Guidelines for managing water quality impacts within UK European marine sites

October 1999

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This report is produced as part of the UK Marine SACs Project - a joint venture involving English Nature, Scottish Natural Heritage, Countryside Council for Wales, Joint Nature Conservation Committee, Environment and Heritage Service Northern Ireland and Scottish Association of Marine Science and the financial support of the European Commission's LIFE-Nature Programme.

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Preface

The 1990s are witnessing a “call to action” for marine biodiversity conservation. The global Convention on Biodiversity, the European Union’s Habitats Directive and recent developments to the Oslo and Paris Convention have each provided a significant step forward. In each case, marine protected areas are identified as having a key role in sustaining marine biodiversity.

The Habitats Directive requires the maintenance or restoration of natural habitats and species of European interest at favourable conservation status, with the management of a network of Special Areas of Conservation (SACs) being one of the main vehicles to achieving this goal. Among the habitats and species specified in the Annexes I and II of the Directive, several are marine features and SACs have already been selected for many of these in the UK. But to manage specific habitats and species effectively, there needs to be clear understanding of their distribution, biology and ecology and their sensitivity to change. From such a foundation, realistic guidance on management and monitoring can be derived and applied.

One initiative now underway to help implement the Habitats Directive is the UK Marine SACs LIFE Project, involving a four year partnership (1996-2001) between:

- English Nature
- Scottish Natural Heritage
- Countryside Council for Wales
- Environment and Heritage Service, Department of the Environment for Northern Ireland
- Joint Nature Conservation Committee, and
- Scottish Association of Marine Science.

The overall goal of the Project is to establish management schemes on 12 of the candidate marine SAC sites. A key component of the Project is to assess the interactions that can take place between human activities and the Annex I and II interest features on these sites. This understanding will provide for better management of these features by defining those activities that may have a beneficial, neutral or harmful impact and by giving examples of management measures that will prevent or minimise adverse effects.

Seven areas where human activity may impact on marine features were identified for study, ranging from specific categories of activity to broad potential impacts. They are:

- port and harbour operations
- recreational user interactions
- collecting bait and shoreline animals
- water quality in lagoons
- water quality in coastal areas
- aggregate extraction
- fisheries.

These areas were selected on the grounds that each includes issues that need to be considered by relevant authorities in managing many of the marine SACs. In each case, existing knowledge is often extensive but widely dispersed and needs collating as guidance for the specific purpose of managing marine SACs.

The reports from these studies are the result of specialist input and wide consultation with representatives of the nature conservation, user and interest bodies. This report has, in particular, benefited from the close involvement of the Environment Agency and the Scottish Environment Protection Agency, as members of the steering group overseeing its production. The reports are aimed at staff from the relevant authorities who jointly have the responsibility for assessing activities on marine SACs and ensuring appropriate management. But they will also provide a valuable resource for industry, user and interest groups who have an important role in advising relevant authorities and for practitioners elsewhere in Europe.

The reports provide a sound basis on which to make management decisions on marine SACs and also on other related initiatives such as the Biodiversity Action Plans and Oslo and Paris Convention. As a result, they will make a substantial contribution to the conservation of our important marine wildlife. We commend them to all concerned with the sustainable use and conservation of our marine and coastal heritage.

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Background

UK Marine SACs Project

This guidance manual has been prepared as part of the UK Marine SACs Project. The overall aim of this Project is to promote the implementation of the Habitats Directive in marine areas through trialing the establishment of management schemes on 12 sites in the UK and by providing proven good practice and guidance to UK and European practitioners.

To support the establishment of these management schemes, the Project is undertaking a series of tasks to collate and develop the understanding and knowledge needed. One of the areas for providing guidance to those developing the schemes concerns the interaction between human activities and marine features. Human activities have an important role in the management of marine features and may have both beneficial and damaging impacts. This manual is one of seven studies bringing together guidance on these impacts and promoting the means of avoiding significant damage to features, the others being:

- port and harbour operations
- recreational user interactions
- collecting bait and other shoreline animals
- water quality in lagoons
- water quality in coastal areas
- aggregate extraction
- fisheries

Habitats and Birds Directive

In May 1992, the member states of the European Union adopted the ‘Council Directive 92/43/EEC on the conservation of natural habitats and of wild fauna and flora’. This is more commonly referred to as the Habitats Directive. The main aim of the Directive is to promote the maintenance of biodiversity and, in particular, requires member states to work together to maintain at or restore to favourable conservation status certain rare, threatened, or typical natural habitats and species. These are listed in Annex I and II of the Directive respectively.

One of the ways in which member states are expected to achieve this aim is through the designation and protection of a series of sites, known as Special Areas of Conservation (SACs).

The Birds Directive (Council Directive 79/409/EEC on the conservation of wild birds) complements the Habitats Directive by requiring member states to protect rare or vulnerable bird species through designating Special Protection Areas (SPAs). Together, the terrestrial and marine SPAs and SACs are intended to form a coherent ecological network of sites of European importance, referred to collectively as Natura 2000.

Habitats Regulations

The requirements of the Habitats Directive have been transcribed into UK legislation through the Conservation (Natural Habitats &c.) Regulations 1994 and the Conservation (Natural Habitats &c.) (Northern Ireland) 1995, known as the Habitats Regulations.

On land, SACs and SPAs are underpinned by Sites of Special Scientific Interest. There is no existing legislative framework for implementing the Habitats Directive in marine areas. Therefore, the Regulations have a number of provisions specifically for new responsibilities and measures in relation to marine areas.

The Regulations place a general duty on all statutory authorities to exercise legislative powers in accordance with the Habitats Directive. The term European marine site is defined as any SPA and SAC or part of a site that consists of a marine area where “marine” also includes intertidal areas. The new duties relative to the management of marine sites are summarised below.

Management schemes

In the UK, management schemes may be established on European marine sites as a key measure in meeting the requirements of the Habitats Directive. Each scheme will be prepared by a group of relevant authorities having statutory powers over the marine area. The Regulations set out which authorities have responsibilities for managing these sites and how they are to be managed, as described below:

- Relevant authorities are those who are already involved in some form of relevant marine regulatory function and would therefore be directly involved in the management of a marine site, and may include the following:
    - country conservation agency
    - environment agencies
    - lighthouse authority
    - local authorities
    - navigation authorities
    - port and harbour authorities
    - sea fishery committees
- A scheme may be established by one or more of the relevant authorities. It is expected that one will normally take the lead. Once established, all the relevant authorities have an equal responsibility to exercise their functions in accordance with the scheme.
- Each site can have only one management scheme.

Whilst only relevant authorities have the responsibility for establishing a management scheme, Government policy (DETR guidance on “European marine sites in England and Wales”) strongly recommends that other groups, including owner and occupiers, users, industry and interest groups be involved in developing the scheme. To achieve this, it suggests the formation of advisory groups and a process for regular consultation during the development and operation of the scheme.

Within the Regulations, the nature conservation bodies have a special duty under Regulation 33 (Regulation 28 in Northern Ireland) to advise the other relevant authorities as to the conservation objectives for a site and the operations that may cause deterioration or disturbance to the habitats or species for which it has been designated. This advice forms the basis for developing the management scheme.

The management scheme will encourage the wise use of an area without detriment to the environment, based on the principle of sustainability. European marine sites have been selected with many activities already taking place and it is recognised that these are normally compatible with the conservation interest at their current levels. Only those activities that would cause deterioration or disturbance to the features for which a site has been designated need to be subject to restrictions under a management scheme.

The primary focus of a management scheme is to manage operations and activities occurring within a European marine site, promoting its sustainable use. However, it may also provide guidance for the assessment of plans and projects, particularly those of a minor or repetitive nature. A plan or project is any operation which requires an application to be made for a specific statutory consent, authorisation, licence or other permission. Not all types of plan or project fall within the statutory functions of relevant authorities, but are consented or authorised by other statutory bodies, termed competent authorities (e.g. central Government Departments).

UK marine SACs

In the UK, candidate SACs have been selected for 10 of the marine features listed in Annex I and II of the Directive and shown in Table 1. There are presently 39 sites that have been forwarded to the European Commission as candidate SACs and a further 3 are proposed and subject to on-going consultation (Figure 1).

Table 1 Annex I habitats and Annex II species

Annex I habitat	**Annex II species**
Estuaries	Bottlenose dolphin
Large shallow inlets and bays	Common seal
Sandbanks which are slightly covered by seawater at all times	Grey seal
Mud and sandflats not covered by sea water at low tide	
Reefs	
Lagoons	
Submerged or partially submerged sea caves	

Sites have been selected for other coastal habitats, such as saltmarsh, sand dunes or species such as the shore dock plant. Whilst these are intertidal areas and therefore strictly European marine sites, they are generally part of ecological systems that extend above high water and come under the provisions of the Habitats Regulations relating to terrestrial SACs. **For this reason, these coastal SACs lie outside the remit of this report, although reference may be made to them where considered relevant to the management of human activities on marine SACs selected for the marine features in Table 1 above.**

References

DEPARTMENT OF THE ENVIRONMENT, TRANSPORT AND THE REGIONS. 1998. *European Marine Sites in England and Wales. A Guide to the Conservation (Natural Habitats &c.) Regulations 1994 and to the Preparation and Application of Management Schemes.*

Map 1:

Candidate Special Areas of Conservation for marine interest:~

The sites and their special features:–

S – Sandbanks which are slightly covered by sea water at all times
E – Estuaries
M – Mudflats and sandflats not covered by sea water at low tide
L – Lagoons
I – Large shallow inlets and bays
R – Reefs
C – Submerged or partially submerged sea caves
GS – Grey seal *Halichoerus grypus*
CS – Common seal *Phoca vitulina*
BD – Bottlenose dolphin, *Tursiops truncatus*

Sites included in the UK Marine SACs Project

Information provided by JNCC. October 1999

1. Introduction

Objectives/scope of these guidelines

These guidelines are concerned with damage to species and habitats through deleterious changes to environmental conditions, including water quality. Although the quality of water of European marine sites is fundamental to their integrity, maintaining water quality at an appropriate level for the protection of the site can be difficult. The causes of deleterious changes in water quality are numerous and while some are easily identified and adequately controlled, others are less obvious and remain effectively uncontrolled. Water quality is characterised in terms of physico-chemical parameters. The effects of human activities in the environment can lead to artificial increases and decreases in these parameters and to the introduction of substances not naturally present.

This guidance is intended to be used mainly as a reference manual by nature conservation agencies and other organisations with statutory duties for the management of European marine sites. **This is a technical manual, not a policy document, which is designed to give staff an idea of the chemical properties of toxic and non-toxic chemicals, their fate and behaviour in the marine environment and potential effects on features of European marine sites.** As such, it brings together the scientific knowledge and understanding considered necessary for ensuring the appropriate response to water quality issues affecting these sites. **In particular, this guidance should assist with identifying any water quality issue that potentially or currently affects the interest features for which the SAC/SPA was selected. These include:**

- the identification of human activities that could result in significant alterations to water quality;

- the identification of priorities for water quality monitoring and surveillance;

- the selection of appropriate water quality criteria for the protection of interest features;

- the appropriate assessment of new and existing plans and projects affecting European marine sites.

Many of these issues are to be addressed through management schemes for European marine sites. One method of dealing with water quality problems is the process of reviewing consenting discharges, for which the competent authority is the Environment Agency in England and Wales, the Scottish Environment Protection Agency (SEPA) in Scotland and the Environment and Heritage Service in Northern Ireland.

How to use these guidelines

These guidelines are intended to be used in two ways:

1. to find answers to specific queries on the relevant legal frameworks, the role of statutory bodies, water quality characteristics of particular substances and current standards for the protection of the marine environment.

2. To assist the competent authority and statutory nature conservation agency staff in assessing the impacts of particular water quality issues and providing advice to competent authorities

In dealing with the latter, the guidelines cover two broad areas:

! the legal and decision-making frameworks; and

! assessing and advising on the impacts.

Legal and decision-making frameworks

, Who is involved in the decision-making process

ö *Section 2 - Framework of controls in the UK*

, What information is needed by the competent authorities to make a decision

ö *Section 3 - Decision-making process by relevant authorities*

Assessing and advising on the impacts

You will find the guidelines provides both **generic** principles and practice as well as more detailed and highly **specific** information in the Appendices:

Generic	Specific
, The threats posed by substances to the European marine site features Toxic substances ö *Section 4.2 - overview of generic impacts of substances* ö *Table 4.3 - summary by substance(s)* Non-Toxic substances ö *Section 4.3 - overview of generic impacts of substances* ö *Table 4.4 - summary by substance(s)* , The background levels of toxic substances in the marine environment ö *Appendix D* , Other factors to take into account when assessing impact ö *Section 6 - generic considerations of fate and behaviour*	, Toxic substances formally identified in international conventions and legislation ö *Appendix A* , Detailed review for each substance(s) of: entry into marine environment; recorded levels in marine; environment; fate/behaviour characteristics; toxicity; bioaccumulation; potential effects on features of European marine sites. ö *Appendix B Toxic Substances Profiles* ö *Appendix C Non-Toxic Substances Profiles* , Specific water quality standards being operated for protecting the marine environment ö *Section 5*

The way all this information is brought together with other information concerning the conservation objectives for a site and the sensitivity of its features to provide advice on potential impacts, is addressed through three **case studies** ö *Section 7*

References

GRIMWOOD, M.J. & DIXON, E. 1997. *Assessment of risks posed by List II metals to Sensitive Marine Areas (SMAs) and adequacy of existing environmental quality standards (EQSs) for SMA protection*. Report to English Nature.

PARR, W., CLARKE, S.J., VAN DIJK, P, & MORGAN, N. 1997. *Turbidity in English and Welsh Tidal Waters*. Report to English Nature.

SCOTT, C.R., HEMINGWAY, K.L., ELLIOTT, M., DE JONGE, V.N., PETTWICK, J.S., MALCOLM, S. & WILKINSON, M. 1999. *Impact of nutrients in estuaries - Phase 2*. Report to English Nature and the Environment Agency.

2. Framework of controls in the UK

2.1 Introduction

This Section introduces the major items of legislation that provide the framework of controls on pollution of coastal waters in the UK and identifies the competent authorities charged with implementing these responsibilities. The information provided is current at the time of writing but some aspects of legislation are under review. The text indicates any reviews currently under discussion. Statutory nature conservation agency staff will be consulted as part of the assessment of possible impacts of new/revised authorisations etc. under the Habitats Regulations. The purpose of this Section is to provide background information for staff on:

! on the competent authority responsible for particular consenting activities; and

! the legislation which that competent authority will use in carrying out that assessment.

Staff should contact the relevant competent authority responsible for implementing European Directives and North Sea commitments for progress in achieving targets.

2.2 Legislation

The activities identified in Table 4.1 are controlled to varying extents by a framework of controls comprising UK and European Union (EU) legislation and international agreements to which the Government is committed. These controls on pollution represent tiers of legislation with different legal status and geographical areas of applicability.

For a control to be statutory and therefore legally binding, it must be written into UK legislation which applies to the UK or parts thereof. Commonly, different legislation applies in England and Wales, Scotland and Northern Ireland (although frequently the same, or similar, controls are implemented). UK legislation comprises primary (Acts of Parliament) and secondary (Regulations) legislation. The geographical area within which UK legislation on pollution control can apply extends to the limit of UK territorial waters (12 nautical miles) but commonly applies only in coastal waters (3 nautical miles).

International agreements can apply globally or to more restricted areas, such as parts of oceans or individual seas. They are needed to control pollution or potentially polluting activities in international waters (beyond territorial waters) that threaten the status of these bodies of water, including coastal areas. The provisions of international agreements are not necessarily legally binding but rely on countries honouring their commitments. Some provisions of international agreements have been included in EU and UK legislation and have become statutory controls through that route.

The key items of primary legislation and the parts of the UK to which they apply are indicated in Table 2.1.

Table 2.1 UK primary legislation and the parts of the UK to which they apply

Legislation	England and Wales	Scotland	Northern Ireland
The Merchant Shipping and Maritime Security Act 1997	Y	Y	Y
The Environment Act 1995	Y	Y	N
The Merchant Shipping Act 1995	Y	Y	Y
The Radioactive Substances Act 1993	Y	Y	Y
The Water Resources Act 1991	Y	N	N
The Environmental Protection Act 1990	Y	Y	Y
The Food and Environment Protection Act (FEPA) 1985	Y	Y	Y
The Control of Pollution Act 1974	[1]	Y	N
The Water Act (Northern Ireland) 1972	N	N	Y

Y = Yes N = No

[1] In England and Wales, the Control of Pollution Act (COPA) was largely replaced by the Water Resources Act 1991 though some discharge consents issued under COPA may still be in force (NRA 1994)

The key items of EU legislation providing controls on water quality in the marine environment are:

- Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control (IPPC);
- Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (Nitrates Directive);
- Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment (Urban Waster Water Treatment (UWWT) Directive);
- Council Directive 79/923/EEC of 30 October 1979 on the quality required of shellfish waters (Shellfish Waters Directive);
- Council Directive 76/464/EEC of 4 May 1976 on pollution caused by dangerous substances discharged into the aquatic environment of the Community (Dangerous Substances Directive) and “daughter” Directives;
- Council Directive 76/160/EEC of 8 December 1975 concerning the quality of bathing water (Bathing Waters Directive).

In June 1995, the Council of Minsters and the European Parliament called for a fundamental review of EU water policy. As a result, the Commission proposed a Council Directive Establishing a Framework for Community Action in the field of Water Policy (Water Framework Directive) that same year. This proposed Directive is under discussion with the European Parliament and negotiations over amendments are still taking place. The current estimate for an agreed Directive is during the Portuguese Presidency (January to June 2000).

The important international agreements to which the UK is committed are:

- The Convention on the Protection of the Marine Environment of the North-East Atlantic, 1992 (OSPAR Convention);
- North Sea Conferences;
- Convention on the Prevention of Marine Pollution by Dumping of Waste and Other Matter, 1972 (London Convention);
- International Convention on the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto (MARPOL 73/78).

2.2.1 UK legislation

2.2.1.1 The Environment Act 1995

The Environment Act 1995 established the Environment Agency (EA) in England and Wales and the Scottish Environment Protection Agency (SEPA) in Scotland and transferred responsibilities to these agencies from a number of bodies. These functions were originally conferred by previous legislation. The EA assumed various responsibilities of the National Rivers Authority (NRA), the waste regulation and disposal authorities and Her Majesty's Inspectorate of Pollution (HMIP). SEPA assumed various functions of the river purification authorities, the waste regulation and disposal authorities, local authorities and Her Majesty's Industrial Pollution Inspectorate (HMIPI). The EA and SEPA were formed on 1st April 1996 and at the same time, the Environment and Heritage Service was established in Northern Ireland with similar responsibilities.

2.2.1.2 The Merchant Shipping Act and Merchant Shipping and Maritime Security Act 1997

The Merchant Shipping Act 1995 is a consolidation statute, bringing together the provisions of previous merchant shipping legislation. Part VI of the Act deals with oil and other pollution from ships. The Act provides powers to introduce regulations implementing provisions of international treaties (in particular MARPOL 73/78), to regulate ship-to-ship transfers of potentially polluting material, to require harbour authorities to provide waste reception facilities and prepare waste management plans and to control the discharge from a ship of 'oil or any mixture containing oil.' A number of Regulations has been issued under the powers granted by the Act. **The competent authority for the enforcement of the 1995 Act is the DETR in England and Wales, the Scottish Executive in Scotland and the Northern Ireland Office in Northern Ireland.**

The 1995 Act has been amended by the Merchant Shipping and Maritime Security Act 1997 which provides powers to the Secretary of State to establish temporary exclusion zones for stricken vessels where there is a danger of significant pollution of UK waters. The Act also places a responsibility on port and harbour authorities to provide adequate waste reception facilities and prepare waste management plans as a means of pollution control. **This responsibility was made statutory by the Merchant Shipping (Port Waste Reception Facilities) Regulations 1997 which came into force in January 1998.** These Regulations also revoke and replace earlier legislation on port waste reception facilities. Port and harbour authorities also now have a statutory responsibility to prepare oil spill contingency plans provided they meet certain criteria, one of which being any port or harbour authority within an area of significant environmental sensitivity. **This provision was made in this Act and brought into effect by the Merchant Shipping (Oil Pollution Preparedness, Response and Co-operation Convention) Regulations in May 1998.**

The Act also increased the maximum fine which can be imposed by magistrates (and their equivalents in Scotland and Northern Ireland) for illegal oil pollution from £50,000 to £250,000. **This was brought into force by the Merchant Shipping (Prevention of Oil Pollution) (Amendment) Regulations in September 1997.**

The competent authority for the enforcement of the Merchant Shipping Act 1995 and Maritime Security Act 1997 is the DETR in England and Wales, the Scottish Executive in Scotland and the Environment and Heritage Service in Northern Ireland.

2.2.1.3 The Radioactive Substances Act 1993

This Act provides for the regulation of the keeping and use of radioactive material on premises and for the disposal and accumulation of radioactive waste. **The competent authorities under the Act are the Environment Agency in England and Wales, SEPA in Scotland and the Environment and Heritage Service in Northern Ireland.** These authorities have responsibilities for all of the above duties at hospitals and research and industrial establishments. However, at the major nuclear installations (i.e. Sellafield and Dounreay), these bodies are only responsible for the disposal of radioactive waste to the environment. Discharges of radioactivity into the environment are controlled by authorisations with limits on total emissions and composition of the discharge. The Environment Agency, SEPA and Environment and Heritage Service in Northern Ireland are responsible for environmental monitoring of radioactivity.

2.2.1.4 The Water Resources Act 1991

This Act is the key piece of legislation governing discharges to surface waters from non-prescribed processes under Integrated Pollution Control (IPC) (see Environmental Protection Act 1990) in England and Wales. In Scotland, the powers to consent discharges have their basis in the Control of Pollution Act 1974. In Northern Ireland, these powers were granted under the The Water Act (Northern Ireland) 1972.

The Water Resources Act consolidated much of the legislation governing water pollution which was previously contained in, for example, the Water Act 1989 and the Control of Pollution Act 1974. Some of the main provisions relevant to water quality in estuaries and coastal waters are described below.

Definition of controlled waters

The Act applies to all discharges made to controlled waters in England and Wales. Controlled waters are defined as:

1. Territorial waters - marine waters within three nautical miles of the baseline which marks the territorial sea.

2. Coastal waters - waters between the baseline marking the territorial sea and the limit of high tide on land.

Water Protection Zones and Nitrate Sensitive Areas

Sections 93 and 94 of this Act provide for the establishment of Water Protection Zones (WPZs) and Nitrate Sensitive Areas (NSAs) respectively.

32 NSAs have been designated, mostly in Eastern England. Farmers are compensated if they adopt ‘environmentally friendly’ farming practices that result in a decrease in nitrate application to land.

Offences of Polluting Controlled Waters

Under Section 85 of this Act, it is an offence to cause, or knowingly permit, the entry into controlled waters, either directly or via a drain or sewer, of:

- any poisonous, noxious or polluting matter;
- any solid waste matter;
- any matter, other than trade or sewage effluent, via a drain or sewer pipe, if it has been prohibited by the Environment Agency;
- trade or sewage effluent;
- any matter likely to impede the flow;
- any effluent through a pipe into the sea outside the seaward limit of controlled waters.

A person shall not be guilty of an offence if the discharge is consented by the Environment Agency. Therefore, an offence is committed as a result of unconsented discharges and accidental spillages which result in the entry of polluting matter to water. Anyone committing such an offence is subject to prosecution.

Discharge Consents

The Environment Agency in England and Wales can place consent conditions on any discharge containing a compound likely to cause pollution in the aquatic environment. The Act also outlines the procedure for obtaining, reviewing and charging for the issue of discharge consents and requires the Agency to keep a public register of all data relevant to the discharge and the receiving water. **The Act identifies the Environment Agency in England and Wales as the competent authority for the control of discharges to controlled waters.**

In Scotland, the discharge of trade and sewage effluent to rivers and tidal waters is controlled under the Rivers (Prevention of Pollution) Scotland Acts 1951 and 1965. The control and monitoring of the discharges is the function of SEPA.

In Northern Ireland, the Water and Sewerage (Northern Ireland) Order 1973 contains provisions for the Environment and Heritage Service to grant consents to discharge trade effluents to public sewers and sewage and trade effluents to surface waters.

Abstraction licences

Part II of the Water Resources Act 1991 provides for the requirement for the licensing of abstractions from inland waters in England and Wales.

2.2.1.5 The Environmental Protection Act 1990

This Act introduced two new pollution control systems:

- Integrated Pollution Control (IPC);
- Local Authority Air Pollution Control (LAAPC).

The most important system with respect to water quality in the marine environment is IPC.

Integrated Pollution Control is intended to promote a more integrated approach to environmental protection by considering releases to all three environmental compartments (air, water and land) together. An IPC authorisation, therefore, replaces any existing consents covering releases to these media. Discharges to sewer will additionally require a trade effluent consent from the appropriate sewerage undertaker. IPC initially applies to releases from the ‘most polluting industrial processes’ (as defined by the Secretary of State) and is designed to tighten pollution control requirements by introducing a number of new measures. These include:

- releases of the most polluting (prescribed) substances must be prevented or, where this is not possible, minimised and rendered harmless by applying Best Available Techniques Not Entailing Excessive Costs (BATNEEC);
- for processes resulting in releases to more than one environmental medium, the Best Practicable Environmental Option (BPEO) has to be identified in order to minimise the impact of the process on the environment as a whole;
- one regulatory authority (the Environment Agency in England and Wales, SEPA in Scotland) issues an authorisation for discharges to all three media (air, water and land) after consultation with other relevant environment authorities (a trade effluent consent will still be required from the appropriate sewerage undertaker);
- the ‘polluter pays principle’ will be applied, allowing the environment agencies to recover from industry the costs associated with administering the IPC system;
- public participation is significantly greater than in previous pollution control schemes;
- self-monitoring is required in authorisations and the results recorded in a public register; and
- tougher enforcement measures are available to the environment agencies.

The IPC systems are limited in application to Great Britain. A comparable system of industrial pollution control has been introduced in Northern Ireland under Regulations introduced in 1998. **The competent authority is the Environment and Heritage Service.**

The UK Government is proposing to modify the system of IPC in the light of the EC Directive on Integrated Pollution Prevention and Control (IPPC) by the introduction of a new Act of Parliament and associated regulations (see Section 2.2.2.1).

2.2.1.6 The Food and Environment Protection Act 1985

The Food and Environment Protection Act 1985 Part II provides controls for the disposal of waste at sea (as opposed to discharge into the sea via pipelines) under a system of licences. Certain other activities resulting in the deliberate deposit of articles or substances in the sea below the mean high water spring mark also require a licence under this legislation. This includes certain construction projects or laying of pipelines. The types of wastes involved can vary from the disposal of dredged material and sewage sludge to the use of tracers and biocides and burials at sea. The main types of wastes for which licences are issued are:

- minestone (colliery wastes);
- sewage sludge;
- dredged material; and
- offshore installations (i.e. oil rigs)

This legislation applies to the UK Continental Shelf (as defined by the Continental Shelf Act 1964 (as amended)) and beyond that if the waste is loaded in the UK or is deposited from a British registered vessel. Licences for these activities are issued by MAFF in England and Wales (see Section 3.1.2), the Scottish Executive Rural Affairs Department (SERAD) in Scotland (see Section 3.2.2) and the Environment and Heritage Service in Northern Ireland (see Section 3.3.1).

2.2.1.7 The Control of Pollution Act (COPA) 1974

The former water authorities were responsible for issuing consents for discharges of trade and sewage effluent. They also had a duty to review consents and conditions from time to time and could revoke the consent if it was reasonable to do so or modify the conditions if pollution caused by the discharge was ‘injurious to fauna and flora’.

Under COPA, a person is guilty of an offence if he causes, or knowingly permits:

- any poisonous, noxious or polluting matter to enter any stream or controlled waters;
- any matter to enter a stream so as to impede the proper flow of water within the stream in a manner leading or likely to lead to a substantial aggravation of pollution;
- any solid waste matter to enter a stream or restricted water.

The Water Resources Act 1991 largely replaced COPA. The aforementioned responsibilites are now discharged by the Environment Agency in England and Wales and SEPA in Scotland.

2.2.1.8 The Water Act (Northern Ireland) 1972

Under this Act, the Environment and Heritage Service is responsible for protecting fresh and tidal waters, principally through the application of consents for discharges to controlled waters.

2.2.2 EU legislation

2.2.2.1 Directive on Integrated Pollution Prevention and Control (IPPC)

This Directive was adopted by the Council of Ministers in 1996 and has been introduced as a harmonisation measure in response to the existence of several national integrated pollution management systems (such systems operate in the UK, Belgium, Denmark, France and the Netherlands). The Directive has been strongly influenced by the UK IPC system, not least as it is the most recent and comprehensive system of integrated pollution management. Whilst IPC appears to be at least as comprehensive as IPPC, there are a number of elements of IPPC that may lead to the extension of IPC in the UK. These are discussed below.

Prescribed Processes and Substances

IPPC will apply to “installations” rather than “processes”. These are listed in Annex I of the Directive and fall into the same broad categories as IPC. The list is not as detailed or comprehensive as the IPC list, but suggests that IPPC will require some extension to the application of IPC. For example, IPPC will apply to all processes included in the Annex and will not allow for exclusion where the release of prescribed substances is trivial. In addition, some of the size exclusions for IPC will not apply under IPPC. For example, IPPC will apply to all plants manufacturing chemical pesticides, compared to IPC which applies only to plants likely to release prescribed substances to water.

As for IPC, IPPC requires that releases of certain substances which are prescribed for each media and listed in an Annex to the Directive are prevented, or where that is not possible, minimised. The list for air is similar to that for IPC. However, for water and land, where IPC lists specific substances, IPPC will apply to the broad groups of dangerous/hazardous substances defined, respectively, in the Dangerous Substances Directive and the Hazardous Waste Directive. IPPC will also require that Best Available Technology (BAT) be used to reduce the release of energy and of substances “with a bearing on global pollution problems”. These approaches will require that the release of a much broader range of substances must be prevented, or if that is not possible, minimised by the use of BAT, thus tightening the present requirements on a wide range of substances.

In addition, IPPC requires that materials and substances generated in the installation must be recovered and recycled wherever possible.

Authorisations

As IPPC applies to installations rather than to processes, it anticipates a single authorisation for an installation irrespective of the number of processes operated.

The information required in an application for authorisation is broadly similar to that for an IPC authorisation, but there are areas of discrepancy. For example:

- IPPC applications must include information on energy use, raw material consumption and opportunities for recycling or re-using materials. These will be taken into account when assessing BAT;
- IPPC applications must also include details about the decommissioning of the installation; however,
- IPPC applications will not have to include detailed programmes for continued improvements and investment plans.

Best Available Techniques (BAT)

Best Available Techniques (BAT), in the context of IPPC, must be practically suitable, industrially feasible (both from a technical and an economic point of view) and proven at a scale which allows for its implementation in the relevant industrial context. The economic element of IPC's BATNEEC is therefore retained in IPPC within the concept of 'available'. BAT under IPPC will have a broader scope and take into account use of raw materials and energy consumption as well as emission reduction.

Early drafts of the Directive suggested BAT would be set in EU "daughter" Directives. However, in line with subsidiarity, the Directive allows each member state to define BAT separately, taking into account guidance on BAT published by the European Commission. Member states will be required to submit reports to Brussels every three years on the definition of BAT being applied to each industrial sector. Every permit will contain an implied condition that BAT will be used even where this is not specifically stated in the permit.

In order to ensure that there is some harmonisation of approaches across the EU, the European Commission, via the IPPC Centre in Seville, is preparing BAT Reference Notes (BREFs) for each of the industrial sectors covered by IPPC. These will function in a similar manner to the UK's present IPC Guidance Note approach (Chief Inspector's Guidance Notes, Series 2. 1993 ff).

Implementation Timetable

Member states have to ensure that all the industrial activities listed in Annex I to the Directive are controlled by IPPC permits three years after the Directive's entry into force, i.e September 1999. The Directive was adopted under Article 130 of the Maastricht Treaty and, therefore, member states will be able to maintain stricter national standards if they so choose.

The Government issued its third consultation paper on the implementation of the Integrated Pollution Prevention and Control (IPPC) Directive in December 1998. The Government has decided to implement the IPPC Directive as primary legislation and accompanying Regulations. Consequently, the Pollution Prevention and Control (PPC) Bill was introduced into the House of Lords on 30 November 1998, giving the Secretary of State the power to:

- repeal Part I of the Environmental Protection Act 1990 and replace it with a single pollution regime, bringing under the new system those IPC and LAAPC processes not caught by the Directive; and

- apply key IPPC concepts such as Best Available Techniques (BAT) to all installations covered by the new regime, rather than the IPC/LAAPC regimes continuing to operate with the concept of Best Available Techniques Not Entailing Excessive Cost (BATNEEC).

The second consultation paper outlined a number of options for the involvement of English and Welsh local authorities in IPPC Regulation. The favoured option was for the division of regulatory responsibilities between local authorities and the Environment Agency. The current paper gives more detail on how this partnership will work. Local authorities would retain regulatory responsibilities for the bulk of the 1,500 IPPC installations they currently control under the LAAPC regime, as well continuing to regulate emissions to air from the 11,500 non-Directive processes. The Environment Agency will regulate all other IPPC installations. However, the Government recognises that local authorities lack the expertise of the Environment Agency regarding the regulation of polluting emissions to water. **The Agency will, therefore, act as a statutory consultee for the IPPC permits issued by the local authorities.**

In Scotland, the Scottish Environment Protection Agency (SEPA), will be the regulator for all installations.

2.2.2.2 Nitrates Directive

In 1991, the Council of Ministers adopted a Directive on the protection of waters against pollution caused by nitrates from agricultural sources (the Nitrates Directive).

The Directive aims to protect fresh, coastal and marine waters against pollution caused by nitrates from diffuse sources. It requires member states to identify waters, either actually or potentially affected by nitrate pollution. These are to include :

- surface waters, particularly those for the abstraction of drinking water, where nitrate concentrations exceed 50 mg/l nitrate;

- groundwaters actually or potentially containing more than 50 mg/l nitrate;

- freshwater lakes, other freshwater bodies, estuaries, coastal waters and marine waters which are, or may in the future be, eutrophic.

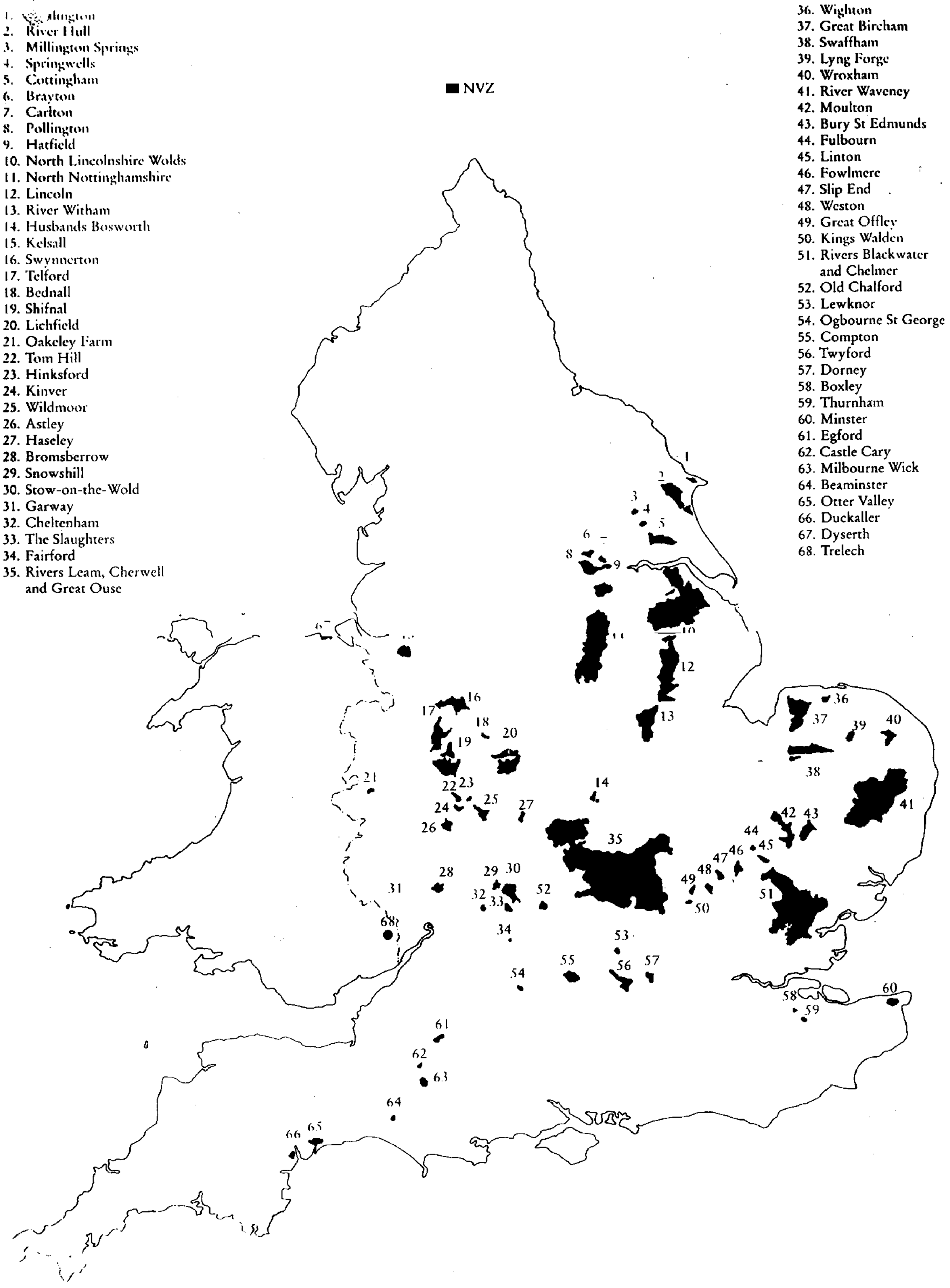
Member states had to designate all areas draining into such waters as vulnerable zones by 19 December 1993 and establish Action Programmes to control the timing and rate of application of manure and chemical fertilisers in these zones.

The provisions of the Nitrates Directive for the identification of vulnerable zones were transcribed into UK legislation primarily under the provisions of the Water Resources Act 1991 and subsequent Regulations. 68 Nitrate Vulnerable Zones (see Map 2) were identified in England and Wales under the Protection of Water Against Agricultural Nitrate Pollution

Regulations 1996 and one, at Balmalcolm in Fife, under similar regulations in Scotland. Three Nitrate Vulnerable Zones have been designated in Northern Ireland.

The provisions for Action Programmes were implemented in UK legislation under the Action Programme for Nitrate Vulnerable Zones Regulations 1998 which came into force on 19 December 1998. These Regulations, which aim to reduce the leaching of nitrate from farmland into ground and surface waters, require farmers in Nitrate Vulnerable Zones to control the timing and rate of applications of nitrogen fertilisers and manures used on their land and to keep supporting records.

Map 2. Nitrate Vulnerable Zones in England and Wales



1. Bridlington
2. River Hull
3. Millington Springs
4. Springwells
5. Cottingham
6. Brayton
7. Carlton
8. Pollington
9. Hatfield
10. North Lincolnshire Wolds
11. North Nottinghamshire
12. Lincoln
13. River Witham
14. Husbands Bosworth
15. Kelsall
16. Swynnerton
17. Telford
18. Bednall
19. Shifnal
20. Lichfield
21. Oakeley Farm
22. Tom Hill
23. Hinksford
24. Kinver
25. Wildmoor
26. Astley
27. Haseley
28. Bromsberrow
29. Snowshill
30. Stow-on-the-Wold
31. Garway
32. Cheltenham
33. The Slaughters
34. Fairford
35. Rivers Leam, Cherwell and Great Ouse
36. Wighton
37. Great Bircham
38. Swaffham
39. Lyng Forge
40. Wroxham
41. River Waveney
42. Moulton
43. Bury St Edmunds
44. Fulbourn
45. Linton
46. Fowlmere
47. Slip End
48. Weston
49. Great Offley
50. Kings Walden
51. Rivers Blackwater and Chelmer
52. Old Chalford
53. Lewknor
54. Ogbourne St George
55. Compton
56. Twyford
57. Dorney
58. Boxley
59. Thurnham
60. Minster
61. Egford
62. Castle Cary
63. Milbourne Wick
64. Beaminster
65. Otter Valley
66. Duckaller
67. Dyserth
68. Trelech

The European Commission is currently pursuing legal action against the UK for non-compliance of the Nitrates Directive. The UK has limited the application of Nitrate Vulnerable Zones to drinking water sources, whereas the Directive states that the criteria should be applied to all surface and ground waters. In order to address this shortcoming in the application of the Directive, the UK has extended monitoring to investigate such waters but this will not be completed until 2000 (several years after the Directive's deadline). Furthermore, no action plans have been established for the Nitrate Vulnerable Zones in Northern Ireland.

2.2.2.3 Urban Waste Water Treatment Directive

On 18 March 1991, EU Environment Ministers adopted the Urban (formerly Municipal) Waste Water Treatment Directive. The provisions of the Directive have been transcribed into UK legislation by the Urban Waste Water Treatment Regulations 1994 in England, Wales and Scotland. DETR and the Welsh Office issued a guidance note (DETR 1997) providing agreed interpretation of the Regulations between the Environment Agency and the Water Service plcs (the largest group of dischargers).

The main aim of the Directive is to ensure that all signficant discharges of sewage are treated before they are discharged, either to inland surface waters, groundwaters, estuaries or coastal waters. Significant discharges are defined, for the purposes of the Directive, as those to fresh waters or to estuaries serving agglomerations with population equivalents (commonly abbreviated to "pe") of more than 2,000 or those to coastal waters serving agglomerations with population equivalents of more than 10,000 (1 pe = the organic biodegradable load having a five day biological oxygen demand (BOD_5) of 60 g per day). Sewage will normally be treated to secondary treatment standards (see Box 1, page 50) (normally a biological process). Discharges into areas identified as 'sensitive' because of the risk of eutrophication will require more stringent treatment which will usually include the removal of nitrogen in coastal waters and phosphorus in freshwaters. The timetable for the implementation of these improvements in estuarine and coastal waters is as follows:

- secondary treatment for discharges above 15,000 pe must be provided by 31 December 2000;

- discharges between 2,000 and 15,000 pe in estuaries and between 10,000 and 15,000 pe in coastal waters must receive secondary treatment by 2005;

- smaller discharges must receive appropriate treatment by 2005.

The Directive and the UK Regulations allowed for the designation of High Natural Dispersion Areas (HNDAs) in coastal waters. In these areas, only primary treatment of sewage is required. 85 HNDAs have been identified in the UK: 58 in England and Wales, 24 in Scotland and 3 in Northern Ireland. However, the Government has recently decided to withdraw all HNDAs which will require all discharges covered by UWWT Regulations to undergo secondary treatment as a minimum. Any discharges affected by this change of policy may be allowed longer to comply with the secondary treatment requirements.

Five estuarine eutrophic 'sensitive' areas have been identified in the UK and these are all in England and Wales: Chichester Harbour, Langstone Harbour, Truro, Tresillian and Fal estuaries, Taw estuary and Tawe estuary. **Where 'sensitive area' designations coincide with European**

marine sites, the implications for the features of interest should be considered. Designations are to be reviewed in 2001. In Northern Ireland, Inner Belfast Lough is to be designated as a eutrophic 'sensitive' area.

All qualifying discharges under the Directive have specific conditions written into the discharge consents specifying the appropriate level of treatment.

The Directive also requires member states to take action to limit pollution from storm water overflows. This requires measures to be undertaken to improve unsatisfactory intermittent discharges, although no specific requirements are imposed, nor is a timetable set.

The Directive also requires appropriate treatment to be provided from smaller agglomerations and effluents from industrial processes with characteristics similar to sewage. The Directive also required the ending of disposal of sewage sludge at sea on 31 December 1998.

2.2.2.4 Shellfish Waters Directive

The Shellfish Water Directive (adopted in 1979) outlines the requirements for the quality of designated waters which support shellfish (defined as bivalve and gastropod molluscs) and aims to protect these shellfish populations from the harmful consequences resulting from the discharge of polluting substances into the sea. **This Directive has been transcribed into UK legislation under the Surface Waters (Shellfish) (Classification) Regulations 1997 and The Surface Waters (Shellfish) Directions 1997.**

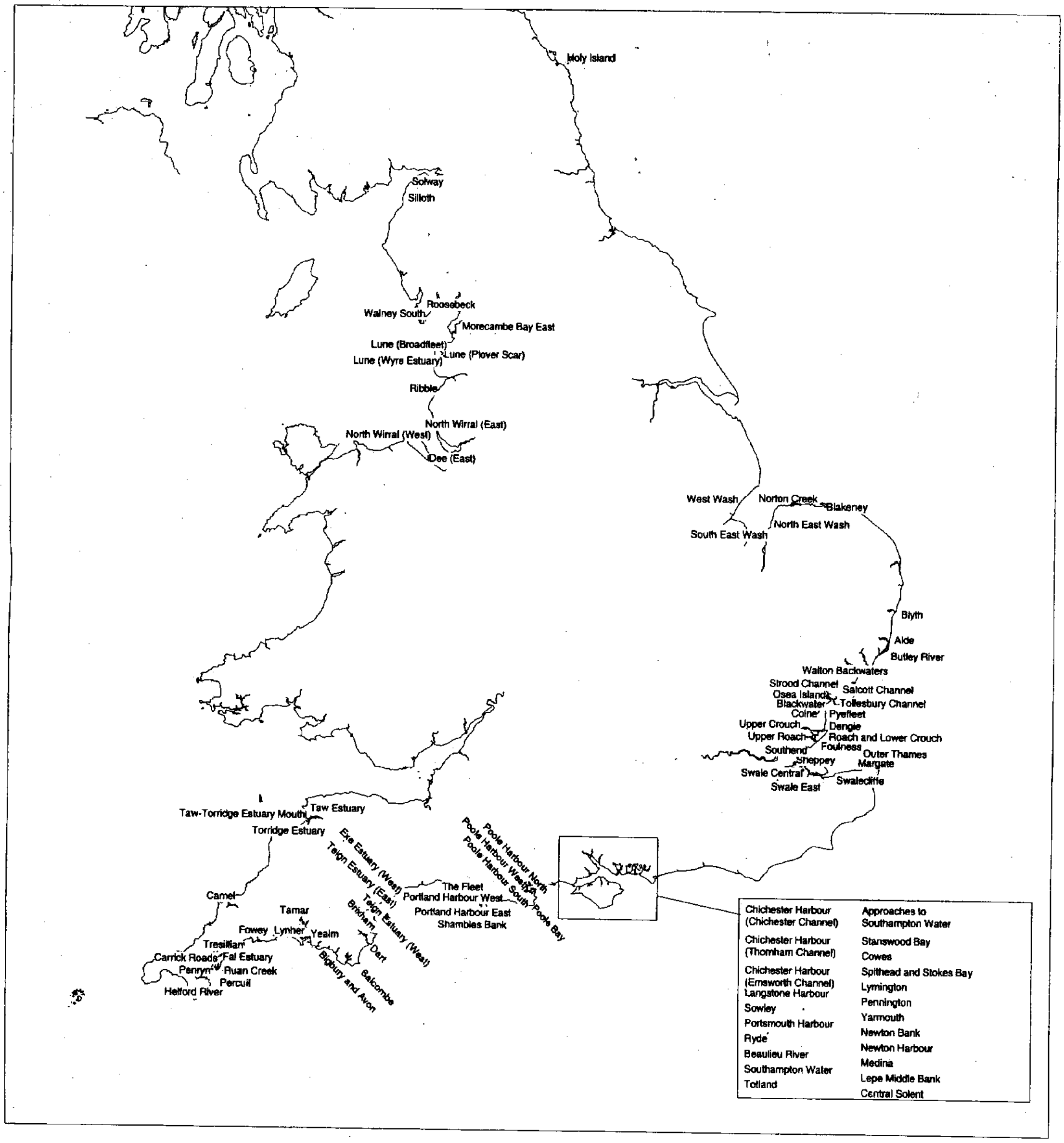
In July 1999, DETR announced the designation of 76 new shellfish waters and the extension of the existing 17 designations. The total number of protected areas in England is now 93 (see Map 3). There is one designated shellfish area in Wales (although more are expected to be designated by the National Assembly for Wales in the near future - CEFAS, Weymouth pers. comm.), 11 in Scotland and 1 in Northern Ireland.

There are also plans to increase the number of designated waters in Northern Ireland. **The competent authority for the implementation of this Directive is the Environment Agency in England and Wales, SEPA in Scotland and the Environment and Heritage Service in Northern Ireland.**

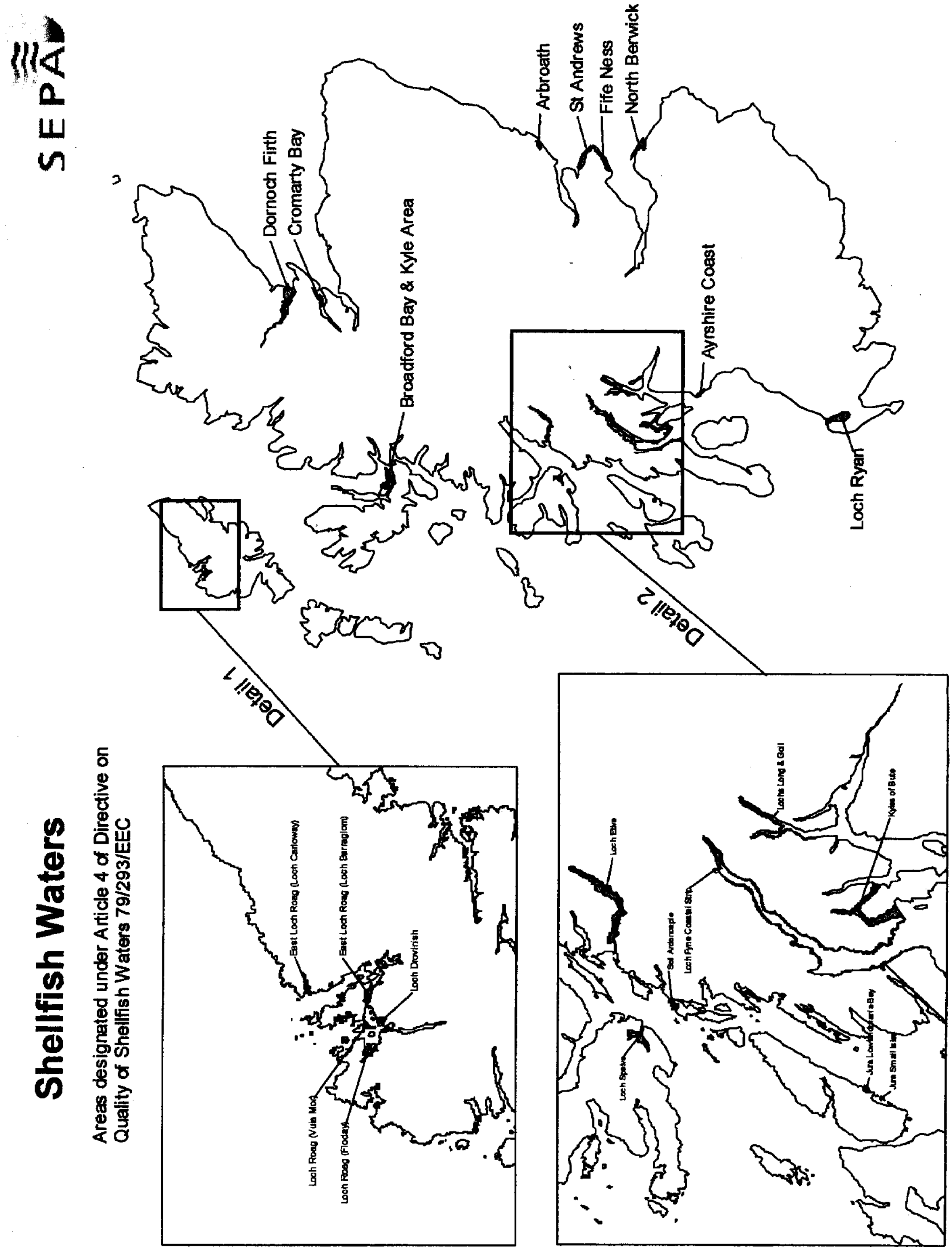
The Directive lays down Imperative (I) values for certain parameters (see Section 5) of water quality which must be attained in designated waters. It also sets Guideline (G) values (Section 5) which member states must 'endeavour to observe' in establishing programmes for improvement of designated waters. The Regulations set mandatory minimum standards equal to the I values in the Directive. In practice, it is intended that local operational standards will be set (after 2001) which are at least as stringent as the I values but take into account current water quality such that no deterioration is allowed. No deterioration in this context means that water quality currently better than the proposed I values will not be allowed to deteriorate, regardless of the I values.

Shellfish waters are monitored throughout the year ranging from monthly, quarterly, six-monthly to annually, depending on the relevant parameter. The parameters measured include physico-chemical determinands and a range of toxic organic and metal contaminants. Where shellfish waters are located within or close to European marine sites, the results of monitoring of shellfish waters provide an indication of the concentration of some key physico-chemical determinands and a range of toxic contaminants in the water column and the degree of compliance with standards designed to protect shellfish.

Map 3. Designated shellfish waters in England and Wales



Map 4. Designated shellfish waters in Scotland



The related Directive laying down the health conditions for the production and the placing on the market of live bivalve molluscs (Shellfish Hygiene Directive) is aimed at ensuring shellfish are fit for human consumption and involves monitoring for faecal bacteria contamination. The Directive does not impose any obligation to achieve or maintain a particular standard, but classifies shellfish harvesting areas according to the level of faecal bacteria present in the shellfish. **MAFF, SERAD in Scotland and Department of Agriculture for Northern Ireland (DANI) in Northern Ireland are the competent authorities for the implementation of this Directive.**

2.2.2.5 Dangerous Substances Directive

In 1976, the EU Council of Ministers adopted the Dangerous Substances Directive to control pollution caused by certain dangerous substances discharged to the aquatic environment. The Directive established two lists of compounds:

- List I dealing with substances regarded as being particularly dangerous because of their toxicity, persistence and bioaccumulation. Pollution by List I substances must be eliminated; and

- List II containing substances which are less dangerous but which nevertheless have a deleterious effect on the aquatic environment. Pollution by List II substances must be reduced.

For List I substances, the Directive stipulates two approaches for control: uniform emission standards (UESs) (also known as limit values) and environmental quality standards (EQSs). Both types of standard are set on a Community level but member states are given discretion to select which approach to adopt. Most EU member states prefer the UESs, whereas the UK has adopted the EQS approach. For List II substances, member states are required to set environmental quality standards (EQSs) developed on a national level.

EQSs for List I substances have been established in a series of 'daughter' Directives (Table 2.3).

EQSs for List II substances have been derived in the UK and implemented by the Surface Waters (Dangerous Substances)(Classification) Regulations 1997 and 1998.

In 1980, the EU adopted the Groundwater Directive (Protection of Groundwater Against Pollution Caused by Certain Dangerous Substances - 80/68/EEC). The substances to be controlled fall into two lists:

List 1 substances are the most toxic and must be prevented from entering groundwater. They include pesticides, sheep dip, solvents, hydrocarbons, mercury, cadmium and cyanide.

List 2 substances are less dangerous but, if disposed of in large amounts, could be harmful to groundwater. They include some heavy metals and ammonia (which is present in sewage effluent), phosphorous and its compounds. Entry of these substances into groundwater must be restricted to prevent pollution.

Control is also required where water is recharged to ground for later drinking water use.

On 1 January 1999, Regulations completing the implementation of the 1980 Directive were introduced (EA has responsibility for the Groundwater Regulations in England and Wales with SEPA exercising similar responsibilities in Scotland). From the above date, anyone who disposes of listed substances (including materials which contain these substances) onto or into land should apply for an authorisation if they want to continue with that disposal. An application made before 1 April 1999 will be deemed granted until fully determined by the EA. Where applications are made on or after 1 April 1999, these will need to be considered by the Agency and a formal authorisation issued before any disposal can be made. Where disposal is acceptable, the EA will authorise this with appropriate conditions. In some cases, it will be necessary to refuse the application because of the risks to groundwater. **This advice on authorisations under the Regulations is subject to finalisation of DETR guidance on interpretation of the Regulations. The reader should contact Sarah Peaty (EA, 0191 203 4000) for further information.**

Table 2.2 Dangerous substances 'daughter' Directives for List I substances

Substance	Directive	Formal compliance
Cadmium	83/513/EEC	1/1/89
Mercury	82/176/EEC	1/7/86
	84/156/EEC	1/7/89
Lindane (hexachlorocyclohexane)	84/491/EEC	1/10/88
Pentachlorophenol	86/280/EEC	1/1/91
DDT	86/280/EEC	1/1/91
Carbon tetrachloride	86/280/EEC	1/1/91
Chloroform	88/347/EEC	1/1/90
Hexachlorobenzene	88/347/EEC	1/1/90
Hexachlorobutadiene	88/347/EEC	1/1/90
Dieldrin	88/347/EEC	1/1/89
Aldrin	88/347/EEC	1/1/89
Isodrin	88/347/EEC	1/1/89
Endrin	88/347/EEC	1/1/89
1,2-dichloroethane	90/415/EEC	1/1/93 and 1/1/95
Trichloroethylene	90/415/EEC	1/1/93 and 1/1/95
Perchloroethylene	90/415/EEC	1/1/93 and 1/1/95
Trichlorobenzene	90/415/EEC	1/1/93 and 1/1/95

The requirement to comply with EQSs in controlled waters governs the conditions on discharge consents containing List I substances. The Environment Agency undertakes monitoring of controlled waters around discharges known to contain these substances in order to demonstrate compliance with the requirements of the Directive. An annual summary of this information is submitted to DETR.

2.2.2.6 Bathing Waters Directive

This Directive covers the quality of bathing waters for protecting human health and for reasons of amenity and seeks to ensure that quality is raised over time largely by ensuring sewage is not present or has been adequately diluted or destroyed. Bathing waters are defined as "fresh or sea water in which bathing is explicitly authorised or is not prohibited and is traditionally practised by a large number of bathers." A total of 448 coastal and estuarine sites have been designated as bathing waters in England and Wales, 23 in Scotland and 16 in Northern Ireland. The Scottish Executive is expected to designate further bathing waters in Scotland before the start of the 1999 bathing season (SEPA 1998). SEPA monitored an additional 93 coastal and inland and as yet undesignated bathing waters in 1998 (SEPA 1998).

The Directive lists 10 parameters: total coliforms, faecal coliforms, salmonella, enteroviruses, pH, colour, mineral oils, surface-active substances reacting with methylene blue (essentially detergents), phenols and water clarity for which there are mandatory standards for all member states. The Directive also gives guideline values for some of the parameters, including the two coliform groups and faecal streptococci, which are stricter than the mandatory values and which member states should endeavour to observe. **The mandatory requirements of this Directive were transcribed into UK legislation under the provisions of the Water Resources Act 1991 (Section 2.2.1) by the Bathing Waters (Classification) Regulations.**

The UK Government bases compliance with the Directive's mandatory standards on the counts of total coliforms and faecal coliforms (both parameters must comply to achieve a pass) and with guideline values on the counts of total coliforms, faecal coliforms and faecal streptococci (all three parameters must comply to achieve a pass). **The competent authority for the implementation of this Directive is the Environment Agency in England and Wales, SEPA in Scotland and the Environment and Heritage Service in Northern Ireland.**

Bathing waters are monitored regularly during the bathing season (15 May to 30 September in England and Wales and 1 June to mid-September in Scotland and Northern Ireland) for a range of microbiological and physico-chemical parameters. Where bathing waters are located within or close to European marine sites (see JNCC Coastal Directory Series for locations of designated bathing waters), the monitoring of bathing waters provides an indication of the degree of pollution (principally from sewage). However, sampling is limited to the bathing season only and is located on the designated bathing beach regardless of the position of outfalls. The results of bathing water monitoring are published annually by the Environment Agency in England and Wales (see Environment Agency website at www.environment-agency.gov.uk), SEPA in Scotland (SEPA 1998 and SEPA website at sepa.org.uk) and the Environment and Heritage Service in Northern Ireland.

The requirement to achieve compliance with mandatory standards is one of the major pressures leading to significant improvements in Secondary Treatment Works (STW) discharges in the vicinity of designated bathing waters. SEPA adopted a new policy in 1998 on microbiological standards in marine waters which aims to ensure that all new or modified discharges are designed to achieve compliance with guideline values of the Directive at identified bathing waters in Scotland.

2.2.2.7 Water Framework Directive

The European Commission adopted a proposal for a Water Policy Framework Directive (WFD) on 26 February 1997. The overall aim of the Directive is to establish a framework for the protection and management of surface waters, including estuaries, coastal waters and groundwaters in the EU. The main objectives of the proposed Directive are to:

- prevent further deterioration and to protect and enhance the aquatic environment;

- achieve ‘good’ water quality for all surface waters and groundwaters unless it is impossible or prohibitively expensive;

- promote sustainable water management based on long-term protection of water resources.

These objectives are to be achieved by managing the water environment on the basis of river basins by applying the combined approach of limit values (LV) and environmental quality standards (EQSs) to the control of discharges and by controlling water abstractions from both surface and groundwaters. The Directive will effectively provide the legal basis for the management of Community waters. Whereas previously adopted water-related Directives addressed individual issues (e.g. the control of sewage effluents), the WFD aims to provide an overall framework for the management of water, both in terms of quality and quantity, thus enabling an integrated approach to be taken to achieve the objective of sustainable water management. It aims to balance the needs of water uses within a catchment, using command and control measures, planning and economic instruments.

The Directive will, therefore, have a fundamental impact on existing and proposed legislation. It is likely to incorporate the requirements of current use-related or quality-objective Directives (e.g. the Freshwater Fish, Shellfish, Groundwater, Surface Water, and also the proposed Ecological Directive) and the quality standards laid down in the Dangerous Substances Directive. However, the Urban Waste Water Treatment (UWWT), Nitrates, Bathing Water and the IPPC Directives will remain in force. The proposed Directive will also provide the framework for the integration into water policy of the measures required under other Community legislation, such as the Pesticides, Habitats, Birds (conservation) and Seveso Directives. Many of the Directives will provide some of the measures required to implement the WFD (e.g. to control pollution from certain activities).

Some of the key times for implementation of parts of the proposed Directive are:

- 10 years to develop river basin management plans by a river basin authority (likely to be EA/SEPA) (coastal waters will be assigned to the river basin district). These management plans must register all Protected Areas (which includes European marine sites) in the river basin district.

- A further 6 years to achieve improvements to “good” status with a possible extension for a further 18 years.

“Good surface water status” means the status achieved by a surface water body when both its ecological and chemical status are at least “good”.

“Good ecological status” means the ecological status achieved by a body of water which is demonstrated to be significantly influenced by human activity, but which nevertheless has a rich, balanced and sustainable ecosystem.

“Good chemical status” means the chemical status achieved by a body of water in which concentrations of the substances from Annex VIII of the Directive do not exceed the environmental quality standards established in Annex X of the Directive and other relevant Community legislation setting environmental quality standards and in which the trends in the monitoring data do not suggest that such environmental quality standards will be exceeded in the future.

Surface waters are intended to include ‘transitional waters’ (a general term adopted for estuaries, coastal lagoons etc) and coastal waters out to a limit of 1 nautical mile.

2.2.3 International agreements

2.2.3.1 The Convention on the Protection of the Marine Environment of the North-East Atlantic (the OSPAR Convention)

The OSPAR Convention came into force on 25 March 1998 and replaced the 1972 Oslo Convention on Waste Dumping at Sea and the 1974 Paris Convention on Pollution of the North Sea and Adjacent Areas from Land-Based Sources. The original Oslo and Paris Conventions were administered by the Oslo and Paris Commissions and these also ceased to exist when the OSPAR Commission, commonly abreviated to OSPARCOM, was created to administer the new Convention. There is considerable continuity in the work of OSPARCOM from the work of the former Commissions.

The OSPAR Convention requires signatory countries, including the UK and the European Union, to prevent and, where possible, eliminate pollution of the marine environment (previous Conventions merely required a reduction in pollution). The text of the new Convention places particular emphasis on the use of the ‘polluter pays principle’ and the ‘precautionary approach’. The Convention places particular emphasis on preventing pollution from diffuse sources and, to this end, a list of substances contributing to diffuse pollution has been identified as priority substances for control (see Section 4 and Appendix A).

The Convention's goals are to be achieved by the use of Action Plans that prioritise the most polluting substances and industries and require the application of Best Available Technology (BAT) and Best Environmental Practice (BEP) to eliminate pollution. BAT will be applied to industrial sources whilst BEP will be used to control pollution from diffuse sources. BEP will include increased use of labelling to indicate the polluting potential of products to purchasers, the introduction of collection and recycling systems and the use of economic instruments. Other areas covered by the Convention include:

- a prohibition on waste incineration at sea;
- waste dumping at sea will be prohibited, except for dredged materials, inert materials of a natural origin, fish waste from processing operations and dumping from vessels and aircraft. These exceptions will be banned at the end of 2004. Dumping of sewage sludge at sea was banned from the end of 1998 in line with the Urban Waste Water Treatment Directive;
- the dumping of waste from offshore installations is to be prohibited. BAT and BEP must be applied to eliminate other sources of pollution;
- contracting parties will be required to make information on the state of the sea available to the public, including activities affecting it and control measures to prevent pollution. This requirement is in line with the EU’s Freedom of Information Directive;

- the new Convention tightens up the legal basis for implementing measures agreed under its auspices. Decisions will be binding on countries that voted for them, whilst recommendations will be non-binding. Both are to be agreed unanimously or, where this is not possible, by a three-quarter majority vote;

- signatory countries are required to provide information on their compliance with the Convention.

- the Convention lays down a process for resolving disputes about transboundary pollution.

Implementation of any actions agreed under the Convention requires adoption of UK legislation.

Following a meeting of Ministers of signatory countries in Sintra, Portugal, on 23 July 1998 within the framework of OSPARCOM, a statement was released detailing some priorities for action in the immediate future. The issues meriting further action were:

- Ecosystems and Biological Diversity.

- Hazardous Substances.

- Radioactive Substances and Eutrophication.

Perhaps the most significant of these issues for UK marine waters was the commitment made by Government to be bound by the agreement to ‘ensure that discharges, emissions and losses of radioactive substances are reduced by the year 2020 to levels where the additional concentrations in the marine environment above historic levels, resulting from such discharges, emissions and losses, are close to zero.’ This agreement will have greatest impact on the composition of permitted discharges from Sellafield and Dounreay.

At Sintra, OSPAR member states also committed themselves to:

- ending all opt-outs on the sea dumping of nuclear waste;

- banning the dumping of all steel offshore installations.

2.2.3.2 North Sea Conferences

Concern about the quality of the North Sea resulted in a series of Conferences of the Environment Ministers of countries bordering the North Sea. The decisions reached at these Conferences have had a significant impact on the development of policy and legislation for the protection of the aquatic environment in Western Europe. There have been four Conferences to date and some outstanding commitments remain from the Third Ministerial Conference held in the Hague in 1990 (see Appendix A for a summary of commitments). One of the commitments undertaken by the UK was to reduce the inputs of potentially dangerous substances, subsequently known as the Red List (see Section 4 and Appendix A). At the Fourth Ministerial Conference held in Esjberg in June 1995, Ministers maintained their commitment to reach the reduction targets set by the Third Conference as soon as possible. They agreed to ensure that all permits covering hazardous substances are at least in accordance with internationally agreed BAT (processes) or BEP (activities) by the year 2000. Ministers also agreed to take action to phase out the use of the following hazardous substances by promoting the use of less- or non-hazardous alternatives:

- highly chlorinated short-chained paraffins;
- trichlorobenzene;
- musk xylenes;
- nonyl phenols and nonyl phenolethoxylates, and related substances; and
- brominated flame retardants.

The next conference will be held in Norway at some date during 2000-2002.

Implementation of agreements reached at Ministerial Conferences also requires adoption of UK legislation and/or revision of consents.

2.2.3.3 Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, 1972 (London Convention)

The provisions of the London Convention are global in nature and prohibit the dumping of certain hazardous materials, require a special permit for the dumping of a number of other identified materials and a prior general permit for other wastes or matter. The Convention also bans the dumping of low-level radioactive waste and the incineration of industrial wastes at sea and is administered by the International Marine Organisation (IMO).

A further revision of the Convention (the 1996 Protocol) has been agreed and ratified by the UK which ‘prohibits the dumping of any wastes or other matter with the exception of those listed in Annex I’ (Dredged material, sewage sludge, fish waste or material resulting from industrial fish processing operations, vessels and platforms or other man-made structures at sea is administered by the International Maritime Organisation (IMO), inert, inorganic geological material, organic material of natural origin, and bulky items, primarily comprising iron, steel, concrete and similar unharmful materials). The 1996 Protocol has been ratified by 4 states and requires ratification by 26 countries before it enters into force.

Some of the provisions of the London Convention were incorporated in the Food and Environment Protection Act (FEPA) 1985 and other provisions are covered by other Conventions or international agreements with a more limited geographical scale of application (OPSAR and North Sea Conferences).

2.2.3.4 International Convention on the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto (MARPOL 73/78)

The provisions of MARPOL 73/78 are global in nature and have been adopted by many countries, including the UK. The objective of the measures introduced in the MARPOL 73/78 Convention is to regulate and minimise pollution from ships, ashore and afloat, by oil and other harmful substances. The Convention is administered by the International Maritime Organisation

(IMO) through its Marine Environmental Protection Committee. MARPOL 73/78 deals with the main forms of ship generated waste in five specific annexes:

I - Oil;
II - Noxious liquid substances in bulk;
III - Harmful substances carried by sea in packaged form;
IV - Sewage from ships;
V - Garbage from ships;
VI - Air pollution from ships (under development).

Annexes I, II, IV and V provide specific requirements for the handling and discharge of ship generated wastes and these Annexes are currently in force. Annex IV (Sewage fom ships) is not currently in force but has been signed up to by many member states, including the UK. The provisions of this Annex will apply to ships over 200 tonnes gross or a ship carrying more than 10 persons.

In 1998, the Marine Environmental Protection Committee of the IMO agreed to draft mandatory regulations to phase out the use of toxic antifoulant paints containing organotins, such as tributyltin (TBT), and to propose a timetable for their prohibition. They also agreed to prepare a draft Assembly Resolution for adoption at the 21st Assembly in November 1999 which would urge member states to encourage the use of alternatives to organotin antifouling systems pending the entry into force of the mandatory instrument. One option for the introduction of the mandatory legal instrument is the adoption of a new annex to MARPOL 73/78.

The provisions of MARPOL 73/78 are translated into UK legislation in the Merchant Shipping Acts and Regulations. Further information on the implications of MARPOL 73/78 on Port and Harbour Operations are contained in ABP Research Ltd (1999).

2.3 Competent authorities

For each of the activities identified in Table 4.1, the appropriate legislation identifies a competent authority that exercises the statutory control of that activity. Some legislation also specifies other regulatory bodies that must be consulted by the competent authority in exercising those legislative powers and these are generally termed statutory consultees. Often, consultation with other legislative bodies is undertaken on an informal or non-statutory basis. Where activities involve the construction of a land-based (above Mean High Water) structure, for which planning permission will be required, many of the regulatory bodies will be consulted as part of the planning process.

Tables 2.3, 2.4 and 2.5 identify the competent authorities in England and Wales, Scotland and Northern Ireland respectively and other regulatory bodies involved in the consultation processes. The tables indicate the legislative basis for the role of each regulatory body in relation to the identified activities.

Table 2.3. Common activities and the role/function of regulatory authorities in England and Wales with some responsibility for the control of activities with a potential to degrade water quality at European marine sites
(CA - Competent authority; SC - Statutory consultee; NSC - Non-statutory consultee; PL - influence through the planning process)
(refer to Table 4.1 for the effects of these activities on water quality)

	Environment Agency	**MAFF**	**DETR**	**National Assembly for Wales**	**English Nature**	**Countryside Council for Wales**	**Local authorities**	**Other**
Discharge via pipes of sewage, sewage effluent, storm water and liquid effluents from industry (including cooling waters from power stations) to rivers, estuaries and coastal waters;	CA[1], SC[2]	SC[3]	PL[4]	SC[3], PL[4]	SC[5]	SC[5]	PL[6], SC[7]	WSplc: SC[8]
Abstraction of freshwater for irrigation, industrial processes and drinking water purposes;	CA[9], SC[2]		PL[4]	PL[4]	SC[5]	SC[5]	PL[6]	WSplc: SC[10]
Abstraction of saltwater for cooling and drinking water purposes;	SC[2]		PL[4]	PL[4]	SC[5]	SC[5]	PL[6]	
Maintenance dredging in estuaries and coastal waters;			CA[11]	CA[11]	SC[5]	SC[5]	CA[35]	Port and harbour authorities: CA[12]
Capital dredging in estuaries and coastal waters	SC[2]	NSC	PL[4]	PL[4]	SC[5]	SC[5]	PL[6]	Port and harbour authorities: CA[12]
Aggregate extraction in estuaries and coastal waters	NSC	NSC	CA[13]	CA[13], NSC	SC[5]	SC[5]	NSC	Crown estate: CA[14]
Disposal of wastes (including dredge spoil) in estuaries and coastal waters;	NSC	CA[15]	CA[11]		SC[5]	SC[5]	PL[6]	
Aquaculture in estuaries and coastal waters;	CA[1], SC[2]	CA[16]	CA[11], PL[4]	CA[16], PL[4]	SC[5]	SC[5]	PL[6]	Crown Estate: CA[17]
Oil/ gas exploration in estuaries and coastal waters; pollution from offshore installations	NSC	NSC	NSC	NSC	SC[5]	SC[5]	PL[6]	DTI: CA[18]

	Environment Agency	**MAFF**	**DETR**	**National Assembly for Wales**	**English Nature**	**Countryside Council for Wales**	**Local authorities**	**Other**
Pollution arising from shipping in estuaries and coastal waters.	CA[19]	NSC[20]	CA[21]	NSC[20]	SC[20, 5]	SC[20, 5]	NSC[20]	Port and harbour authorities: CA[22]
Commercial fishing for fin and shell fish in estuaries and coastal waters.	CA[23]	CA[24]		CA[24]				Sea Fisheries Committees: CA[25]
Land reclamation, marine construction works (including harbours and marinas) and beach replenishment in estuaries and coastal waters.	SC[26]	CA[26]	CA[11,28] PL[4]	PL[4]	SC[5,26]	SC[5,26]	PL[6], SC[26]	Crown Estate: SC[28]
Flood defence in estuaries and coastal waters.	CA[29]	CA[30]		CA[30]	SC[5]	SC[5]	CA[29]	Internal Drainage Boards: CA[29]
Placement of structures in the sea (including windfarms).	SC?	CA[27]	CA[11]	CA[27]?	SC[5]	SC[5]		Crown estate: CA[17] DTI: CA[18]
Land use in the catchments of estuaries and coastal waters.	NSC[31]	CA[32]	PL[4]	CA[32], PL[4]	SC[5]	SC[5]	PL[6]	
Discharge of gaseous emissions to the atmosphere.	CA[33]		PL[4]	PL[4]	SC[5]	SC[5]	CA[34], PL[6]	

Notes

[1] The Environment Agency is the competent authority for the consenting of discharges via pipes (including cage fish farms) to controlled waters and for the authorisation of discharges to water from certain industrial processes;

[2] The Environment Agency is a statutory consultee for certain planning applications;

[3] MAFF (and the National Assembly for Wales Agriculture Department) is a statutory consultee with respect to possible impacts of sea fisheries. Consent applications are also referred to Sea Fisheries Committees at the request of MAFF (WEAD). Some Environment Agency regions have sea fisheries powers in estuaries;

[4] The Secretary of State at DETR (and the National Assembly for Wales (NAW)) is the final arbiter in planning applications which cannot be resolved by local planning authorities.

[5] English Nature in England and CCW in Wales are statutory consultees under the Conservation (Habitats &c.) Regulations 1994 where a ‘plan or project’ is likely to have a significant effect on a European (marine) site;

[6] Local authorities are the local planning authority and are responsible for dealing with planning applications for works associated with a discharge, an abstraction or other land-based works. Some works may require an Environmental Assessment;

[7] Local authorities are consulted for all consent applications;

[8] The appropriate Water Service plc (WSplc) is a statutory consultee in relation to water supply issues;

[9] The Environment Agency is the competent authority for the granting of abstraction licences from rivers and estuaries;

[10] Persons applying for a licence to abstract are required to serve a notice to the appropriate WS plc;

[11] Consent from DETR Ports Division is required where there are implications for the provision of safety of navigation;

[12] Port and harbour authorities administer maintenance and capital dredging and are governed by their own legislation;

[13] Minerals and Land Reclamation Division of DETR (and NAW Transport, Planning and Environment Group in Wales) administers the 'Government View' procedure which determines whether an application for aggregate extraction is granted;

[14] Crown Estate issues a licence for aggregate extraction from the sea bed following a favourable 'Government View' of the proposed operation;

[15] MAFF is responsible for the issue of a disposal licence under the provisions of Part II of FEPA 1985;

[16] MAFF registers fish farming (and saltwater shellfish farming) businesses under fish diseases legislation;

[17] Crown Estate acts as a landowner leasing the sea bed for various uses;

[18] DTI Oil and Gas Directorate issues licences to explore for and exploit the petroleum resources of Great Britain, the United Kingdom territorial sea and the UK Continental Shelf. The Department is also responsible for the granting of consents for certain activities carried out under those licences and for the decommissioning of oil and gas installations. Prior to offering petroleum licences, the Department consults widely with other Government Departments and (through the JNCC) the nature conservation agencies, i.e. EN and CCW. The DTI is also responsible for giving consent to the siting of offshore wind farms in excess of 50 megawatts capacity under Section 36 of the Electricity Act 1989.

[19] The Environment Agency has powers to prosecute for a pollution incident in controlled waters;

[20] MAFF (and NAW), the statutory nature conservation agencies and local authorities are consulted in the event of a pollution incident affecting coastal waters;

[21] DETR is the competent authority for enforcing Merchant Shipping legislation;

[22] Port and harbour authorities are required to provide waste reception facilities for ships entering ports and harbours;

[23] The Environment Agency is responsible for licensing migratory species, eg eel, salmon and sea trout. Some Environment Agency regions have Sea Fishery Committee powers;

[24] MAFF regulates fisheries within UK territorial waters (12 miles) through national and EU legislation;

[25] Sea Fisheries Committees regulate commercial sea fisheries (to the 6 mile limit) by introducing and enforcing byelaws;

[26] The Environment Agency, DETR, the statutory nature conservation agencies, local planning authorities and the Crown Estate would be consulted by MAFF in consideration of a licence for these activities which is required under FEPA 1985.

[27] MAFF is the competent authority for issuing licences for these activities under FEPA 1985;

[28] If the activity is to be undertaken on seabed owned by the Crown Estate, then DETR administer an approval process which, if favourable, results in the issue of licence by the Crown Estate;

[29] The Environment Agency, local authorities and Internal Drainage Boards are operating authorities responsible for planning, design, construction, maintenance and operation of flood defence measures;

[30] MAFF (and NAW) has overall policy responsibility for flood defence and coastal protection in England and Wales;

[31] The Environment Agency produces Local Environment Agency Plans (LEAPs) on a sub-catchment basis to inform land-use and planning issues affecting water, land and air quality;

[32] MAFF (and NAW) implements policies influencing agricultural activities in catchments;

[33] The Environment Agency is responsible for issuing authorisations for emissions to the atmosphere for certain ‘heavy’ industrial processes;

[34] Local authorities are responsible for the Local Air Pollution Control (LAPC) system controlling emissions from ‘light’ industrial processes.

[35] Some local authorities are harbour authorities.

Table 2.4. Common activities and the role/function of regulatory authorities in Scotland with some responsibility for the control of activities with a potential to degrade water quality at European marine sites

(CA - Competent authority; SC - Statutory consultee; NSC - Non-statutory consultee; PL - influence through the planning process)

(refer to Table 4.1 for effects of these activities on water quality)

	SEPA	**SERAD**	**Scottish Executive**	**Scottish Natural Heritage**	**Local authority**	**Other**
Discharge via pipes of sewage, sewage effluent, storm water and liquid effluents from industry (including cooling waters from power stations) to rivers, estuaries and coastal waters;	CA[1], SC[2]	SC[3]	PL[4]	SC[5]	PL[6], SC[7]	Water Authority: SC[8]
Abstraction of freshwater for irrigation, industrial processes and drinking water purposes;	CA[9], SC[2]		PL[4]	SC[5]	PL[6]	Water Authority: SC[10]
Abstraction of saltwater for cooling purposes in power stations	SC[2]		PL[4]	SC[5]	PL[6]	
Maintenance dredging in rivers, estuaries and coastal waters;		CA[11]		SC[5]		Port and harbour authorities: CA[12]
Capital dredging in estuaries and coastal waters	SC[2]	NSC	PL[4]	SC[5]	PL[6]	
Aggregate extraction in estuaries and coastal waters	NSC	NSC, CA[13]		SC[5]	NSC	Crown Estate: CA[14]
Disposal of waste (including dredge spoil) in estuaries and coastal waters;	NSC	CA[15]		SC[5]		
Aquaculture in estuaries and coastal waters;	CA[1], SC[2]	CA[16]	PL[4]	SC[5]	PL[6]	Crown Estate: CA[17]
Oil/ gas exploration and mineral extraction in estuaries and coastal waters; pollution from offshore installations	NSC	NSC	CA[18]	SC[5]		DTI CA[18]
Pollution arising from shipping in estuaries and coastal	CA[19]	SC[20]	CA[21]	SC[20]	SC[20]	Port and harbour

	SEPA	**SERAD**	**Scottish Executive**	**Scottish Natural Heritage**	**Local authority**	**Other**
waters;						authorities: CA[22]

	SEPA	SERAD	Scottish Executive	Scottish Natural Heritage	Local authority	Other
Commercial fishing for fin and shell fish in estuaries and coastal waters.		CA[23]		SC[5]		
Land reclamation, marine construction works (including harbours and marinas) and beach replenishment in estuaries and coastal waters;	SC[24]	CA[25]	PL[4]	SC[5]	PL[6]	Crown Estate: CA[26]
Flood defence in estuaries and coastal waters;		CA[27]		SC[5]	CA[28]	
Placement of structures in the sea (including windfarms)	SC	CA[25]	CA[11]	SC[5]		Crown Estate: CA[26] DTI CA[18]
Land use in the catchments of estuaries and coastal waters.	NSC[29]	CA[30]	PL[4]	SC[5]	PL[6]	
Discharge of gaseous emissions to the atmosphere from industrial processes.	CA[31]		PL[4]	SC[5]	PL[6]	

Notes

[1] SEPA is the competent authority for consenting discharges via pipes (including cage fish farms) to controlled waters and for the authorisation of discharges to water from certain industrial processes;

[2] SEPA is a statutory consultee for certain planning applications;

[3] Scottish Executive Rural Affairs Department (SERAD) is a statutory consultee with respect to possible impacts of sea fisheries;

[4] The Scottish Executive is the final arbiter in planning applications which cannot be resolved by local planning authorities.

[5] Scottish Natural Heritage (SNH) is a statutory consultee under the Conservation (Habitats &c.) Regulations 1994 where a ‘plan or project’ is likely to have a significant effect on a European (marine) site;

[6] Local authorities are the local planning authority and are responsible for dealing with planning applications for works associated with a discharge, an abstraction or other land-based works. Some works may require an Environmental Assessment;

[7] Local authorities are consulted for all consent applications;

[8] The appropriate Water Authority is a statutory consultee in relation to water supply issues;

[9] SEPA is the competent authority for the granting of abstraction licences from rivers and estuaries;

[10] Persons applying for a licence to abstract are required to serve a notice to the appropriate Water Authority;

[11] Consent from the Scottish Executive is required where there are implications for the provision of safety of navigation;

[12] Port and harbour authorities administer maintenance dredging and are governed by their own legislation;

[13] The Scottish Development Department administers the ‘Government View’ procedure which determines whether an application for aggregate extraction is granted;

[14] Crown Estate issues a licence for aggregate extraction from the sea bed following a favourable ‘Government View’ of the proposed operation;

[15] SERAD is responsible for the issue of a disposal licence under the provisions of Part II of FEPA 1985;

[16] SERAD registers fish farming (and saltwater shellfish farming) businesses under fish diseases legislation;

[17] Crown Estate acts as a landowner leasing the sea bed for various uses;

[18] DTI Oil and Gas Directorate issues licences to explore for and exploit the petroleum resources of Great Britain, the United Kingdom territorial sea and the UK Continental Shelf. The Department is also responsible for the granting of consents for certain activities carried out under those licences and for the decommissioning of oil and gas installations. Prior to offering petroleum licences, the Department consults widely with other Government Departments and (through the JNCC) the nature conservation agencies, i.e. SNH. The DTI also has responsibility for giving consent to the siting of offshore wind farms in excess of 50 megawatts capacity under Section 36 of the Electricity Act 1989;

[19] SEPA has powers to prosecute for a pollution incident in controlled waters;

[20] SERAD, statutory nature conservation agencies and local authorities are consulted in the event of a pollution incident affecting coastal waters;

[21] The Scottish Executive is the competent authority for enforcing Merchant Shipping legislation;

[22] Port and harbour authorities are required to provide waste reception facilities for ships entering ports and harbours;

[23] SERAD is the competent authority for commercial sea fisheries in coastal waters (to the 12 mile limit);

[24] SEPA, Scottish Executive Departments, local planning authorities and the Crown Estate would be consulted by SERAD in consideration of a licence for these activities which is required under FEPA 1985.

[25] SERAD is the competent authority for issuing licences for these activities under FEPA 1985;

[26] If the activity is to be undertaken on seabed owned by the Crown Estate, then SERAD administers an approval process which, if favourable, results in the issue of licence by the Crown Estate;

[27] The Scottish Executive has some policy responsibility for flood defence and coastal protection in Scotland;

[28] Local authorities are responsible for planning, design, construction, maintenance and operation of flood defence measures with respect to non-agricultural land. Landowners have responsibility for agricultural land;

[29] SEPA provides advice to farmers on the protection of water and soil from pollution from agricultural activities;

[30] SERAD implements policies determining agricultural activities in catchments;

[31] SEPA is responsible for issuing authorisations for emissions to the atmosphere.

Table 2.5. Common activities and the role/function of Regulatory authorities in Northern Ireland with some responsibility for the control of activities with a potential to degrade water quality at European marine sites
(CA - Competent authority; SC - Statutory consultee; NSC - Non-statutory consultee; PL - influence through the planning process)
(refer to Table 4.1 for effects of these activities on water quality)

	Environment and Heritage Service	DANI	Northern Ireland Office	Local authorities	Other
Discharge via pipes of sewage, sewage effluent, storm water and liquid effluents from industry (including cooling waters from power stations) to rivers, estuaries and coastal waters;	CA[1], SC[2,5]	SC[3]	PL[4]	PL[6, 7]	Water Service: SC[8]
Abstraction of freshwater for irrigation, industrial processes and drinking water purposes;	CA[9], SC[2,5]		PL[4]	PL[6]	Water Service: SC[10]
Abstraction of saltwater for cooling water purposes;	SC[2,5]		PL[4]	PL[6]	
Maintenance dredging in rivers, estuaries and coastal waters;	SC[5]		CA[11]		Port and harbour authorities: CA[12]
Capital dredging in rivers, estuaries and coastal waters	SC[2,5]	NSC	PL[4]	PL[6]	
Aggregate extraction in estuaries and coastal waters	SC[5], NSC	NSC	CA[13]	NSC	Crown Estate: CA[14]
Disposal of wastes (including dredge spoil) in estuaries and coastal waters;	CA[15], SC[5], NSC	NSC	CA[11]		
Aquaculture in estuaries and coastal waters	CA[1], SC[2,5]	CA[16]	CA[11], PL[4]	PL[6]	Crown Estate: CA[17]
Oil/ gas exploration and mineral extraction in estuaries and coastal waters; pollution from offshore installations	NSC, SC[5]	NSC			DTI: CA[18]
Pollution arising from shipping in estuaries and coastal waters	CA[19], SC[5,20]	SC[20]	CA[21]	SC[20]	Port and harbour authorities: CA[22]
Commercial fishing for fin and shell fish in estuaries and coastal waters.	SC[5]	CA[23]			

	Environment and Heritage Service	DANI	Northern Ireland Office	Local authorities	Other
Land reclamation, marine construction works (including harbours and marinas) and beach replenishment in estuaries and coastal waters;	CA[24]	SC[25]	SC[25], PL[4]	PL[6]	Crown Estate: SC[26]
Flood defence in estuaries and coastal waters;	SC[5]	CA[27]			Rivers Agency: CA[28]
Placement of structures in the sea (including windfarms)	CA[24], SC[5]	NSC	CA[11]		Crown Estate: CA[17] DTI, CA[18]
Land use in the catchments of estuaries and coastal waters.	NSC[29]	CA[30]	PL[4]	PL[6]	
Discharge of gaseous emissions to the atmosphere	CA[31], SC[5]		PL[4]	PL[6]	

Notes

[1] The Environment and Heritage Service is the competent authority for the consenting of discharges via pipes (including cage fish farms) to controlled waters and for the authorisation of discharges to water from certain industrial processes;

[2] The Environment and Heritage Service is a statutory consultee for certain planning applications;

[3] The Department of Agriculture for Northern Ireland (DANI) is a statutory consultee with respect to possible impacts of sea fisheries;

[4] The Secretary of State for Northern Ireland is the final arbiter in planning applications which cannot be resolved by local planning authorities.

[5] The Environment and Heritage Service is a statutory consultee under the Conservation (Habitats &c.) Regulations 1994 where a ‘plan or project’ is likely to have a significant effect on a European (marine) site;

[6] Local authorities are the local planning authority and are responsible for dealing with planning applications for works associated with a discharge, an abstraction or other land-based works. Some works may require an Environmental Assessment;

[7] Local authorities are consulted for all consent applications;

[8] The Water Service is a statutory consultee in relation to water supply issues;

[9] The Environment and Heritage Service is the competent authority for the granting of abstraction licences from rivers and estuaries;

[10] Persons applying for a licence to abstract are required to serve a notice to the Water Service;

[11] Consent from the Northern Ireland Office is required where there are implications for the provision of safety of navigation;

[12] Port and harbour authorities administer maintenance dredging and are governed by their own legislation;

[13] The Northern Ireland Office administers the ‘Government View’ procedure which determines whether an application for aggregate extraction is granted;

[14] Crown Estate issues a licence for aggregate extraction from the sea bed following a favourable ‘Government View’ of the proposed operation;

[15] The Environment and Heritage Service is responsible for the issue of a disposal licence under the provisions of Part II of FEPA 1985;

References

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3. Decision-making process by relevant authorities

This Section contains summary information on the issues taken into consideration by the main authorities when making decisions on potential impacts of water quality.

3.1 England and Wales

3.1.1 Environment Agency

The Environment Agency was established on 1st April 1996 under the provisions of the Environment Act 1995 and has duties which include the following:

- to monitor the state of pollution and other aspects of the environment;
- to regulate industrial processes with the greatest pollution potential so as to prevent or minimise pollution to the environment as a whole;
- to regulate the disposal of radioactive waste;
- to regulate the treatment, keeping, movement and disposal of controlled waste so as to prevent pollution of the environment or harm to human health;
- to preserve or improve the quality of rivers, estuaries and coastal waters through powers to regulate, prevent, mitigate or remedy pollution of water;
- to take any action to conserve, redistribute, augment and secure the proper use of water resources;
- to exercise a general supervision over all matters relating to flood defence;
- to maintain, improve and develop salmon, trout, freshwater and eel fisheries;
- to promote the conservation and enhancement of inland and coastal waters, and their use for recreation;
- to maintain or improve non-marine navigation.
- to regulate the remediation of contaminated land designated as special sites.

The Environment Agency's powers to control pollution of tidal waters are underpinned in large part by the provisions of the Water Resources Act 1991 (Section 2.2.1.4). Pollution of tidal waters from the land can arise from pollution incidents (e.g. accidental spillages), diffuse sources (e.g. agricultural run-off) and from point sources (e.g. from a fixed pipe discharge). The Environment Agency has various powers to control, prevent, mitigate or remedy pollution from these sources.

3.1.1.1 Pollution incidents

The Environment Agency has powers (under Section 161 of the Water Resources Act 1991) to remedy or mitigate the effects of pollution in controlled waters (see definition of such waters in Section 2.2.1.4), and to remove or dispose of polluting matter in them. The Environment Agency co-operates with the Counter Pollution Branch (formerly the Marine Pollution Control Unit) of the Maritime and Coastguard Agency in responding to accidental spillages of substances from ships or pipelines (see Section 3.1.3). The lead organisations for responding to spills depend on the location and scale of the incident.

3.1.1.2 Pollution from diffuse sources

Pollution from diffuse sources is the most difficult to control since the sources of the polluting substances cannot be readily identified and therefore cannot be consented or treated. Diffuse source pollution enters the marine environment direct from land adjacent to estuarine or coastal waters, from freshwater inputs draining the land and from the atmosphere.

The most common groups of pollutants from land drainage are nutrients (principally from agricultural use of fertilisers), pesticides (mainly from agricultural use) and suspended solids (from land management activities).

Control of pollution from diffuse sources is exercised by a combination of standards applying to the use of particular products, by pollution prevention advice provided to potential polluters (e.g. farmers) and by the control of activities in designated areas.

A number of Product Directives have been adopted by the EU to prohibit the use of certain products or restrict the type of product which may be used. For example, the Detergent Directive requires a certain degree of biodegradability before a surfactant may be marketed in detergents. Similarly, the Pesticides Directive restricts the use of pesticides and specifies the purpose and application rate. However, even though the Directives or voluntary bans (e.g. the ban by local authorities to use the herbicides atrazine and simazine for road verge treatment) may prohibit or restrict the use of a substance, it may nevertheless still be present by being imported with raw materials or finished products (e.g. pesticides on imported wool).

Pollution prevention advice is provided by the Environment Agency, in collaboration with other appropriate regulatory bodies as necessary in the form of Pollution Prevention Guidance (PPG) notes and codes of good practice. For example, such advice for farmers and land managers has been provided with the collaboration of MAFF and representatives from the industry in the form of the Codes of Good Agricultural Practice for Water, Air and Soil.

Existing legislation allows for the designation of Water Protection Zones (WPZs) and Nitrate Sensitive Areas (NSAs). WPZs can be designated by Ministerial order and, within this, specific restrictions or prohibitions on particular activities can be applied. Only one WPZ has been designated in 1999 dealing with the storage of chemicals near the River Dee. NSAs have only been designated to date in relation to water supply sources with elevated nitrate concentrations and have not been used to protect controlled waters from nitrate contamination. The Environment Agency acknowledges that enforcement and monitoring of measures to control diffuse pollution is much more difficult than for point sources (Environment Agency 1998).

Atmospheric deposition introduces nitrogen, metals, persistent organic substances and radionuclides to the marine environment. These substances reach the atmosphere from point source emissions with the control mechanisms being applied at the point of discharge. These are controlled by two systems established by the Environmental Protection Act 1990. The system of IPC addresses emissions from heavy industry and is enforced by the Environment Agency. The Local Authority Air Pollution Control (LAAPC) system addresses emissions from other point sources and is enforced by local authorities in England and Wales. Emissions of radionuclides to the atmosphere are controlled by the Environment Agency under the provisions of the Radioactive Substances Act 1993.

3.1.1.3 Pollution from point sources

Pollution from point sources is controlled, either by the application of a discharge consent granted by the Environment Agency under the provisions of the Water Resources Act 1991, or by the issue of an IPC 'authorisation' for 'prescribed' processes by the Environment Agency under the provisions of the Environmental Protection Act 1990. These procedures aim to ensure that substances legitimately discharged to the environment do not cause pollution.

a. Discharge consents

The Environment Agency's approach to discharge consents largely follows that explained in *Discharge consents and compliance. The NRA's approach to control of discharges to water* produced by the NRA (NRA 1994). **The Environment Agency has produced a discharge consents manual which sets out detailed policies and technical information for the setting of all discharge consents. Many recent consents and all new authorisations will be set with reference to this manual**. For discharges from sewage treatment works which have to comply with the requirements of the UWWTD, recent guidance from DETR provides information on the setting of appropriate consents (DETR 1997).

Point source discharges to the marine environment comprise sewage and industrial effluent from non-prescribed processes. Occasionally, discharges from industrial processes (trade effluent) are made directly to sewer. This is licensed by the appropriate water company and conditions are set in relation to the discharge consent for the combined effluent when it is eventually discharged to a receiving water. Marine cage fish farm installations are also considered point source discharges and are controlled by the consents process. Marine cage fish farming occurs mainly in Scotland and is considered with respect to the duties of SEPA (see Section 3.2.1) and will not be considered further here.

The procedure for obtaining a discharge consent from the Environment Agency is described in Schedule 10 of the Water Resources Act 1991 for England and Wales. Application for a consent must contain all information related to the discharge required by the authority including the location of the discharge, and the composition and quantity of effluent. The Agency is required to advertise the consent application in the local newspaper and the London Gazette and to inform the appropriate local authorities. Representations and objections to the application must be received within six weeks of advertising. The Agency will subsequently decide whether a discharge consent should be given. However, before a formal discharge consent can be given, the Agency must notify all those who have made representations or an objection to their decision. 21 days are then allowed, during which the Secretary of State may be asked to review the application.

If a consent is issued, it may be subject to conditions, in particular relating to the:

- location of the discharge;
- design and construction of the outlet;
- composition and quantity of effluent;
- sampling requirements;
- flow metering requirements;
- records which must be kept.

The discharger can appeal to the Secretary of State regarding the conditions placed on the consent. The Agency can grant a consent without publishing or advertising an application if it considers that the proposed discharge will have not appreciable effect on the receiving water. The Agency can also grant an unconditional consent.

It is the duty of the Agency to review consents periodically (every two years). This can lead to:

- revocation of the consent;
- modification of the consent; and
- amendment of an unconditional consent to one containing conditions.

The consents may also be modified:

- to allow the UK Government to implement EU legislation and international agreements;
- to protect public health or fauna and flora dependent on the aquatic environment;
- in response to any representation or objection made to the Secretary of State or otherwise.

However, each consent must state the period for which the consent is valid.

The Agency must keep a register of all data relevant to the discharge and the receiving water. The information must contain details of any water quality objectives, the discharge consent and the monitoring data for the discharge and the receiving water. The register must also be readily accessible to the public.

Sewage discharges

Sewage effluent can vary in nature depending on the degree to which the sewage has been treated (see Box 1). Discharges of sewage effluent can arise from a number of different sources and be continuous or intermittent in nature:

- treated effluent from urban sewage treatment plants (continuous);

- storm discharges from urban sewage treatment plants (intermittent);
- effluent from ‘package’ sewage treatment plants serving small populations (continuous);
- combined sewer and emergency overflows from sewerage systems (intermittent);
- septic tanks (intermittent);
- crude sewage discharges at some estuarine and coastal locations (continuous).

Box 1. Sewage treatment

Treatment of sewage ranges from:

- none at all (crude sewage);
- preliminary (screening and/or maceration to remove/disguise solid matter);
- primary (settling to remove suspended solids as sewage sludge). Typically removes 40% of BOD, 60% of suspended solids; 17% of nitrogen and 20% of phosphorus from the untreated sewage;
- secondary (settling and biological treatment to reduce the organic matter content). Typically removes 95% of BOD, 95% of suspended solids; 29% of nitrogen and 35% of phosphorus from the untreated sewage. Nutrient removal steps can be incorporated into secondary treatment which can reduce ammonia -N down to 5 mg/l, nitrogen to 10 mg/l and phosphorus to 2 mg/l.
- tertiary (settling, biological treatment and an effluent polishing step which may involve a reed bed (unlikely for a coastal works) or a treatment to reduce the load of micro-organisms in the effluent). Typically removes 100% of BOD, 100% of suspended solids, 33% of nitrogen and 38% of phosphorus from the untreated sewage.

The form of the consent for these discharges depends both on the type of effluent discharged and their periodicity. In general, discharges of continuous sewage effluent (i.e. effluent discharged at all times) have consents with numeric conditions for substances or groups of substances among other conditions on the consent. For intermittent discharges (usually of sewage effluent or storm sewage), consents are descriptive and relate to the number of discharge events in a specified time period (termed the spill frequency).

Numeric consents for sewage effluents are generally expressed in terms of a 95 percentile, which means that samples of the effluent must not exceed the numeric condition for that substance on more than 95 percent of occasions, and an upper tier, which means that exceedance must not occur on more than 99.5% of occasions. Look-up tables are used by the regulator to enable this condition to be translated into the number of samples that are allowed to exceed the conditions. The use of the 95 percentile reflects the fact that dischargers of sewage have little control on the variability in composition of sewage entering treatment works such that, occasionally, the treatment process will not be able to deliver the typical reductions in the main components of the sewage. The use of the upper tier prevents flagrant abuse of the 5% of occasions when 95 percentile consent limits can be exceeded.

The numeric limits in discharge consents are set such that the quality of the receiving water is maintained for all existing uses and to comply with relevant statutory requirements. The process of relating concentrations of a substance in the receiving water to numeric limits in a discharge consent can be complex, especially in tidal waters. The concept of the mixing zone is applied to allow consent conditions to be related to environmental concentrations of polluting substances (see Section 6.2.1 for further details). The mixing zone is an area of receiving water around the discharge point within which EQSs can be exceeded. The choice of the size of a mixing zone is somewhat arbitrary and a diameter of 100 m is commonly used. For the majority of situations, mass-balance or modelling approaches are adopted. Mass-balance calculations essentially involve defining the effective volume of the receiving water and calculating the amount of a substance that can be discharged into that volume to achieve a desired concentration. More complicated modelling approaches can be undertaken but these are usually reserved for particularly sensitive situations, e.g. where more than one discharge is under consideration, where discharges are close to bathing waters and when compliance with appropriate standards is likely to be borderline.

Decisions on appropriate consent conditions include consideration of the uses to which the receiving waters are put and the application of a policy of ‘no deterioration’ under the Shellfish Waters Directive.

For tidal waters, the following receiving water uses are considered:

- basic amenity and conservation of the general ecosystem;
- passage of migratory fish;
- commercial fisheries for fish, molluscs and crustacea for public consumption;
- bathing and other water contact based recreation;
- other recognised uses, such as industrial abstractions and harvesting of edible seaweed.

In addition, the requirements of the following legislation and commitments must be considered:

- EC Bathing Waters Directive and UK Regulations (appropriate mandatory or indicative standards must be met at designated bathing waters in the vicinity of the discharge);
- EC Urban Waste Water Treatment Directive and UK Regulations (the appropriate level of treatment should be applied to the sewage, based on the population equivalent of the agglomeration served by the sewerage system and on the nature of the receiving water (HNDA or a sensitive area);
- EC Dangerous Substances Directive and UK Regulations (EQSs for List I and II substances in receiving waters must be met, including standstill provisions);
- EC Shellfish Directive and UK Regulations (appropriate standards must be met for designated shellfish waters in the vicinity of the discharge);
- North Sea Conference and OSPAR commitments (commitments on the reduction in loads of toxic substances in discharges to the marine environment must not be compromised).

The policy of ‘no deterioration’ as it applies to estuaries and coastal waters encompasses statutory requirements and includes provisions not to allow an increase in consented loads in existing discharges (particularly for ammonia and BOD in estuaries) and for all discharges not to allow more than a 10% change in receiving water quality unless there is insignificant environmental change as a consequence (particularly for bacteriological parameters in coastal waters in relevant circumstances).

For intermittent discharges of sewage from Combined Sewer Overflows (CSOs), the spill frequency is based on the uses of the receiving waters. Where discharges are likely to affect bathing waters, the spill frequency on the discharge consent will vary between 3 spills per bathing season where the discharge is below Mean Low Water Springs (MLWS) to 1 spill every 5 years for discharges above Mean High Water Springs (MHWS). For the majority of CSOs, the consent conditions will only relate to bathing seasons, that is, at a time when rainfall is usually lowest and when spill frequencies are likely to be less frequent. Control of CSO discharges in other waters is less well defined but should be sufficient to avoid nuisance and protect existing uses.

Industrial discharges

Industrial discharges are regulated by the Environment Agency under Integrated Pollution Control (IPC) if the process is ‘prescribed’; under UWWT Regulations if the effluent is similar in nature to sewage; or under the provisions of the Water Resources Act 1991.

In practice, the approach to granting consents or authorisations is similar to that for sewage discharges. The main difference being that it is recognised that there is a greater degree of control on the composition of the effluent arising from industrial processes and, therefore, the numeric limits on the consents are set as absolute limits which must not be exceeded under any circumstances. Industrial effluents also tend to contain more toxic substances and numeric limits in consents and authorisations are set to ensure compliance with EQSs, where they exist, in receiving waters. There are many substances for which there is no EQS. In such cases, dischargers are required to provide as much information as possible on concentrations and loads in the effluent, and ecotoxicological effects in the environment, to support the consent application on which basis the Environment Agency will set appropriate consent conditions.

Some industrial discharges contain complex and varying mixtures of toxic substances, making the approach of setting consent conditions for each component problematic. The difficulties include:

- Cost and potential difficulties of chemical determination of all constituents;
- Frequent lack of ecotoxicological data for identified substances; and
- Difficulties in predicting the interaction between chemicals and how they combine to affect the environment.

In these circumstances, an alternative approach to consent setting is used, namely direct assessment and control of the toxicity of the whole effluent - Direct Toxicity Assessment (DTA). Samples are taken of an effluent and toxicity tests performed to assess the potential impact of the effluent. If toxicity is detected but considered acceptable, a toxicity based consent can be derived and applied. If the toxicity of the effluent is not acceptable, remedial action may be needed (i.e.

eliminate, substitute, treat) and then a toxicity based consent can be applied (or a chemical consent if more appropriate).

b. Abstraction licences

Abstraction licences are issued by the Environment Agency under the provisions of the Water Resources Acts 1963 and 1991 (see Section 2) and provide authorisation for the impoundment and/or abstraction of water from inland waters. Abstractions of less than 5 cubic metres do not require a licence and those less than 20 cubic metres require approval but not a formal licence. All abstractions greater than 20 cubic metres require a licence, with the exception of the removal of water for land drainage, mining, quarrying and related activities and for such uses as fire fighting.

The process for issuing a licence begins with an application from the abstractor (with the assistance of the Environment Agency) who should provide the correct information to enable the decision to be made within the agreed timescale. The application is advertised locally and in the London Gazette to enable representations to be made by interested parties. Statutory consultation is also carried out with Internal Drainage Boards, Navigation, Harbour and Conservancy authorities, and with English Nature/CCW where an SSSI or a European site is likely to be affected. Once respresentations have been received, the application is circulated within the Environment Agency for consideration of implications for fisheries, flood defence and water quality.

The key consideration in considering an application for water abstraction is the flow or level in the water body providing the supply. The Environment Agency has a duty to ensure that interests downstream of the abstraction will not be compromised. The Agency has the power to set conditions on the licence to ensure that the abstraction does not compromise such interests. A common condition on a licence is one that sets a prescribed flow or level in the water body below which abstraction is not permitted. This can be associated with a “hands off” condition which means that an appropriate structure of weirs or sluices has been put in place that automatically ensures that water is not abstracted when the flow or level falls below the prescribed level. The “hands off” condition is preferred because it is more reliable than a system involving human intervention to prevent abstraction. The legislation refers to minimum acceptable flows in water bodies but these have not been determined in practice and so are not used when considering abstraction applications.

Abstraction licences remain in force until revoked by the applicant or the Environment Agency. However, the Government is consulting on new legislation that would allow abstraction licences to be reviewed on a more regular basis.

The requirements for abstraction licences from estuaries and coastal waters are more complicated than for surface freshwaters. Abstractions from estuaries and coastal waters where the intake is below mean low water do not usually require abstraction licences. There are no limits on the amount of water that can abstracted. However, if the abstractor constructs an impoundment to collect water on high tides and then abstracts from the impoundment, a licence to abstract from the impoundment will be required. This is to protect any features that might exist within the impoundment. Abstractions from above mean low water in estuaries do require licences but no charge is made for the water and few limits on the amount of water abstracted will be applied.

The Environment Agency’s abstraction licensing manual details the guidance and technical procedures used when considering licences to abstract.

3.1.2 MAFF

The Ministry of Agriculture Fisheries and Food (MAFF) has the following responsibilities related directly to water quality in the marine environment:

! Licensing of the deposit of wastes and other substances at sea under Part II of the Food and Environment Protection Act (FEPA) 1985 (see Section 2.2.1.6);

! Statutory consultee in the consent setting process for discharges from pipelines to sea.

3.1.2.1 FEPA licences

MAFF is the competent authority in England for the issue of licences for the disposal of wastes and other substances to sea, e.g. those used during construction of, for example, pipelines (the sea includes beaches, mudflats and any other areas submerged at Mean High Water Springs). MAFF also acts under an administrative arrangement with the National Assembly for Wales for applications in Wales (see Section 3.1.5). Such wastes include colliery wastes, dredged materials, offshore installations (such as oil rigs), fish waste, and, up until the end of 1998, sewage sludge. Applications for licences to dispose of wastes are sent to MAFF with details of the chemical (e.g. concentrations of contaminants, such as metals, butyl tins and PCBs (See Section 4)) and physical (e.g. particle size distribution) nature of the waste and the proposed disposal site. MAFF refers the application to the Centre for Environment, Fisheries and Aquaculture Science (CEFAS) for consideration of the scientific issues and they make an expert judgement in asessing the suitability of the waste for sea disposal. CEFAS report the result of the scientific consideration to MAFF who considers this in light of the following statutory obligations:

! to protect the marine environment, the living resources which it supports and human health,

! to prevent interference with legitimate uses of the sea, and

! to other such matters as the authority consider relevant.

Wastes are deposited at disposal sites identified in the licence and MAFF sponsors some monitoring of major sites to ensure compliance with licence conditions. MAFF collates returns on the amounts of material deposited and associated contaminants to fulfill obligations under the OSPAR and London Conventions (see Section 2). Information on licensing and monitoring activities are reported in the Aquatic Environment Monitoring Reports produced by CEFAS (e.g. CEFAS 1997, 1998). Other chemicals requiring licences are tracers and biocides. Licences are also required for certain construction projects and beach nourishment schemes.

Certain operations are exempt from licensing under the Deposits in the Sea (Exemptions) Order 1985. These include deposit of fishing gear and fish discards by fishermen; certain deposits from the offshore oil and gas industry, deposit of navigational aids and deposit of scientific instruments.

The use of dispersants, sorbents and other products to treat oil found at sea and on beaches etc. is also exempt, provided that these products have been approved by MAFF and are used in accordance with any specified conditions. Approved products are required to pass specified tests for efficacy and toxicity. Oil treatment products may only be used in water of a depth of less than 20 metres, or within 1 nautical mile of the 20 metre contour, with the specific agreement from the relevant Fisheries Department (MAFF in England and Wales). Such agreement is normally only given after consultation with English Nature or the Countryside Council for Wales as appropriate.

Further information is given in the following booklets available from MAFF (Malcolm Peddar, Marine Policy Branch, Tel: 0171 238 5879):

PB3180:	The Approval and Use of Oil Dispersants in the UK (1997).
PB4296:	Oil Spill Contingency Plans - Guide to MAFF Requirements (1999).
	The Control of Deposits of Materials at Sea and Approval of Oil Dispersants - Guidance Notes. Marine Resources and Licensing Branch (updated annually).

3.1.2.2 Discharge consents

MAFF is a statutory consultee under the Water Resources Act 1991 and the Environmental Protection Act 1990 for the issue of discharge consents and IPC authorisations to water for discharges to sea via pipelines. It is MAFF’s duty to ensure there will be no adverse impact on sea fisheries or on shellfish. MAFF consults the Sea Fisheries Committees on consent applications in exercising their duties.

3.1.3 The Department of the Environment, Transport and the Regions (DETR)

DETR has major policy and financial oversight relating to water quality in the marine environment. Two main groups of DETR are involved: the Environmental Protection Group and the Rail, Aviation and Shipping Group.

The Environmental Protection Group has policy and financial oversight for the Environment Agency and also co-ordinates marine environmental policy, including international agreements on the North-East Atlantic (OSPAR) and North Sea (See Section 2). The Environment Agency is responsible for the decisions relating directly to water quality in the marine environment (see Section 3.1.1).

The Rail, Aviation and Shipping Group includes the Maritime and Coastguard Agency (MCA) which is an executive agency of DETR with a responsibility to minimise pollution from ships to the sea and the coastline. As such, the MCA enforces Merchant Shipping legislation (see Section 2) with the co-operation of port and harbour authorities.

The Counter Pollution Branch (formerly known as the Marine Pollution Control Unit) is part of the MCA and is responsible for a National Contingency Plan (currently under revision) which outlines the arrangements for managing marine pollution incidents when releases of oil or other hazardous substances in the marine environment threaten UK interests.

Local and port/harbour authorities and the Environment and Heritage Service (Northern Ireland) can ask the Counter Pollution Branch for permission to set up a Shoreline Response Centre (SRC) to deal with a major incident if all parties agree that such action is necessary (usually if a spill cannot be handled by the resources available to local authorities etc.) The MCA will bear the costs of the resources provided from its own stockpiles which the Environment and Heritage Service/port and local authorities cannot reasonably supply.

The SRC is established locally to deal with shoreline pollution and co-ordinates the activities of relevant organisations, including local authorities, statutory nature conservation agencies, MAFF and Environment Agency/SEPA. Key decisions about tackling the spill (including the use of dispersants, mechanical removal etc.) are made by the SRC in relation to protecting environmental and fisheries interests, together with public amenity sites (including beaches). A Marine Response Centre (MRC) is responsible for co-ordinating the at sea response to major incidents and will propose response actions to deal with the spill. The MRC will maintain close links with the SRC and those involved in salvage operations. The role of the MRC is to be clarified within the revised National Contingency Plan.

3.1.4 DTI

The Oil and Gas Direcorate of the Department of Trade and Industry (DTI) is responsible for maximising the economic benefits to the nation from the exploitation of the nation's hydrocarbon resources, having due regard to the potential impact of such activities on the environment and on other land and sea users (DTI 1997).

Exploration and production in the oil industry is regulated primarily through a licensing system which is managed by the Exploration and Licensing Branch of the Oil and Gas Directorate. The licensing system applies throughout the UK in territorial waters and beyond to the UK Continental Shelf whose boundaries are determined through negiotation with neighbouring states. Two types of licences are issued: seaward and landward licences. Seaward licences are issued for blocks of approximately 250 square kilometres of the UK Continental Shelf and landward licences are issued for blocks comprising the 10 by 10 km grid squares of the National Grid down to the low water mark. Exploration and production under both types of licence could therefore affect European marine sites.

Seaward production and landward licences for blocks are awarded in licensing rounds. Prior to offering petroleum licences, the Department consults widely with other Government Departments and (through the JNCC) the nature conservation agencies. For Landward licences, the local authority is the principal environmental consultant.

Once blocks are offered in the licensing round, the applicant is required to undertake an Environmental Assessment of the blocks applied for and provide details of their Company Environmental Policy and Environmental Management System. These are taken into consideration in the award of the licence. Once awarded, compliance with the conditions of the licence is checked by inspectors. These licences do not prevent all losses of oil to the sea but do seek to minimise and quantify the loss.

DTI (1997) summarises the procedures for Oil and Gas licensing the UK and is available from DTI.

3.1.5 National Assembly for Wales

The National Assembly for Wales (NAW) was established under The National Assembly for Wales (Transfer of Functions) Order 1999 and powers were assumed on 1 July 1999. The Assembly has the following duties in relation to the marine environment:

- Oversee land drainage, flood prevention and coast protection in Wales (jointly with UK Government in areas which straddle the England - Wales border);
- Control marine pollution up to 12 nautical miles from the coast;
- Control water quality and river pollution in Wales;
- Oversee the activities of Dwr Cymru throughout its operational area.

The National Assembly for Wales has powers to determine and implement policy. The Executive part of the Assembly currently has the same departmental structure as the former Welsh Office.

With respect to water quality in the marine environment, the Transport, Planning and Environment Group and the Agriculture Department have relevant responsibilities.

Environment Division of the Transport, Planning and Environment Group has a general co-ordination responsibility for environmental issues. It has the lead responsibility for sustainable development; sponsorship of the Environment Agency in Wales; water resources and protection, other than fisheries; land drainage, flood and coastal defence; environmental pollution, including air quality and waste.

Operational decisions in relation to water quality in the marine environment in Wales are made by the Environment Agency (see Section 3.1.1), the Maritime and Coastguard Agency (see Section 3.1.3) and the DTI Oil and Gas Directorate (see Section 3.1.4).

The Animal and Plant Health, Fisheries and Countryside Division of the Agriculture Department deals with fisheries and pollution matters. The NAW has taken responsibility for the control of fisheries in Welsh inland waters and in the sea within 12 nautical miles of the Welsh coast.

Operational decisions in relation to the issue of FEPA licences are currently made under an administrative arrangement by MAFF (see Section 3.1.2) but issued under the name of the NAW Agriculture Department. This is likely to continue for the time being. Statutory consultation for discharge consents and IPC authorisations are dealt with by the NAW Environment Group in the first instance.

3.2 Scotland

3.2.1 SEPA

The Scottish Environment Protection Agency (SEPA) was established on 1st April 1996 under the provisions of the Environment Act 1995. SEPA has duties which include the following:

- Water
  - To control discharges to surface waters and groundwaters by the issue of legally binding consents;
  - To conserve water resources as far as possible;
  - To promote conservation and enhancement of the natural beauty and amenity of controlled waters and associated flora and fauna.
- Air
  - To control atmospheric emissions from certain types of process, which are prescribed in Regulations, and which are expected to have a medium pollution risk by means of a legally binding ‘authorisation’;
- Integrated Pollution Control
  - To control discharges (to land, air and water) from larger and more complex ‘prescribed’ processes through Integrated Pollution Control (IPC) authorisations;
- Waste
  - Responsibilities for the management of waste in Scotland are shared by SEPA and local authorities. SEPA has specific duties to produce a national waste strategy and for the licensing of waste disposal sites.
- Radioactivity
  - To register the keeping and use of radioactive substances and to authorise disposal of radioactive waste from all users, including nuclear establishments in Scotland. SEPA undertakes environmental monitoring for radioactivity in Scotland.

SEPA’s duties for water quality in the marine environment are to control discharges to surface waters (which include tidal waters out to the three-mile limit) by issuing discharge consents, to control prescribed processes through IPC authorisations and to authorise disposal of radioactive wastes.

3.2.1.1 Discharge consents

SEPA is responsible for the regulation of discharges to controlled waters under Part II of the Control of Pollution Act 1974 (as amended) and for the granting of consents and service of instruments to discharge under that Act. It inherited these functions under the Environment Act 1995 from the river purification authorities.

Since its inception, SEPA has been formulating policies to discharge these responsibilities, including :

- Consenting policy for discharges to controlled waters (SEPA Policy No. 3, Version 1, July 1996) (draft);
- Microbiological standards in marine waters (excluding shellfish waters) in relation to design criteria for discharges (SEPA Policy No. 27, Version 1, September 1998);
- Initial dilution and mixing zones for discharges from coastal and estuarine outfalls (SEPA Policy No. 28, Version 1, September 1998).

Point source discharges for which consents are required include sewage and industrial discharges from non-prescribed processes (trade effluent). Prescribed processes require an IPC authorisation which is also issued by SEPA. Discharges from marine fish farm installations are considered to be trade effluent and require a discharge consent.

The procedure for the application for a discharge consent and the form of consent conditions (95 percentiles, upper tiers and absolute limits) is similar to that in England and Wales (see Section 3.1.1.).

There is a requirement for all existing discharges to meet the following statutory requirements:

- EC Bathing Waters Directive and UK Regulations (appropriate mandatory standards must be met at designated bathing waters);
- EC Urban Waste Water Treatment Directive and UK Regulations (the appropriate level of treatment should be applied to the sewage, based on the population equivalent of the agglomeration served by the sewerage system);
- EC Dangerous Substances Directive and UK Regulations (EQSs for List I and II substances in receiving waters must be met, including standstill provisions);
- EC Shellfish Directive and UK Regulations (appropriate standards must be met for designated shellfish waters).
- North Sea Conference and OSPAR commitments (reduction in loads of toxic substances in discharges to the marine environment must be demonstrated).

SEPA’s policy on initial dilution and mixing zones (see Section 6.2) (SEPA Policy No 28) sets out requirements to be met in the design of new or modified discharges.

For discharges with greater than 100 population equivalent, outfalls should be designed and constructed to provide the following minimum initial dilution to reduce both the visibility of density slicks and the occurrence of smell nuisance to acceptable levels:

- minimum initial dilution of 100 times (95 percentile) for primary treated effluent;
- minimum initial dilution of 50 times (95 percentile) for secondary treated effluent, including septic effluent;
- minimum initial dilution of 50 times (95 percentile) for significant new or modified industrial discharges (to be judged on an individual basis).

Modelling studies are required to determine the best location and design of the outfall and to demonstrate achievement of the minimum initial dilution requirements. SEPA specifies the requirements for modelling studies and recommends the use of one of 3 models: ELSID, PLUMES or CORMIX (see SEPA Policy No. 28).

Requirements for mixing zones are also specified to inform the design of an outfall and the consent conditions to be set to achieve compliance with statutory requirements and to protect the environment. These requirements include:

- a limitation on the size of a mixing zone to 100 m in any direction;
- UK or SEPA Environmental Quality Standards (EQSs) should not be breached outwith the mixing zone;
- where toxicity-based criteria are used, there should be no residual toxicity outwith the mixing zone;
- neighbouring mixing zones should not merge and ideally should be at least 100 m apart;
- no mixing zone should impinge on the Mean Low Water Springs (MLWS) shoreline;
- no mixing zone should plug an estuary, sea loch or small bay;
- the mixing zone will not be allowed to jeopardise the integrity of any European marine site;
- the mixing zone should not give rise to significant slicks or other aesthetic problems;
- accumulation of solids on the sea bed must not threaten the achievement of standstill clauses for List I substances outwith the mixing zone and not cause acute toxic effects to sediment-dwelling organisms within the mixing zone.

SEPA has developed a policy for microbiological standards in marine waters (except shellfish waters) in relation to design criteria for discharges (SEPA policy No 27). This policy has some influence on all marine waters in Scotland.

For all marine waters, no new or modified discharges will be allowed to result in deterioration of the class which is currently achieved under the coastal classification scheme nor threaten progress in improving class C and D marine waters identified in SEPA's corporate plans.

For identified bathing waters, existing discharges must enable mandatory standards to be achieved and, for new or modified discharges, the outfalls must be designed so as to achieve guideline standards.

SEPA may also designate 'recreational waters' where significant water contact activities are practised outwith identified bathing waters. SEPA will require mandatory microbiological standards to be achieved at relevant times of year and promote the achievement of guideline standards where appropriate.

SEPA will also adopt a strong presumption that mandatory microbiological standards are achieved at 'shoreline waters' (i.e. those visited by the public).

As in England and Wales, the primary driver for the derivation of consent conditions is compliance with statutory requirements, in particular bathing water, Urban Waste Water Treatment and shellfish water standards. SEPA has supplemented these requirements in Scotland to some extent with their policies. These policies enable Scottish Natural Heritage (SNH) to verify that consent conditions for new or modified discharges in or close to European marine sites have been set according to the procedures outlined in these documents.

The approach to the regulation and monitoring of cage fish farming in Scotland has been comprehensively laid out in a manual of procedures (SEPA 1998). This manual provides details of the application process, the assessment of the application, setting consent limits, process for granting and refusing a consent, monitoring, data management and use of information and review of consents. **Conservation agency staff should have access to this document to ensure that all cage fish farming consents have been set according to the process.**

3.2.2 Scottish Executive Rural Affairs Department (SERAD)

The main responsibilities of the Department in relation to water quality in the marine environment are:

! Policy responsibility for the quality of the environment in Scotland;

! Licensing of the deposit of wastes and other substances at sea under Part II of the Food and Environment Protection Act (FEPA) 1985 (see Section 2);

! Statutory consultee in the consent setting process for discharges from pipelines to sea.

SERAD has policy responsibility for the quality of the marine environment and is the sponsoring department for SEPA. SEPA is responsible for decisions relating directly to water quality in the marine environment (see Section 3.2.1).

SERAD is the competent authority for the issue of licences under Part II FEPA 1985. The decision-making process is similar to that operated by MAFF (see Section 3.1.2).

SERAD is a statutory consultee for consent applications for discharges to tidal waters and is responsible for ensuring that fisheries interests and other genuine uses of the sea are not compromised.

3.3 Northern Ireland

3.3.1 Environment and Heritage Service

The Environment and Heritage Service was established as an executive agency within the Department of the Environment for Northern Ireland on 1st April 1996. The main responsibilities of the Environment and Heritage Service include:

- the control of air, water and land pollution;
- the identification and management of sites of nature conservation value;
- the management of country parks, countryside centres and historic monuments;
- the protection and recording of historic monuments and buildings.

The Environment and Heritage Service is responsible for:

- protecting fresh and tidal waters under the Water Act (Northern Ireland) 1972 (principally through the application of consents for discharges);
- protecting marine waters under the Food and Environment Protection Act 1985 by the issue of licences for the disposal of wastes and other substances at sea; and
- engineering works which may affect the marine environment and for the discharge of radioactive substances under the Radioactive Substances Act 1993.

3.3.1.1 Discharge consents

The Environment and Heritage Service's approach to setting discharge consents is broadly similar to that in Great Britain. Discharges of sewage and trade effluent, including cage fish farms, are consented or in the case of Water Service discharges registered.

Modelling studies are undertaken for new or upgraded continuous sewage discharges to coastal waters in order to determine the environmental impact of the discharge and to establish the optimum location for the outfall, and to ensure that at, at designated bathing waters, compliance with the guide standards in the Bathing Water Directive are taken into account (see Section 5). For those discharges which fall within the Urban Waste Water Treatment (UWWT) Regulations, the appropriate degree of treatment to comply with the requirements of the Regulations will be the minimum acceptable. These are set out in the Guidance Notes to the Regulations. For discharges to designated sensitive areas (see Section 2.2.2.3), nutrient removal may be required in the treatment process and appropriate standards for nutrients will be included in the discharge conditions. In determining discharge standards, it is necessary to check that EQSs for controlled substances will be met outside any mixing zone. The Environment and Heritage Service is also in the process of adopting the Association of Directors and River Inspectors in Scotland (ADRIS)

Coastal Waters Classification Scheme (see Section 3.2.1) which states that no deterioration in quality class will be acceptable. The highest priority in the classification system is improving and maintaining water quality.

For intermittent discharges, the primary concern is to limit their discharge under storm conditions and their impact on water quality when a discharge does occur. Discharge standards are set on performance criteria determined from hydraulic sewer studies and impact assessments on receiving water quality. The impact assessment may be based on simple dilution or spill frequency criteria, in complex situations modelling tools are employed. The discharge standards state the design conditions under which a discharge is allowed to take place. This may be the pass-forward flow in the sewer above which a discharge can occur or relate to a spill frequency over a year or a bathing season. Additional conditions, such as screening storage, telemetry or other precautions to minimise impact are included in the discharge standard. Further details are set out in Annex 8 of the Guidance Notes to the UWWT Regulations.

Trade effluents include those from industrial discharges and from cage fish farms. There are few such discharges in Northern Ireland and those that do exist are small. In general, no modelling or mass balance calculations are undertaken to determine consent conditions. These are based on expert judgement with the relevant EQS for controlled substances used as a guideline to setting the consent conditions. Consent conditions are set as absolute limits. Some toxicity testing of effluents has been undertaken but the Direct Toxicity Assessment (DTA) approach has not yet been applied in Northern Ireland.

There are few cage fish farm installations in Northern Ireland. The approach to consenting is based on the requirement to comply with EQSs for controlled substances and to ensure that the water column and sea bed in the vicinity of the cage installation is not damaged.

3.3.1.2 FEPA Licences

The Environment and Heritage Service is the competent authority for the issue of licences for the disposal of materials at sea in Northern Ireland.

The approach to the issue of licences is compatible with that adopted by MAFF in England and Wales (see Section 3.1.2).

3.3.3 DANI

The Department of Agriculture for Northern Ireland (DANI) has responsibilities for agriculture, fisheries and food in Northern Ireland. As such, the Department is consulted in the discharge consent application process about possible impacts on fisheries.

References

SEPA Policy No. 3, Version 1, July 1996 (draft). Stirling, Scotland.

DTI. 1997. *Oil and Gas licensing in the UK. The Right Framework.* DTI, Oil and Gas Directorate, London.

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MAFF. 1998. *Controls over the deposit of materials at sea and approval of oil dispersants. Guidance Notes*. MAFF, Rural and Marine Environment Division, Marine Resources and Licensing Branch, London.

SEPA. 1998. *Regulation and Monitoring of Marine Cage Fish Farming in Scotland. A Procedures Manual*. SEPA, Stirling, Scotland.

SEPA Policy No. 27, Version 1, September 1998. Stirling, Scotland.

SEPA Policy No. 28, Version 1, September 1998. Stirling, Scotland.

4. Principal water quality issues likely to affect the interest features of European marine sites in the UK

4.1 Introduction

The principal activities with the potential to cause a degradation of water quality in European marine sites and their possible mechanisms are listed in Table 4.1. The likely mechanisms include those resulting in either a change in the concentration of naturally occurring substances or the introduction of substances not found naturally in the marine environment. These latter substances are termed synthetic or xenobiotic. For the purposes of this report, the term synthetic will be used for these substances and the term non-synthetic will apply to those naturally occurring substances.

Langford (1990) defines biological impacts as:

! lethal effects (direct mortalities);

! controlling effects (on growth, reproduction etc);

! directive effects (behavioural responses);

! indirect effects (through effects on other biota or chemistry).

Any one of the above may be significant for features within a Natura 2000 site. Generally, there is very much less information on indirect or directive effects than on controlled or lethal effects. Available relevant information on all these has been summarised as far as possible in Appendices B and C.

The effects of synthetic substances on marine organisms are generally toxic in that they interfere with one or more essential processes resulting in effects ranging from death of the organism (lethal) to changes in sub-cellular structures (sub-lethal). Non-synthetic (naturally occurring) substances can also be present at concentrations that are toxic to marine organisms (e.g. ammonia and heavy metals). The majority of non-synthetic (naturally occurring) substances result in effects by changing the natural balance of the physico-chemical environment resulting in structural and functional shifts in community composition.

Many thousands of chemicals are released into the environment as a result of human activities. For example, the European Inventory of Existing Commercial Chemical Substances (EINECS) contains more than 100,000 chemicals and a good proportion of these is likely to be released into the environment to some extent. However, only 61 synthetic substances, or groups of substances, have been identified on priority lists for control (Table 4.2). These substances have been selected on the basis of persistence, bioaccumulation and toxicity.

Table 4.1 Principal activities and related threats to water quality at European marine sites

Activity	Potential threat to water quality
1. Discharge via pipes of sewage, sewage effluent, storm water and liquid effluents from industry (including cooling waters from power stations) to rivers, estuaries and coastal waters;	Introduction of organic matter, nutrients, contaminants (including radionuclides and biocides), heated water and micro-organisms. Alteration of flow and salinity regime from power station cooling water discharges
2. Abstraction of freshwater for irrigation, industrial processes and drinking water purposes;	Alteration to flow regime in rivers affecting the salinity regime in estuaries
3. Abstraction of saltwater for cooling and drinking water purposes;	Alteration to flow regime
4. Maintenance dredging in estuaries and coastal waters;	Resuspension of particulate matter and contaminants into the water column
5. Capital dredging in estuaries and coastal waters;	Resuspension of particulate matter and contaminants into the water column
6. Aggregate extraction in estuaries and coastal waters;	Resuspension of particulate matter and contaminants into the water column
7. Disposal of wastes (including dredge spoil) in estuaries and coastal waters;	Introduction of particulate matter and contaminants
8. Aquaculture in estuaries and coastal waters;	Introduction of organic matter, nutrients, and contaminants (including veterinary medicines and antifoulants)
9. Oil/ gas exploration in estuaries and coastal waters;	Introduction of particulate matter, contaminants and oil
10. Pollution arising from shipping in estuaries and coastal waters;	Introduction of oil and petrochemicals, sewage (organic matter, nutrients and micro-organisms) and contaminants (antifoulants); Introduction of dispersants to combat spills
11. Commercial fishing for fin and shell fish in estuaries and coastal waters;	Resuspension of particulate matter into the water column
12. Land reclamation, marine construction works (including harbours and marinas[1]) and beach replenishment in estuaries and coastal waters;	Introduction of particulate matter during construction and change in water circulation
13. Flood defence in estuaries and coastal waters;	Introduction of particulate matter during construction and change in water circulation
14. Placement of structures in the sea (including windfarms);	Introduction of particulate matter and contaminants during construction and operation
15. Land use in the catchments of estuaries and coastal waters;	Introduction of particulate matter, organic matter, nutrients and agrochemicals
16. Discharge of gaseous emissions to the atmosphere.	Introduction of nutrients and contaminants through atmospheric deposition

[1] For more information refer to the report on Port and Harbour Operations (ABP Research Ltd 1999)

The concepts of hazard and risk are widely used in the identification of substances of concern. The hazard associated with a substance is its potential to cause harm and is assessed by collecting data on properties, such as physical-chemical characteristics, mobility and persistence in environmental media, bioaccumulation and acute and chronic toxicity. Risk is the probability that harm will be caused and requires information on likely environmental concentrations of the substance derived from known rates of release and dilution factors in the environment. Reliable information on known release rates of many substances is extremely difficult to find and consequently risk assessments for chemicals already in the environment are not commonly done. Substances on priority lists have been identified primarily in terms of characteristics associated with hazard (persistence, bioaccumlation and toxicity).

For the purposes of this guidance manual, the 61 synthetic substances, or groups of substances, from the priority lists, together with several groups of substances identified by the conservation agencies, have been arranged into groups of toxic (Section 4.2) and non-toxic substances (Section 4.3). For each substance, or group of substances, a profile has been prepared outlining entry to the marine environment, fate and behaviour in the marine environment and main effects on marine organisms. This information has then been used to indicate potential effects on interest features of European marine sites. Information on levels of toxic and non-toxic substances has been collated for most substances and is provided, either in the substance profile or in Appendix D to indicate the levels that might be expected to occur.

The reader is referred to a nine volume report series which provide an overview of dynamics and sensitivity characteristics for conservation management of marine SACs for the following sub-features:

Vol. I	Zostera Biotopes
Vol. II	Intertidal Sand and Mudflats & Subtidal Mobile Sandbanks
Vol III	Sea Pens and Burrowing Megafauna
Vol IV	Subtidal Brittlestar Beds
Vol V	Maerl
Vol VI	Intertidal Reef Biotopes
Vol VII	Infralittoral Reef Biotopes with Kelp Species
Vol VIII	Circalittoral Faunal Turfs
Vol IX	Biogenic Reefs

All the above reports include references to impacts of water quality which will serve as a valuable source of further information.

4.2 Toxic substances

4.2.1 Identification of toxic substances

Toxic substances, or groups of toxic substances, were identified on the basis of the level of concern expressed by the regulatory authorities and the statutory nature conservation agencies. Toxic substances of concern to UK and European regulatory authorities appear on various lists of chemicals identified for priority action for their control. These lists include Lists I and II of the Dangerous Substances Directive, the Red List established by the North Sea Conferences and a priority list for substances contributing to diffuse pollution established by OSPAR. Details of these lists are provided in Appendix A. Table 4.3 summarises the toxic substances, or groups of substances, and indicates the source list for that substance.

The following toxic substances of concern were identified by the nature conservation agencies and these, together with most of those listed in Table 4.2, are dealt with in detail in Appendix B.

! Ammonia
! Other pesticides (e.g. synthetic pyrethroids)
! Radioactive substances
! Oils (in general)
! Surfactants (in general)
! Fish farming chemicals (in general)
! Biocides used in disinfection (in general, covering chlorine and bromine)
! Booster biocides
! Phthalates (general)
! Algal toxins
! Microbial pathogens

Table 4.2 Toxic substances, or groups of substances, identified from priority lists

Chemical	**List I**	**List II**	**Red List**	**North Atlantic**
Aldrin	U		U	U
Arsenic		U		U
Atrazine		U	U	
Azinphos-methyl		U	U	
Bentazone		U		
Benzene		U		
Biphenyl		U		
Boron		U		
Brominated flame retardants				U
4-chloro-3-methyl phenol		U		
2-chlorophenol		U		
Chlorinated paraffins				U
2,4-dichlorophenol		U		
2,4-D (ester)		U		
2,4-D (non-ester)		U		
Cadmium	U		U	U
Carbon Tertrachloride	U			
Chloroform	U			
Chloronitrotoluenes		U		
Chromium		U		U
Copper		U		U
1,2-dichloroethane	U		U	
DDT	U		U	
Demeton		U		

Chemical	List I	List II	Red List	North Atlantic
Dichlorvos		U	U	
Dieldrin	U		U	
Dimethoate		U		
Endosulphan		U	U	
Endrin	U		U	
Fenitrothion		U	U	
Hexachlorobenzene	U		U	
Hexachlorobutadiene	U		U	
Isodrin	U			
Iron		U		
Lead		U		U
Lindane	U		U	
Linuron		U		
Malathion		U	U	
Mecoprop		U		
Mercury	U		U	U
Mothproofers		U		
Naphthalene		U		
Nickel		U		
Organotins (tributyltin (TBT) and triphenyltin (TPT)		U	U	U
Polyaromatic hydrocarbons (PAHs)				U
Polybrominated naphthalenes				U
Penatachlorophenol (PCP)	U		U	
Perchloroethylene	U			
Polychlorinated biphenyls (PCBs)			U	U
Simazine		U	U	U
1,1,1-trichloroethane		U		
1,1,2-trichloroethane		U		
Toluene		U		
Triazophos		U		
Trichloroethylene	U			
Trichlorobenzene	U		U	
Trifluralin		U	U	
Timber treatment chemicals				U
Vanadium		U		
Xylene		U		
Zinc		U		U

4.2.2 Hazard assessment of toxic substances

A profile of each toxic contaminant, or group of contaminants, has been prepared providing information on the major sources, fate and behaviour in the marine environment, main biological effects and potential impact on interest features of European marine sites. These profiles are located in Appendix B.

The profiles have been compiled using information on each substance, or group of substances, already collated in major reviews, including those prepared by the World Health Organisation and, for those List II substances with EQSs, the report prepared by WRc for the derivation of the EQS (Grimwood and Dixon, 1997). Extensive literature reviews on each substance have not been carried out. **The profiles, therefore, indicate the most sensitive groups of organisms but do not purport to summarise all of the available toxicity information for all groups of organisms**. The most common groups of organisms used for toxicity testing are invertebrates, fish and, to a lesser extent, algae. Consequently, most of the toxicity information is available for these groups of organisms. Information for marine macrophytes, seabirds and sea mammals is not generally available in these reviews but has been included where such data exist.

Table 4.3 summarises the key features of the profile of each substance, or group of substances, and identifies the toxic effects on the main groups of marine organisms.

The standardised terms used in Table 4.3 for fate and behaviour, persistence, bioaccumulation and toxicity have been based on consistent criteria summarised in paragraphs 4.2.2.1 to 4.2.2.4 below.

In applying these criteria to the identified toxic substances, or groups of substances, there are cases where the required information is not available or has been estimated or where classifications have been borderline. **The reader is urged to use Table 4.3 only as an initial indication of the hazard posed by a substance and to consult the profile in Appendix B and, if necessary, the supporting literature referenced in the profile.**

4.2.2.1 Fate and behaviour

The fate and behaviour of a substance entering the water column is determined to a large extent by its physical-chemical properties. Properties, such as solubility, volatility and its affinity for organic matter determine whether a substance remains dissolved in the water column, evaporates into the atmosphere or becomes associated with suspended or deposited organic material or sediment. Affinity for organic material or sediment is measured for a substance in the laboratory, or estimated by modelling, by determining the extent to which the substance partitions between water and octanol (an organic solvent) and is expressed as a partition coefficient (log Kow). **Log Kow values of greater than 4 indicate that a substance is likely to sorb strongly to sediments/suspended solids**. As such, these substances may disappear relatively quickly from the water column, but persist in sediments where they may continue to be available to sediment fauna, or risk re-suspension when sediment is disturbed.

The fate and behaviour of non-synthetic substances, such as metals, are influenced by the chemical form of the metal. Certain forms are soluble in water and are likely to remain in the water column. Others are insoluble and are likely to be deposited and incorporated into sediments. Soluble forms might be transformed into insoluble forms, and vice versa, by chemical or biological processes such that metals can cycle between sediments and the water column over a period of many years. For these substances, fate and behaviour is dependent on its chemical form and environmental conditions and cannot be classified with respect to a partition coefficient.

4.2.2.2 Persistence

Many of the synthetic organic substances are broken down by natural processes, such as photolysis (reaction with light), hydrolysis (reaction with water) or by biological processes (biodegradation). The rate at which this occurs is measured in terms of the half-life (the time taken for the concentration of the substance to reduce by half). Persistence in water or sediments can be measured in the laboratory. The following criteria have been used:

! half life <10 days - low persistence

! half-life >10 and <100 days - moderate persistence

! half-life >100 days - high persistence

Non-synthetic (naturally occurring) toxic substances, such as metals, do not break down but undergo chemical transformations and cycle between sediment, water column and organisms. Persistence in any one environmental medium is dependent on the chemical form and prevailing conditions. Such substances cannot be classified with respect to a half-life.

4.2.2.3 Bioaccumulation

Bioaccumulation of a substance occurs when it is taken up by an organism and not metabolised or excreted to a large extent such that the concentration of the substances in the body tissues increases over time. The extent to which a substance bioaccumulates in an organism is expressed as a bio-concentration factor (BCF) which is a ratio of the concentration in an organism after a period of exposure relative to the concentration in the environment. The higher the concentration in the organism relative to the surrounding environment, the greater the BCF. Many substances that bioaccumulate are stored in fatty tissues and so a substance that has an affinity for organic matter is more likely to bioaccumulate that one that does not. Consequently, expectation to bioaccumulate is assessed by a combination of BCF and log Kow. The following criteria have been used:

! CF value of <100 or log Kow <3 - not expected to bioaccumulate

! CF value of >100 but <1,000 or log Kow >=3 and <=4 - has the potential to bioaccumulate

! CF value of >1,000 or log Kow >4 - has the potential to bioaccumulate significantly.

These criteria do not apply to ionic chemicals that are generally metabolised or excreted or to organic chemicals with molecular weights greater than 700 as these molecules are too large to pass through cell walls.

4.2.2.4 Toxicity

Toxicity has been classified as follows for major groups of organisms using available information. The criteria used for the classification are those currently being used in the development of the Environment Agency Substance Information System (EA-SIS) which will be used by EA staff to readily access information on substances of concern.

The following criteria have been applied:

! Very toxic to aquatic organisms - acute effect data #1 mg l^{-1} or chronic effect data #0.1 mg l^{-1}

! Toxic to aquatic organisms - acute effect data >1 mgl^{-1} and #10 mgl^{-1} or chronic effect data >0.1 mgl^{-1} and #1 mgl^{-1}

! Unlikely to be toxic to aquatic organisms - acute effect data >10 mgl^{-1} or chronic effect data >1 mgl^{-1}

4.2.2.5 Effects of different substances in combination

Very little is known about interactive effects of many of the substances listed in Appendices B and C, although some, such as effects of pH on toxicity of ammonia, are well understood. Where interactions such as this are well known, they have generally been referred to in the Appendices, but, in most cases, the toxicity of individual substances has been considered in isolation.

This whole area is one of great uncertainty so it is difficult to provide advice on particular risks. **The Environment Agency is currently considering the applicability of Toxicity-Based Consents for discharges where toxicity of contaminants is uncertain; this approach may be useful for some Natura 2000 sites (see Section 3.1.1).**

4.2.3 Hormone (endocrine) disruption

Information is available which suggests that some of the toxic substances considered in this Section may have endocrine modulating effects. The Environment Agency has recently undertaken a review of the scientific evidence on endocrine modulating substances in wildlife (Environment Agency 1998a). The Agency has also produced a consultative report on the potential controls of these substances which contains a straightforward explanation of the issues (Environment Agency 1998b). The former report makes a critical assessment of the evidence for endocrine disruption and its potential effects on the environment in England and Wales, and aims to establish a strategy for their management and control.. The report focuses on wildlife species and reported effects in laboratory and field investigations. However, they do recognise that the report can only be taken as an interim assessment of what is a rapidly developing issue. **(The reader is referred to the Environment Agency publications for a detailed account of the mode and evidence of endocrine modulation).**

The endocrine system is a complex internal system of hormone, secretory glands and receptors responsible for the growth, metabolism and reproduction both in plants and animals. Substances can interfere with the functioning of the endocrine system and have been shown to interfere with these processes. Such substances termed ‘endocrine-disrupting’ or ‘endocrine-modulating’ have emerged in recent years as a major issue of concern for the environment and human health.

Environmental monitoring programmes and research confirm that potential endocrine disrupting substances are being released into the environment. Most of these substances are under some regulatory control due to their toxicity and environmental quality standards already exist for the aquatic environment for some substances. What is not known is whether these standards adequately protect against endocrine-modulating effects.

An impairment of endocrine function can have far-reaching consequences and lead to clear biological effects as measured at the individual, population, community or even ecosystem level. The Agency (Environment Agency 1998a) has summarised substances currently implicated as having endocrine modulating properties in published literature, from *in vitro* screening assessments (tests on cultures of specially bred cell lines or tissue taken from living organisms) or from *in vivo* toxicological evaluations (tests on living animals). Of the synthetic substances considered in this guidance manual, the substances in Section 4.2.3.1 have been identified as having some endocrine modulating effects. These effects have been characterised as:

- oestrogenic - mimic the feminising effects in animals of the natural female sex hormones called oestrogens;
- anti-oestrogenic - block the feminising effects of oestrogens;
- anti-androgenic - block the masculinising effects of male sex hormones called androgens.

Extensive research is being conducted world-wide in order to provide more information on the potential effects of endocrine-modulating substances. However, the Agency has proposed (Environment Agency 1998a) a precautionary approach in addressing this issue. A dual approach has been proposed, in which the Agency will take a number of specific preventative actions, taking account of relative cost and benefits and, at the same time, continue to make its contribution to improving scientific understanding through research and development and environmental monitoring programmes.

4.2.3.1 Potential endocrine modulating substances identified in *in vitro* tests

Oestrogenic substances

Organochlorine substances: DDT (and o,p’-DDD; p,p’-DDT and o,p’DDT); Various Alkylphenols; Various phthalates; endosulfan; dieldrin

Anti-oestrogenic substances

PCBs

Anti-androgenic substances

p,p’DDE; p,p’DDT; permethrin

4.2.3.2 Potential endocrine modulating substances identified from *in vivo* assessments

Endosulfan; tributyltin (TBT); trifluralin; lindane; p,p’DDE; o,p’DDT; atrazine; aldrin; dieldrin; various organophosphates (diazinon, chlorfenvinphos)

4.2.4 Effects of toxic substances on interest features of European marine sites

Each of the profiles of toxic substances in Appendix B contains a summary of the potential effects on interest features of European marine sites.

The following sections explain the types of effects of toxic substances for Annex I habitats, Annex II species and birds.

4.2.4.1 Annex I Habitats

Annex I habitats on SACs in the UK (see Table 1) include interest features that are either physiographic (estuaries, shallow inlets and bays, lagoons) or major habitats (subtidal sandbanks, intertidal sand and mudflats, reefs and caves) and each comprises possible sub-features. The sub-features are biotopes comprising physical aspects of the habitat and associated marine communities. Toxic substances can alter the ability of sub-features to support marine communities (e.g. toxic substances can accumulate in sediments and pose a threat to marine organisms associated with the sediment). Toxic substances can directly affect marine organisms through lethal and sub-lethal (including endocrine disruption) effects via exposure in the water column, the sediment and in the food supply.

The hazard assessment of the identified toxic substances for this guidance manual has indicated the degree of toxicity to the most sensitive groups of organisms, i.e. algae, macrophytes, invertebrate phyla and fish. In many cases, this assessment will have been based on very few species that have been tested in the laboratory and it is unlikely that many of the species associated with sub-features will have been tested. Given this mis-match of information, it is only possible to use the degree of toxicity to the main groups of organisms as an indication of likely toxic effects to species associated with sub-features belonging to these groups. For example, atrazine has been identified as very toxic to algae, macrophytes and crustacea (Table 4.3) based on tests on a range of algae including *Laminaria*, some plants including *Zostera marina* and some crustacea including the copepod *Acartia* and mysids (Section 12, Appendix B). **In seeking to protect a sub-feature comprising algae, macrophytes and associated crustacea, whatever the component species, from a discharge containing atrazine, it is only possible to use the available information to suggest that this substance is very toxic to these groups of organisms and, therefore, the levels of atrazine in the discharge should be stringently controlled.**

4.2.4.2 Annex II Species

Marine SACs have been identified in the UK for the Annex II species: bottle-nose dolphins, otters and for common and grey seals. The exposure routes of these organisms to toxic substances include uptake via the skin (including grooming), ingestion of water and of food. The primary exposure route for toxic substances is likely to be via food. Consequently, the toxic substances posing the greatest hazard to these species are likely to be those that have the potential to bioaccumulate and that are toxic to fish (the primary food source of these species) and possibly also those that have been identified as having potential endocrine disrupting effects.

4.2.4.3 Birds

SPAs are designated for bird species and the exposure routes for these animals include ingestion of water and sediment and via the food. The primary uptake route for toxic substances is likely to be via the food. Consequently, the substances posing the greatest hazard are those that have the potential to bioaccumulate and that are toxic to invertebrates and fish (the main food sources of these animals) and possibly also those identified as having potential endocrine disrupting effects.

For Annex II species and birds, consideration also needs to be given to the indirect effects of toxic substances, e.g. acting via depletion of their food supply.

4.2.5 Background levels of toxic substances

Background levels for those toxic substances contained in monitoring programmes undertaken by the environment agencies in the UK are summarised in Appendix D.

Table 4.3 Hazard assessment of identified toxic substances in relation to European marine sites

Substance	Sources		Fate and Behaviour	Persistence		Effects on biota	
	Point	**Diffuse**	**Partitioning to air, water and sediments**	**Water**	**Sediments**	**Bioaccumulation**	**Toxicity**
Ammonia	Sewage discharges	Agricultural run-off	Found dissolved in water column	Variable. Longer in estuaries		Does not bioaccumulate	Invertebrates: very toxic Fish: very toxic
Mercury	Industrial discharges	Sediments	Can be found in dissolved in water column or associated with sediments	Variable	High	Inorganic mercury: likely to bioaccumulate Organic mercury: likely to bioaccumulate significantly	Macrophytes: very toxic Invertebrates: very toxic Fish: very toxic
Cadmium	Industrial discharges Mine drainage water	Atmospheric deposition	Can be found in dissolved in water column or associated with sediments	Variable	High	Likely to bioaccumulate significantly	Crustacea: very toxic Fish: very toxic
Lead	Industrial discharges Sewage discharges	Atmospheric deposition	Likely to be associated with sediments	Variable	High	Likely to bioaccumulate	Algae: very toxic Invertebrates: very toxic Fish: very toxic
Chromium	Industrial discharges	Atmospheric deposition Natural catchment runoff	Likely to be associated with sediments	Variable	High		Invertebrates: toxic Fish: toxic

Substance	**Sources**		**Fate and Behaviour**	**Persistence**		**Effects on biota**	
	Point	**Diffuse**	**Partitioning to air, water and sediments**	**Water**	**Sediments**	**Bioaccumulation**	**Toxicity**
Zinc	Sewage discharges Industrial discharges Waste disposal	Atmospheric deposition	Likely to be associated with sediments	Variable	High	Likely to bioaccumulate	Algae: very toxic Invertebrates: very toxic Fish: very toxic
Copper	Sewage discharges Industrial discharges Waste disposal	Atmospheric deposition Natural catchment runoff	Likely to be associated with sediments. Can be present in complexes in the water column	Variable	High	Likely to bioaccumulate	Invertebrates: very toxic Fish: very toxic
Nickel	Sewage discharges Industrial discharges Waste disposal	Atmospheric deposition Natural catchment runoff	Likely to be associated with sediments. Can be present in complexes in the water column.	Variable	High	Not likely to bioaccumulate	Algae: very toxic Invertebrates: very toxic Fish: very toxic
Arsenic	Industrial discharges	Sediments	Likely to be associated with sediments	Variable	High	Not likely to bioaccumulate	Algae: very toxic Invertebrates: very toxic Fish: very toxic
Vanadium	Industrial discharges of coal wastes	Atmospheric deposition	Likely to be associated with sediments	Variable	High	Not likely to bioaccumulate	Invertebrates: unlikely to be toxic

Substance	Sources		Fate and Behaviour	Persistence		Effects on biota	
	Point	Diffuse	Partitioning to air, water and sediments	Water	Sediments	Bioaccumulation	Toxicity
Boron	Sewage discharges Industrial discharges		Likely to be associated with sediments	Variable	High	Not likely to bioaccumulate	Invertebrates: unlikely to be toxic
Iron	Sewage discharges Industrial discharges Mining discharges and wastes	Atmospheric deposition	Likely to be associated with sediments	Variable	High	Not likely to bioacumulate	Invertebrates: unlikely to be toxic
Atrazine	Sewage discharges	Agricultural run-off	Likely to be dissolved in water but can be associated with sediments	Low to moderate	Moderate	Not expected to bioaccumulate	Algae: very toxic Macrophytes: very toxic Crustacea: very toxic Others: moderate to low toxicity No data for sediment dwelling organisms
Simazine	Sewage discharges	Agricultural run-off	Likely to be dissolved in water but can be associated with sediments	Low to moderate	Moderate	Not expected to bioaccumulate	Algae: very toxic Macrophytes: very toxic Others: moderate to low toxicity No data for sediment dwelling organisms

Substance	Sources		Fate and Behaviour	Persistence		Effects on biota	
	Point	**Diffuse**	**Partitioning to air, water and sediments**	**Water**	**Sediments**	**Bioaccumulation**	**Toxicity**
Diuron		Urban run-off	Likely to be dissolved in water	Moderate		Not expected to bioaccumulate	Algae and macrophytes: likely to be very toxic. No data for sediment dwelling organisms
Linuron		Agricultural run-off	Likely to be dissolved in water	Moderate		Not expected to bioaccumulate	Algae: likely to be very toxic Macrophytes: likely to be very toxic No data for sediment dwelling organisms
Trifluralin		Agricultral run-off	Likely to be associated with sediment	Low	Moderate to high	Likely to bioaccumulate significantly	Crustacea:very toxic Molluscs: very toxic Fish: very toxic No data for sediment dwelling organisms
Bentazone		Agricultural run-off	Likely to be dissolved in water	Low		Not expected to bioaccumulate	Algae: low toxicity Macrophytes: low toxicity Others: low toxicity No information for sediment dwelling organisms
Lindane	Industrial discharges	Agricultural run-off	Likely to be dissolved in water with some association with sediments	Low to high	Low to high	Likely to bioaccumulate significantly	Invertebrates: very toxic Fish: very toxic

Substance	Sources		Fate and Behaviour	Persistence		Effects on biota	
	Point	Diffuse	Partitioning to air, water and sediments	Water	Sediments	Bioaccumulation	Toxicity
Endosulphan		Agricultural run-off	Likely to be associated with sediments	Low to moderate	Low to moderate	Potential to bioaccumulate (particularly in fish)	Algae: toxic Molluscs: toxic Crustacea: very toxic Sediment dwelling animals: toxic
Synthetic pythrethroids	Fish farming installations	Agricultural run-off	Likely to be associated with sediments	Low	Moderate to high	Potential to bioaccumulate but not expected to due to rapid metabolism	Insects:very toxic Crustacea:very toxic Fish: very toxic
Azinphos-methyl		Agricultural run-off	Likely to be associated with sediments	Low	Moderate to high	Potential to bioaccumulate	Crustacea: very toxic Fish: very toxic
Malathion	Industrial discharges	Agricultural run-off Atmospheric deposition	Likely to be associated with sediments	Low	Moderate to high	Potential to bioaccumulate but not expected to due to rapid metabolism	Insects: very toxic Crustacea: very toxic Fish: very toxic
Fenitrothion		Agricultural run-off	Likely to be associated with sediments	Low	Moderate to high	Potential to bioaccumulate	Crustacea: very toxic Fish: toxic
Dimethoate	Sewage discharges	Agricultural run-off	Likely to be dissolved in the water column	Moderate		Not expected to bioaccumulate	Algae: very toxic Crustacea: very toxic
Ivermectin	Fish-farming installations	Agricultural run-off	Likely to be associated with sediments	Low	Low to moderate	Potential to bioaccumulate though large molecule size may prevent this	Crustacea: very toxic Sediment dwelling animals: toxic
Dichlorvos	Fish-farming installations Industrial discharges	Agricultural run-off	Likely to remain in water column	Low		Not likely to bioaccumulate	Algae: unlikely to be toxic Crustacea: very toxic Fish: very toxic

Substance	Sources		Fate and Behaviour	Persistence		Effects on biota	
	Point	Diffuse	Partitioning to air, water and sediments	Water	Sediments	Bioaccumulation	Toxicity
Mothproofing chemicals - PCSDs Cyfluthrin Sulcofuron Flucofuron Permethrin	Industrial discharges Sewage discharges		Not known	Not known		Likely to bioaccumulate significantly	Invertebrates: very toxic Fish: very toxic
Antifoulants - TBT	Marinas Boatyards Discharges of timber treatment chemicals Fish-farming installations	Leaching from vessels and fish farm installations	Likely to be associated with sediments		High	Potential to bioaccumulate significantly	Algae: very toxic Invertebrates: very toxic Fish: very toxic Sediment dwelling organisms: very toxic
Biocides used in cooling water disinfection - Chlorine Bromine	Power station discharges		Likely to be in the water column	Low to moderate		Not expected to bioaccumulate	Unlikely to be toxic to marine organisms
Benzene	Sewage discharges Industrial effluent discharges	Atmospheric deposition Urban run-off	Likely to be lost to the atmosphere	Low to moderate		Potential to bioaccumulate	Fish: moderately toxic Others: expected to be of low toxicity No data for sediment dwelling organsms

Substance	Sources		Fate and Behaviour	Persistence		Effects on biota	
	Point	Diffuse	Partitioning to air, water and sediments	Water	Sediments	Bioaccumulation	Toxicity
Biphenyl	Sewage discharges (?) Industrial effluent discharges Landfill leachate		Likely to be lost to the atmosphere	Low	Moderate	Low to moderate potential to bioaccumulate	Invertebrates: moderately toxic Fish: moderately toxic Others: low toxicity expected No data for sediment dwelling organisms
4-chloro-3-methyl phenol	Industrial effluent discharges		Likely to dissolved in water	Low to moderate		Not expected to bioaccumulate	Moderate toxicity expected for aquatic organisms No data for sediment dwelling organisms
Carbon tetrachloride	Industrial discharges	Atmospheric deposition	Likely to be lost to the atmosphere	Low		Not expected to bioaccumulate	Low toxicity expected to aquatic organisms. No data for sediment dwelling organisms
Chlorinated ethylenes	Industrial discharges Landfill leachate	Atmospheric deposition	Likely to be lost to the atmosphere	Low		Not expected to bioaccumulate	Low to moderate toxicity to aquatic organisms
Chloronitrotoluenes	Industrial discharges		Likely to be lost to the atmosphere. Some adsorption to sediments	Low		Potential to bioaccumulate (little information)	Low to moderate toxicity to freshwater organisms. No data for marine organisms.

Substance	**Sources**		**Fate and Behaviour**	**Persistence**		**Effects on biota**	
	Point	**Diffuse**	**Partitioning to air, water and sediments**	**Water**	**Sediments**	**Bioaccumulation**	**Toxicity**
Chlorinated paraffins	Sewage discharges Industrial discharges		Likely to be associated with sediments	Low	High	Low molecular weight: potential to bioaccumulate. High molecular weight (>600): not expected to bioaccumulate	Low molecular weight: very toxic to marine organisms High molecular weight: low toxicity to marine organisms
Chlorophenols (CP) and dichlorophenols (DCP)	Industrial discharges; Paper mill discharges; By-product of chlorination of sewage and industrial discharges		Likely to be found in the water column and associated with sediment	Low to moderate	Moderate	Not expected to bioaccumulate	Moderate to high toxicity to marine organisms
Dichlorobenzenes	Sewage discharges Industrial discharges	Atmospheric deposition	Likely to lost to the atmosphere. Likely to associated with sediments.	Low to moderate	High	Potential to bioaccumulate	Moderate toxicity to invertebrates and fish

Substance	**Sources**		**Fate and Behaviour**	**Persistence**		**Effects on biota**	
	Point	**Diffuse**	**Partitioning to air, water and sediments**	**Water**	**Sediments**	**Bioaccumulation**	**Toxicity**
Chlorinated ethanes	Sewage discharges Industrial discharges	Atmospheric deposition	Likely to be lost to the atmosphere	High		Slight potential to bioaccumulate.	Low to moderate toxicity to algae, invertebrates and fish
Hexachlorobutadiene	Industrial discharges Waste leachates		Likely to be lost to the atmosphere. Likely to be associated with sediments	Low	High?	Potential to bioaccumulate significantly	Moderate to high toxicity to invertebrates and fish
PAHs	Sewage discharges Indusrial discharges Oil spillages	Urban runoff Atmospheric deposition	Likely to be associated with sediments (except naphthalene)		High	Potential to bioaccumulate significantly	Moderate toxicity to marine organisms. Can produce carcinogenic metabolites in organisms
Naphthalene	Sewage discharges Industrial discharges	Atmospheric deposition	Likely to be lost to the atmosphere. Some likelihood of association with the water column and sediments	Low to moderate	Low to moderate	Potential to bioaccumulate	Moderate to high toxicity to invertebrates and fish
PCBs	Sewage discharges Industrial discharges	Atmospheric deposition	Likely to be associated with the sediment	High	High	Potential to bioaccumulate significantly	Can be very toxic to marine invertebrates. Can have endocrine disrupting effects.

Substance	Sources		Fate and Behaviour	Persistence		Effects on biota	
	Point	Diffuse	Partitioning to air, water and sediments	Water	Sediments	Bioaccumulation	Toxicity
Phthalates	Industrial discharges Waste leachates		Likely to be associated with the sediment		Low to high	Ranges from not expected to bioaccumulate to potential to bioaccumulate significantly depending on the phthalate	Moderate to low toxicity to marine organisms. Can have endocrine disrupting effects.
Polybrominated naphthalenes	Flame retardant chemicals, Chlorination by-product.		Not known	Not known		Not known	Not known
Oil and petrochemicals	Sewage discharges, Industrial discharges, Spillages, Leisure craft	Atmospheric deposition,	Volatile components will evaporate to the atmosphere. Long-chain hydrocarbons will be associated with the sediment. Oil/water emulsions can be found in the water column.	Low to high	High	Some hydrocarbons have the potential to bioaccumulate significantly	Moderate to high toxicity to invertebrates and fish. Indirect effects on intertidal biotopes through smothering/coating with oil deposits. Indirect effects on birds and seals through damage to plumage and inhalation of aromatic fractions respectively.

Substance	Sources		Fate and Behaviour	Persistence		Effects on biota	
	Point	Diffuse	Partitioning to air, water and sediments	Water	Sediments	Bioaccumulation	Toxicity
Surfactants	Sewage discharges Industrial discharges	Agricultural run-off	Likely to concentrate at air/water and water/sediment interfaces	Low		Potential to bioaccumulate	Can be very toxic to marine algae, invertebrates and fish. Can have endocrine disrupting effects.
Toluene	Sewage discharges, Industrial discharges	Atmospheric deposition	Likely to be lost to the atmosphere Can be associated with sediments	Low to moderate		Not expected to bioaccumulate	Moderate toxicity to marine invertebrates and fish.
Xylenes	Sewage discharges Industrial discharges Oil/petrochemical spillages	Atmospheric deposition	Likely to be lost to the atmosphere. Can be associated with the water column and sediments	Moderate to high		Not expected to bioaccumulate.	Moderate toxicity to marine invertebrates and fish.
Radioactivity	Nuclear power stations, nuclear reprocessing industry, research sites	Atmospheric deposition (from nuclear explosions and fires at nuclear facilities), primordial and natural.	More usually associated with sediment than the water column.	Isotope-specific.	Isotope-specific.	Isotope-specific.	Not at the concentrations found in UK coastal waters.

Substance	Sources		Fate and Behaviour	Persistence		Effects on biota	
	Point	**Diffuse**	**Partitioning to air, water and sediments**	**Water**	**Sediments**	**Bioaccumulation**	**Toxicity**
Algal toxins		Generated within the water column	Predominantly stored within algal cells, and released upon cell lysis.	Probably low-moderate	Probably low-moderate (not known to be accumulated).	High risk for some toxins, e.g. PSP, ASP, DSP; lower for others, e.g. NSP	Spectrum of toxicity from low to very high, dependent on algal species and concentration
Microbial pathogens	Viruses associated with STW outfalls	Potentially almost anywhere,	Unknown.	Probably low-moderate	Probably low-moderate		Pathogen-specific

4.3 Non-toxic substances

4.3.1 Selection of non-toxic substances

Non-toxic substances do not appear on lists of priority substances (see Table 4.2). However, this should not imply that they are not of concern to the regulatory authorities. The non-toxic substances, or groups of substances of concern, have been identified by the nature conservation agencies and include:

- Nutrients: nitrogen, phosphorus, silicon
- Organic carbon
- Oxygen depleting substances: BOD, COD
- pH
- Salinity
- Temperature: thermal discharges
- Turbidity (including suspended solids)

4.3.2 Hazard assessment of non-toxic substances

A profile of each non-toxic substance, or group of substances, has been prepared providing information on the major sources, fate and behaviour in the marine environment and main biological effects. These profiles are located in Appendix C.

The information used for each profile has been drawn partly from reviews undertaken on behalf of English Nature and from other readily available information. Exhaustive literature reviews have not been carried out. **The profiles outline the main primary and secondary effects but do not purport to detail every possible effect**.

Table 4.4 summarises the key features of each non-toxic substance, or group of substances, and so provides an initial indication of the hazard to interest features of European marine sites.

There are no standard criteria that can be applied to non-toxic substances for fate, behaviour and effects and consequently Table 4.4 contains the main points drawn from the profiles in Appendix C.

4.3.3 Effects of non-toxic substances on interest features of European marine sites

Each of the profiles of non-toxic substances in Appendix C contains a summary of the potential effects on interest features of European marine sites. The following Sections explain the types of effects of non-toxic substances for Annex I habitats, Annex II species and birds.

4.3.3.1 Annex I Habitats

Annex I habitats on SACs in the UK (see Table 1) include interest features that are either physiographic (estuaries, shallow inlets and bays, lagoons) or major habitats (subtidal sandbanks, intertidal sand and mudflats, reefs and caves) and each comprises possible sub-features. The sub-features are biotopes comprising physical aspects of the habitat and associated marine organisms.

Non-toxic substances can have profound effects on Annex I habitats because they can be discharged in large quantities. For example, many UK estuaries have been changed fundamentally because of the discharge of sewage effluents containing organic carbon, oxygen depleting substances, nutrients as well as some toxic substances.

The primary effects of the non-toxic substances considered in this guidance manual are to change the physico-chemical nature of the environment. This often leads to secondary effects resulting in changes in the physical aspects of the habitat and associated marine organisms.

The hazard assessment of the identified non-toxic substances has indicated primary and secondary effects on the marine environment.

4.3.3.2 Annex II Species

Marine SACs have been identified in the UK for Annex II species: bottle-nose dolphins, otters and for common and grey seals. These animals are not affected by the primary effects of non-toxic substances but may be by secondary effects. Nutrient and organic enrichment can stimulate fish production and therefore potentially have a positive effect on sea mammal population. **However, excess supply can suppress fish production and potentially have a detrimental effect. The scale of any effect depends largely on the extent to which these animals feed in European marine sites and what proportion of their life they spend there.**

4.3.3.3 Birds

SPAs are designated for bird species and these are not affected by the primary effects of non-toxic substances. However, the secondary effects of many of the non-toxic substances can have a considerable effect on bird populations by influencing the availability of an appropriate food supply. Nutrient and organic enrichment can have a positive effect on populations by increasing the supply of organic carbon to the sediments, stimulating the production of sediment-dwelling invertebrates and enhancing the food supply. Increased temperature from power station effluents can also stimulate greater production of sediment-dwelling organisms. **However, excessive supply of nutrients and organic carbon can result in deoxygenation of the water column and the sediments suppressing the production of food organisms and therefore adversely affect bird populations**.

4.3.4 Background levels of non-toxic substances

Background levels for non-toxic substances are contained within each of the profiles in Appendix C.

Table 4.4 Hazard assessment for non-toxic substances in relation to European marine sites

Substance	Sources		Fate and Behaviour	Effects
	Point	Diffuse	Partitioning to air, water and sediments	
Nitrogen	Sewage discharges; Industrial discharges	Atmospheric deposition, Coastal water inputs, Agricultural run-off	Cycles between sediment, water and the atmosphere. Can accumulate in sediment as organic matter increases (with greater N-load) then dies entering sediment	Can be toxic to invertebrates and fish (NH_3); Can contribute to deoxygenation of the water column and sediments (nitrification and eutrophication); Can contribute to stimulation of algal growth (eutrophication).
Phosphorus	Sewage discharges; Industrial discharges	Coastal water inputs; Agricultural run-off; Natural catchment run-off; Some input from wind-blown pollen and dust.	Cycles between sediment and water. Accumulates in sediments	Can contribute to stimulation of algal growth (eutrophication); Can contribute to deoxygenation of water column and sediments (eutrophication).
Silicon	Has been associated with detergent manufacture	Soil erosion; Weathering of rocks; Sediment mineralisation	Accumulates in sediments. Cycles between water and sediments; never reaches saturation point in water. Spring diatom blooms may strip silicon from the water column.	Can contribute to stimulation of algal growth (eutrophication); Can contribute to deoxygenation of water column and sediments (eutrophication).
Organic carbon	Sewage discharges; Industrial discharges	Agricultural run-off; Natural catchment run-off; Primary productivity within the aquatic environment	Cycles between water column, sediments, and atmosphere through biological and chemical processes. Can accumulate in sediments.	Can contribute to stimulation of production of primary consumers (organic enrichment); Can contribute to deoxygenation of water column and sediments (organic pollution)

Substance	**Sources**		**Fate and Behaviour**	**Effects**
	Point	**Diffuse**	**Partitioning to air, water and sediments**	
Oxygen depleting substances	Sewage discharges; Industrial discharges	Water column: Bacterial and algal respiration. Chemical oxidation Sediments: Agricultural run-off; Natural catchment run-off; Primary production; Decaying algal blooms.	Dissolved and particulate organic matter can deplete oxygen in the water column (measured as BOD). Particlulate organic matter can accumulate in sediments and delete oxygen (measured as SOD) Nitrification in sediments (measured as SOD)	Can be toxic to invertebrates and fish at low concentrations;
pH	Industrial discharges	Atmospheric deposition (acid rain	pH can be decreased in the water column.	Can contribute to transient changes in water chemistry.
Salinity	Major sewage and industrial discharges discharges (reduce salinity)	Coastal water inputs (increase salinity); River inputs (reduce salinity; Atmospheric inputs (reduce salinity).	Salinity can be increased or reduced in the water column and sediments.	Reduced salinity can have lethal and sub-lethal effects on marine organisms; Can influence toxicity of ammonia;
Turbidity	Sewage discharges; Industrial discharges. Dredging operations	Sediment resuspension; Coastal erosion; Phytoplankton; Coastal water inputs; Dissolved and particulate organic matter.	Can remain in water column or accumulate in sediments.	Can contribute to reduction in light penetration; Can reduce primary productivity; Can adversely affect filter feeding organisms.

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5. Water quality guidelines and standards in the marine environment

5.1 Introduction

This Section provides tabulated summaries of the water quality guidelines and standards used for the protection of the marine environment. Once substances of concern have been identified in relation to a particular discharge and some understanding of the fate, behaviour and effects of the substance has been gleaned from Section 4 and Appendices B and C, the appropriate standards, where they exist, can be identified in Tables 5.1, 5.2, 5.3 and 5.4.

The standards listed are those used by the competent authorities in the management of water quality in the marine environment. They have been derived for a number of purposes, including:

- the protection of saltwater life (Environmental Quality Standards) (EQSs) (Section 5.1, Tables 5.1 and 5.2);
- the protection of shellfish populations for human consumption in designated shellfish waters (Section 5.2, Tables 5.3); and
- the protection of human health while bathing in designated waters (Section 5.3, Table 5.4).

These are the statutory standards that must be observed in receiving marine and estuarine waters and are used in setting discharge consents.

All of the standards in Tables 5.1 to 5.4 are only applicable in the water column. There are no equivalent EQSs for sediments in the UK. However, sediment quality standards have been developed elsewhere in Europe and Canada (Table 5.5 and 5.6). Section 5.4 outlines available information on sediment quality standards.

5.2 Environmental Quality Standards (EQSs)

EQSs have been derived under the requirements of the Dangerous Substances Directive (see Section 2.2.2.5) which classifies substances as List I and List II.

Standards for List I substances have been defined in “daughter” Directives to the EC Dangerous Substances Directive. The scientific justification for the standards is not available. Standards for List I substances are given in Table 5.1.

The Dangerous Substances Directive required that standards for List II substances are derived by the member states. The UK has set EQSs for List II substances which have been derived by WRc according to the methodology described in Grimwood and Dixon (1997). For each of the List II substances, reports are available which describe the data used to derive the standards and any uncertainties in the derivation. Where there are uncertainties arising from a lack of information on effects on saltwater organisms, larger safety factors have been used in the derivation of the EQS. Table 5.2 summarises the EQSs for List II substances and includes information on any uncertainties in the derivation of the standard. In the majority of cases, both an annual average (or annual mean) and a maximum allowable concentration were proposed. However, often only the annual average has been made into a statutory standard.

The environment agencies (i.e. the Environment Agency, SEPA and Environment and Heritage Service, Northern Ireland) have a legal obligation to ensure that statutory EQSs are met. **When considering the effect of substances in European marine sites, conservation agency staff should ensure they are aware of the EQS being used, the form of its application (annual average or maximum allowable concentration) and whether uncertainties in the derivation of the EQS have been taken into consideration. Conservation agency staff should refer to the relevant section in Appendices B and C and, if necessary, the additional literature referenced there, before concluding whether an EQS is likely to be adequate for the protection of an SAC or SPA feature. Uncertainties in the applicability of EQSs for the protection of Natura 2000 sites should be drawn to the attention of EA staff during consultation.**

Grimwood and Dixon (1997) assessed the adequacy of EQSs for List II metals in relation to the protection of sites of nature conservation interest. Uncertainties arising from this study have been included in Table 5.2.

Table 5.1. Water quality standards for List I substances

Parameter	Unit	Water quality standard		Standstill Provision [a]
		Estuary[b]	Marine	
Mercury	µg Hg/l	0.5 DAA	0.3 DAA	yes[c]
Cadmium	µg Cd/l	5 DAA	2.5 DAA	yes
Hexachlorocyclohexane[d]	µg HCH/l	0.02 TAA	0.02 TAA	yes
Carbon tetrachloride	µg CCl_4/l	12 TAA	12 TAA	no
Dichlorodiphenyltrichloroethane				
(all 4 isomers, total DDT)	µg DDT/l	0.025 TAA	0.025 TAA	yes
(para, para-DDT)	µg ppDDT/l	0.01 TAA	0.01 TAA	yes
Pentachlorophenol	µg PCP/l	2 TAA	2 TAA	yes
Total ‘drins’	µg/l	0.03 TAA	0.03 TAA	yes
Aldrin[e]	µg/l	0.01 TAA	0.01 TAA	yes
Dieldrin[e]	µg/l	0.01 TAA	0.01 TAA	yes
Endrin	µg/l	0.005 TAA	0.005 TAA	yes
Isodrin[e]	µg/l	0.005TAA	0.005 TAA	yes
Hexachlorobenzene[f]	µg HCB/l	0.03 TAA	0.03 TAA	yes
Hexachlorobutadiene[f]	µg HCBD/l	0.1 TAA	0.1 TAA	yes
Chloroform[f]	µg $CHCl_3$/l	12 TAA	12 TAA	no
1,2-Dichloroethane[g] (ethylenedichloride)	µg EDC/l	10 TAA	10 TAA	no
Perchloroethylene[g] (tetrachloroethylene)	µg PER/l	10 TAA	10 TAA	no
Trichlorobenzene[g] (all isomers)	µg TCB/l	0.4 TAA	0.4 TAA	yes
Trichloroethylene[g]	µg TRI/l	10 TAA	10 TAA	no

Notes

Substances are listed in the order of publication of Directives.

D dissolved concentration, ie usually involving filtration through a 0.45-µm membrane filter before analysis

T total concentration (ie without filtration)

AA standard defined as annual average

a. Most directives include, in addition to the standards for inland, estuary and marine waters, a provision that the total concentration of the substance in question in sediments and/or shellfish and/or fish must not increase significantly with time (the "standstill" provision).
b. In the UK the standards for estuaries are the same as for marine waters - The Surface Waters (Dangerous Substances) (Classification) Regulations 1989
1. In addition to a standstill provision applying to sediments or shellfish there is a further environmental quality standard of 0.3 mg Hg/kg wet flesh "in a representative sample of fish flesh chosen as an indicator".
2. All isomers, including lindane
3. The standard relating to the concentration of this substance came into effect on 1 January 1994.
4. The provisions of the directive on this substance came into force on 1 January 1990.
5. The provision of the directive on this substance came into effect on 1 January 1993.

Table 5.2 Water quality standards for the protection of saltwater life for List II substances

Parameter	Unit	Water Quality Standard (see footnotes)	Uncertainties in the derivation : Details obtained from the relevant EQS derivation reports
Lead	µg Pb/l	25 AD^{1,5}	The preliminary EQS was multiplied by a factor of 2 to account for overestimation of Pb toxicity in laboratory studies compared to the field environment. The EQS was considered tentative as a result of the paucity of reliable data, in particular for sub-lethal chronic studies with invertebrates and fish, and for field studies.
Chromium	µg Cr/l	15 AD^{1,5}	There were limited data on the sub-lethal effect of Cr and long-term exposure to freshwater and saltwater life. Separate standards for different Chronium valences (Cr(VI) and Cr(III)) were not recommended as a consequence of the lack of data for Cr(III). In addition, a comparison of the toxicities of each oxidation state was not possible. Some data were available that indicated higher sensitivity of some saltwater organisms to low salinities. The EQS was based on data generated at salinities typical of normal seawater. Therefore, further research on the effect of Cr at lower salinities was recommended.
Zinc	µg Zn/l	40 AD^{1,5}	The dataset available for the toxicity of Zn to saltwater life illustrated that at the EQS, adverse effects on algal growth had been reported. However, it was considered that there was currently insufficient evidence to suggest that the EQS would not adequately protect saltwater communities.
Copper	µg Cu/l	5 AD^{1}	Further data were considered necessary on the sensitivity of early life stages and life-cycle tests to confirm the sensitivity of saltwater life.
Nickel	µg Ni/l	30AD^{1}	Marine algae were reported to be adversely affected by Ni at concentrations as low as 0.6 mg l^{-1} which is below the EQS to protect saltwater life However, it was considered that there was insufficient evidence to justify a lower EQS based solely on results with algae and that further research into this area was desirable. There was also limited evidence to suggest that invertebrates in estuarine systems may be more susceptible to the effects of Ni than invertebrates in marine systems. Thus, an EQS to protect estuarine life may be needed in future when further data become available.

Parameter	Unit	Water Quality Standard (see footnotes)	Uncertainties in the derivation : Details obtained from the relevant EQS derivation reports
Arsenic	µg As/l	25AD[2]	Based on crab 96 hour LC50, and an extrapolation factor of 10 applied. Standards may need to be more stringent where sensitive algal species are important features of the ecosystem
Boron	µg B/l	7000 AT[1]	Few data available. However the standard was based on Dab 96 hour LC50, with an extrapolation factor of 10 applied
Iron	µgFe/l	1000AD[1,5]	The EQS for the protection of saltwater life was based on observed concentrations and general assessments of water quality. It was recommended, therefore, that the standard should be reviewed as soon as direct observations of water concentrations and biological status become available. Limited data did not allow an assessment of the importance of Fe species.
Vanadium	µgV/l	100 AT[1]	Data on the toxicity of vanadium on saltwater life were limited. As there were limited data for vanadium, it was not possible to recommend standards based on dissolved concentrations or separate standards for migratory fish. With regard to the latter, it may be necessary to base judgement of any risk in applying the EQS on knowledge of local risks and circumstances.
Tributyltin	µg/l	0.002 MT[2]	The standards for TBT weres tentative to reflect a combination of the lack of environmental data, toxicity data or data relating to the behaviour of organotins in the environment.
Triphenyltin (and its derivatives)	µg/l	0.008 MT[2]	The standards for TPT were tentative to reflect a combination of the lack of environmental and toxicity data or data relating to the behaviour of organotins in the environment.
PCSDs	µg/l	0.05 PT[1]	In view of the lack of data for the mothproofing agents, both from laboratory and field studies, the EQSs were reported as tentative values.
Cyfluthrin	µg /l	0.001 PT[1]	In view of the lack of data for the mothproofing agents, both from laboratory and field studies, the EQSs were reported as tentative values

Parameter	**Unit**	**Water Quality Standard (see footnotes)**	**Uncertainties in the derivation : Details obtained from the relevant EQS derivation reports**
Sulcofuron	µg /l	25 PT[1]	As a consequence of the general paucity of data for the mothproofing agents, both from laboratory and field studies, the EQSs were reported as tentative values. The data for sulcofuron suggested that embryonic stages for saltwater invertebrates could be more sensitive than freshwater species and, therefore, the EQS for the protection of marine life, derived from the freshwater value, may need to be lower.
Flucofuron	µg /l	1.0 PT[1]	In view of the lack of data for the mothproofing agents, both from laboratory and field studies, the EQSs were based on freshwater values.
Permethrin	µg /l	0.01 PT[1]	In view of the lack of data for the mothproofing agents, both from laboratory and field studies, the EQSs were reported as tentative values.
Atrazine and Simazine	µg /l	2 AA[2] ; 10 MAC[4]	The EQSs for the protection of saltwater life were proposed as combined atrazine/simazine to take account of the likely additive effects when present together in the environment.
Azinphos-methyl	µg /l	0.01AA[2] ; 0.04 MAC[4]	In view of the relatively high soil organic carbon sorption coefficient, it is likely that a significant fraction of the pesticide present in the aquatic environment will be adsorbed onto sediments or suspended solids. However, it is likely that this form will be less bioavailable to most aquatic organisms. As the adsorbed pesticide is more persistent than the dissolved fraction, it is possible that levels may build up that are harmful to benthic organisms. Insufficient information on saltwater organisms was available to propose a standard. In view of the paucity of data, the standards to protect freshwater life were adopted to protect saltwater life.
Dichlorvos	µg /l	0.04 AA and 0.6 MAC[2]	Based on data for sensitive crustaceans
Endosulphan	µg /l	0.003 AA[2]	There is little evidence on the ultimate fate of endosulfan and its metabolites or degradation products in sediments and on any effects on freshwater benthic organisms. Consequently, it is possible that some sediment-dwelling organisms, such as crustaceans, may be at risk.

Parameter	**Unit**	**Water Quality Standard (see footnotes)**	**Uncertainties in the derivation : Details obtained from the relevant EQS derivation reports**
Fenitrothion	µg /l	0.01 AA[2]; 0.25 MAC[4]	As there were limited data with which to derive EQSs to protect saltwater life, the freshwater values were adopted. However, the annual average for the protection of freshwater life may be unnecessarily stringent in view of the uncertainties associated with the acute toxicity data used in its derivation. The uncertainties exist because the original sources were unavailable for certain studies. Lack of confirmatory data existed in the published literature and data for warm water species were considered in the derivation.
Malathion	µg /l	0.02AA[2] ; 0.5MAC[4]	It was recommended that further investigation for both field and laboratory conditions into the effects of malathion on crustaceans and insects and on UK *Gammarus* species, in particular, should be carried out.
Trifluralin	µg /l	0.1AA[2]; 20 MAC[4]	None mentioned with regard to the annual mean.
4-chloro-3-methyl phenol	µg /l	40 AA[3]; 200 MAC[4]	Insufficient saltwater data were available to propose a standard. Therefore, the standard was based on freshwater value.
2-chlorophenol	µg /l	50 AA[3] ; 250 MAC[4]	Insufficient saltwater data were available to propose a standard. Therefore, the standard was based on freshwater value.
2,4-dichlorophenol	µg /l	20 AA[3]; 140 MAC[4]	Insufficient saltwater data were available to propose a standard. Therefore, the standard was based on freshwater value.
2,4D (ester)	µg /l	1 AA[3]; 10 MAC[4]	For the EQS proposed for 2,4-D esters, comparison of the data and derivation of standards were complicated by the number of esters and organisms for which studies were available. In addition, the toxicity of the esters may have been underestimated in some of the studies due to their hydrolysis. There were limited data on the toxicity of 2,4-D ester to saltwater life. Consequently, the freshwater value was adopted until further data become available.
2,4D	µg /l	40 AA[3]; 200 MAC[4]	There were limited data on the toxicity of 2,4-D non-ester to saltwater life. Consequently, the freshwater value was adopted until further data become available.

Parameter	Unit	Water Quality Standard (see footnotes)	Uncertainties in the derivation : Details obtained from the relevant EQS derivation reports
1,1,1 trichloroethane	µg /l	100 AA[3]; 1000 MAC[4]	The 1,1,1-TCA dataset available for freshwater species contained comparatively few studies where test concentrations were measured and, consequently, comparison of studies using measured concentrations vs. those using nominal values indicated that data from the latter type of study could be misleading.
1,1,2-trichloroethane	µg /l	300 AA[3]; 3000 MAC[4]	For 1,1,2-TCA, few data were available on chronic toxicity to freshwater fish. There were limited data on the toxicity of 1,1,2-TCA to saltwater life and, consequently, the EQS to protect freshwater life was adopted.
Bentazone	µg /l	500 AA[3]; 5000 MAC[4]	In view of the relatively high soil organic carbon sorption coefficient, it is likely that a significant fraction of the pesticide present in the aquatic environment will be adsorbed onto sediments or suspended solids. However, it is likely that this form will be less bioavailable to most aquatic organisms. As the adsorbed pesticide is more persistent than the dissolved fraction, it is possible that levels may build up that are harmful to benthic organisms. Insufficient information on saltwater organisms was available to propose a standard. In view of the paucity of data, the standards to protect freshwater life were adopted to protect saltwater life.
Benzene	µg /l	30 AA[3]; 300 MAC[4]	Limited and uncertain chronic data available.
Biphenyl	µg /l	25 AA[3]	The data available for marine organisms were considered inadequate to derive an EQS for the protection of marine life. However, the reported studies for saltwater organisms indicate that the EQS for freshwater life will provide adequate protection.
Chloronitrotoluenes	µg /l	10 AA[3]; 100 MAC[4]	The dataset used to derive the EQS to protect freshwater life was limited. Toxicity data were available for comparatively few species and there was limited information on the bioaccumulation potential of the isomers. There were few chronic studies available to allow the assessment of the long term impact of CNTs. There were no reliable data for the toxicity to or bioaccumulation of CNTs by saltwater species and, therefore, the EQSs proposed for freshwater life were adopted.
Demeton	µg /l	0.5 AA[3]; 5 MAC[4]	Insufficient saltwater data were available to propose a standard. Therefore, the standard was based on freshwater value.

Parameter	**Unit**	**Water Quality Standard (see footnotes)**	**Uncertainties in the derivation : Details obtained from the relevant EQS derivation reports**
Dimethoate	µg /l	1 AA[3]	The available data for marine organisms were considered inadequate to derive an EQS for the protection of marine life. Crustaceans were considered to be the most sensitive organisms, but more data are required to confirm this. In view of the uncertainties associated with the marine toxicity dataset, the freshwater EQS was adopted. This was based on the toxicity of dimethoate to insects. Although there are no marine insects, there is some evidence that marine organisms are more sensitive than their freshwater counterparts.
Linuron	µg /l	2 AA[3]	In view of the lack of data for saltwater life, the EQS proposed for the protection of freshwater life was adopted until further data become available.
Mecoprop	µg /l	20 AA[3]; 200 MAC[4]	There were limited data relating to the toxicity of mecoprop to aquatic life. The dataset for saltwater life comprised data for one marine alga, a brackish invertebrate and a brackish fish. Consequently, the freshwater values were adopted until further data become available.
Naphthalene	µg /l	5 AA[3]; 80 MAC[4]	Limited and uncertain chronic data available.
Toluene	µg /l	40 AA[3]; 400 MAC[4]	The dataset used to derive the EQS to protect saltwater life relied on static tests without analysis of exposure concentrations. Consequently, the derived values are considered tentative until further data from flow-though tests with analysed concentrations become available.
Triazophos	µg /l	0.005 AA[3]; 0.5 MAC[4]	The dataset available for freshwater life was limited to a few studies on algae, crustaceans and fish. No information was available for the target organisms (insects), on different life-stages or on its bioaccumulation in aquatic organisms. There were no data on the toxicity to or bioaccumulation of triazophos in saltwater organisms. Consequently, the EQSs to protect freshwater life were adopted until further data become available.
Xylene	µg /l	30 AA[3]; 300 MAC[4]	Limited information available. Freshwater data used to ‘ back up’ the standards.

Notes

Substances are listed in the order of publication of Directives.

A	annual
D	dissolved concentration, ie usually involving filtration through a 0.45-µm membrane filter before analysis
T	total concentration (ie without filtration)
µg/l	micrograms per litre
AA	standard defined as annual average
MAC	maximum concentration
1	DoE Circular in 1989 (Statutory standard)
2	Statutory Instrument 1997 (Statutory standard)
3	Statutory Instrument 1998 (Statutory standard)
4	Non- statutory standard
5	revised standards have been proposed but are not statutory

5.3 Standards needed to meet other Directive requirements

Whereas the EQSs discussed in Section 5.2 are set to protect all features of an ecosystem (with the caveats indicated in that Section and Appendices B and C), standards for a range of toxic and non-toxic contaminants have been set separately in order to meet specific Directive requirements. The standards for two of these - the Shellfish Waters and the Bathing Water Directives - are likely to be frequently encountered by conservation agency staff and are presented here. These standards are provided to staff as an indication of the levels that may be set, especially for non-toxic contaminants, to meet specific Directive requirements. They are, however, not necessarily or generally applicable for the protection of SAC or SPA features, but may help in appreciating the broad levels of contamination by some of these substances that may be acceptable, or alternatively which may cause concern.

5.3.1 Standards in the Shellfish Waters Directive

The standards in the Shellfish Waters Directive (Table 5.3) are applicable only in designated shellfish waters (see Section 2.2.2.4) and are designed to protect shellfish populations that are harvested for human consumption.

The standards in Table 5.3 were stipulated in the Directive, although the scientific reasoning for their derivation is unknown. The environment agencies are obliged to meet the imperative (mandatory) (I) standards in designated shellfish waters. **Where such waters have been designated within European marine sites, the conservation agencies should argue that guidelines values, at least, should be met. There may be a requirement for higher standards to secure the favourable condition of SAC features of interest (see Table I).**

Table 5.3. Quality standards stipulated in the Shellfish Waters Directive

Parameter	Unit	G	I
A. GENERAL PHYSIO-CHEMICAL PARAMETERS			
Colour			(a)
Dissolved oxygen	% sat	>80 T95	>70 TAA(b)
pH			7-9 T75
Salinity	g/kg	12-38 T95	40 T95(c)
Suspended solids			(d)
Tainting substances			(e)
Temperature		(f)	
B. METALS AND INORGANIC ANIONS			
Arsenic		(g)	(h)
Cadmium		(g)	(h)
Chromium		(g)	(h)
Copper		(g)	(h)
Lead		(g)	(h)
Mercury		(g)	(h)
Nickel		(g)	(h)
Silver		(g)	(h)
Zinc		(g)	(h)

Parameter	Unit	G	I
C. ORGANIC SUBSTANCES			
Hydrocarbons			(i)
Organohalogens		(g)	(h)
D. MICROBIOLOGICAL PARAMETER			
Faecal coliforms	per 100 ml	300 T75(j)	

Notes:

G	guide value
I	imperative (mandatory) value
T	total concentration (ie without filtration)
D	dissolved concentration ie usually involving filtration through a 0.45-µm membrane filter before analysis
AA	standard defined as annual average
75	standard defined as 75-percentile
95	standard defined as 95-percentile
MA	maximum allowable concentration
Pt/l	concentration of platinum (Pt) determined photometrically on the Platinum/Cobalt scale as a measure of colour in water

a. A discharge affecting shellfish waters must not cause an increase in colouration of more than 10 mg Pt/l compared to the waters not so affected (waters filtered in both cases). This standard is expressed as a 75-percentile.

b. If an individual result indicates a value lower than 70% of saturation, the measurement must be repeated. Concentrations below 60% of saturation are not allowed, unless there are no harmful consequences for the development of shellfish colonies.

c. A discharge affecting shellfish waters must not cause an increase in salinity of more than 10% compared to the water not so affected. This standard is expressed as a 75-percentile.

d. A discharge affecting shellfish waters must not cause an increase in the concentration of suspended solids by more than 30% compared to the water not so affected. This standard is expressed as a 75-percentile.

e. The concentration of substances affecting the taste of shellfish must be lower than that liable to impair the taste of the shellfish.

f. A discharge affecting shellfish waters must not cause an increase in temperature of more than 2 °C compared to the water not so affected. This standard is expressed as a 75-percentile.

g. The concentration of this substance or group of substances in shellfish flesh must be so limited that it contributes to the high quality of shellfish products.

h. The concentration of this substance or group of substances in water or in shellfish flesh must not exceed a level which gives rise to harmful effects in the shellfish or their larvae. Synergistic effects must also be taken into account in the case of metal ions.

i. Hydrocarbons must not be present in water in such quantities as to produce a visible film on the surface of the water and/or a deposit on the shellfish, or to have harmful effects on the shellfish.

j. In shellfish flesh and intervalvular fluid. However, pending the adoption of a directive on the protection of consumers of shellfish products, it is essential that this value be observed in waters from which shellfish are taken for direct human consumption.

5.3.2 Standards in the Bathing Water Directive

The standards in the Bathing Water Directive (Table 5.4) are only applicable in designated bathing waters during the bathing season (see Section 2.2.2.6) and are designed to protect human health from the microbiological components of sewage and, to a lesser extent, the aesthetic appearance of the bathing waters.

The standards in Table 5.4 were stipulated in the Directive and the reasoning behind their derivation is not known. The environment agencies are obliged to meet the imperative (mandatory) (I) standards in designated bathing waters during the bathing season. **However, the Government has indicated that progress towards achievement of guideline values should be made more swiftly. However, conservation agencies should note that, again, higher standards may be required to protect SAC features.**

Table 5.4 Quality standards for fresh and saline waters stipulated in the Bathing Waters Directive

Parameter	Unit	G	I
A. INORGANIC SUBSTANCES AND GENERAL PHYSICO-CHEMICAL PARAMETERS			
Colour			(a, b)
Copper	mgCu/l		
Dissolved oxygen	% saturation	80-120 T90	
pH			6-9 T95(b)
Turbidity	Secchi depth m	>2 T90	>1 T95(b)
B. ORGANIC SUBSTANCES			
Floating waste(c)		(d)	
Hydrocarbons	μg/l	300 T90(e)	(f)
Phenols	μgC_6H_5OH	5 T90(e)	50 T95(e)
Surfactants(g)	μg/l as lauryl sulphate	300 T90(e)	(k)
Tarry residues		(d)	
C. MICROBIOLOGICAL PARAMETERS			
Faecal coliforms	per 100 ml	100 T80	2 000 T95
Total coliforms	per 100 ml	500 T80	10 000 T95
Faecal streptococi	per 100 ml	100 T90	
Salmonella	per 1 l		0 T95
Entero viruses	PFU/10 l		0 T95

Notes

G	guide value
I	imperative (mandatory) value
T	total concentration (ie without filtration)80 standard defined as 80-percentile*
90	standard defined as 90-percentile*
95	standard defined as 95-percentile*
*	It is further stipulated that of the 20, 10 or 5% of samples from designated waters which exceed the standard, none should do so by more than 50% (except for microbiological parameters, pH and dissolved oxygen) and that "consecutive water samples taken at statistically suitable intervals do not deviate from the relevant parametric values" (Article 5 of CEC 1976a).
a.	No abnormal change in colour
b.	May be waived in the event of exceptional weather or geographical conditions
c.	Defined as wood, plastic articles, bottles, containers of glass, plastic, rubber or any other substance
d.	Should be absent.
e.	Applies to non-routine sampling prompted by visual or olfactory evidence of the presence of the substance
f.	There should be no film visible on the surface and no odour
g.	Reacting with methylene blue
h.	There should be no lasting foam

5.4 Sediment quality standards

EQSs are only applicable in the water column and there are no equivalent standards for sediments used in the UK. Some operational standards for toxic substances may be used in specific circumstances by the environment agencies.

The approach to the development of sediment quality standards has been summarised by Grimwood and Dixon (1997) in the context of List II metals. The Canadian/US approach is recommended and involves the derivation of Threshold Effects Levels (TELs) and Probable Effect Levels (PELs) from an extensive database containing direct measurements of toxicity of contaminated sediments to a range of aquatic organisms exposed in laboratory tests and under field conditions. Effects may be observed in some sensitive species exposed to the TEL, whereas the PEL is likely to cause adverse effects in a wider range of organisms. Further information on the approach is given in Long *et al* (1995). Interim sediment quality guidelines have been adopted by Environment Canada for a range of toxic substances (CCME 1999). Table 5.5 summarises some adopted sediment guidelines for List II metals in the Netherlands and Canada.

Table 5.5. Summary of saltwater sediment guidelines adopted for List II metals by VROM and Environment Canada (from Grimwood and Dixon 1997)

	Canadian Guidelines[1]		**Dutch (VROM)**
Metal	**TEL (mg kg^{-1} dry weight)**	**PEL (mg kg^{-1} dry weight)**	**Limit Values**[2] **(mg kg^{-1} dry weight)**
Lead	30.2	112	530
Chromium	52.3	160	380
Zinc	124	271	480
Copper	18.7	108	36
Nickel	15.9	42.8	35
Arsenic	7.2	41.6	55
Vanadium	nv	nv	nv
Boron	nv	nv	nv
Iron	nv	nv	nv

Notes:

1.	Effects based Guidelines. Expressed as bulk sediment concentrations
2.	Guidelines based on equilibrium partitioning (N.B. Particularly unsuitable for metals). Expressed for a standard sediment consisting of 5% organic carbon
nv	no value
TEL	Threshold effects level
PEL	Probable effects level

Table 5.6 summarises interim marine sediment quality guidelines issued by Environment Canada in 1999 for a range of toxic substances. Grimwood and Dixon (1997) stress that these guidelines have not been validated for use in the UK and that a proportion of the test species in the database are not indigenous to the UK and that there may be fundamental differences in sediment geochemistry. **However, in the absence of any UK standards, these guidelines can be used as a first approximation in assessing whether organisms are at risk from sediment concentrations of toxic substances.**

There are certain situations where the background concentrations of toxic substances are higher than normal due to human activities over many years but where the indigenous fauna and flora have successfully adapted to these changed conditions. For example, metal concentrations in the Fal estuary system are elevated due to mining activity in the catchment and organisms have adapted to these conditions.

In general, where sediment concentrations of toxic substances are close to or above the TEL concentration listed in Table 5.6, conservation agency staff should identify sediment

concentrations as a cause for concern and seek to minimise further inputs of these substances to the European marine site.

Table 5.6. Interim marine sediment quality guidelines (ISQGs) and probable effect levels (PELs; dry weight) (from CCME 1999)

Substance	ISQG	PEL
Inorganic (mg·kg^{-1})		
Arsenic	7.24	41.6
Cadmium	0.7	4.2
Chromium	52.3	160
Copper	18.7	108
Lead	30.2	112
Mercury	0.13	0.70
Zinc	124	271
Organic (µg·kg^{-1})		
Acenaphthene	6.71	88.9
Acenaphthylene	5.87	128
Anthracene	46.9	245
Aroclor 1254	63.3	709
Benz(a)anthracene	74.8	693
Benzo(a)pyrene	88.8	763
Chlordane	2.26	4.79
Chrysene	108	846
DDD[2]	1.22	7.81
DDE[2]	2.07	374
DDT[2]	1.19	4.77
Dibenz(a,h)anthracene	6.22	135
Dieldrin	0.71	4.30
Endrin	2.673	62.4[4]
Fluoranthene	113	1 494
Fluorene	21.2	144
Heptachlor epoxide	0.60[3]	2.74[4]
Lindane	0.32	0.99
2-Methylnaphthalene	20.2	201
Naphthalene	34.6	391
PCBs, Total	21.5	189
Phenanthrene	86.7	544
Pyrene	153	1 398
Toxaphene	1.5[3]	—[5]

[1] ISQGs and PELs presented here have been calculated using a modification of the NSTP approach.

[2] Sum of *p,p´* and *o,p´* isomers.

[3] Provisional; adoption of freshwater ISQG.

[4] Provisional; adoption of freshwater PEL.

[5] No PEL derived.

References

CCME. 1999. Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. *In*: *Canadian environmental quality guidelines, 1999*, Canadian Council of Ministers for the Environment, Winnipeg.

GRIMWOOD, M. AND DIXON, E. 1997. *Assessment of risks posed by List II metals to 'Sensitive Marine Areas ' (SMAs) and adequacy of existing environmental quality standards (EQSs) for SMA protection*. WRc Report CO 4278/10435-0 to English Nature.

LONG, E.R. *et al.* 1995. Incidence of adverse biological effects within ranges of chemical concentration in marine and estuarine sediments. *Environmental Management*, 19 (1), 81-97.

6. Factors affecting fate and behaviour of chemicals in the environment

6.1 Introduction

This Section summarises the key variables that must be considered when assessing projects affecting water quality. Their role and significance are considered only briefly here, for a fuller account staff should refer to the separate reports for nutrients, metals and turbidity:

- *Impact of Nutrients in Estuaries - Phase 2* (CCRU and CEFAS, 1999).

- *Turbidity in England and Welsh Tidal Waters* (WRC, 1999).

- *Assessment of Risks Posed by List II Metals to 'Sensitive Marine Areas' and Adequacy of Existing Environmental Quality Standards (EQSs) for SMA Protection* (WRC, 1999).

Chemicals introduced to the marine environment as a result of an activity or a discharge include toxic and non-toxic substances (see Section 4). Toxic substances generally exert their effects on organisms through direct toxicity and the extent of the effect is dependent on the chemical form of the substance (e.g. dissolved forms of metals are most toxic), the concentration and the period of exposure. Non-toxic substances generally exert their effects on organisms through direct or indirect means by changing the natural balance of the physico-chemical environment through a series of chemical and biological transformations. For example, nutrients stimulate growth of planktonic algae which, in turn, affects the light regime in the water column.

The fate and behaviour of a substance once discharged to the marine environment is determined to a large extent by its physico-chemical properties. However, the concentration and period of exposure of toxic substances and the chemical and biological transformations of non-toxic substances are affected by a number of important processes in the receiving environment. These include:

- dilution (including the concept of the mixing zone);
- flushing time;
- stratification;
- sediment type.

The effects of each of these on the behaviour and hazard posed by chemicals introduced into the marine environment are considered in turn below.

6.2 Dilution

When pollutants are introduced into the marine environment, they are subject to a number of physical processes which result in their dilution in the receiving water. Dilution is one of the main processes for reducing the concentration of substances away from the discharge point. Dilution is more important for reducing the concentration of conservative substances (those that do not undergo rapid degradation, e.g. metals) than for non-conservative substances (those that do undergo rapid degradation, e.g. some organic substances).

Dilution capacity of the receiving water can be defined as the effective volume of receiving water available for the dilution of the effluent. The effective volume can vary according to tidal cycles and transient physical phenomena such as stratification. In estuaries, in particular, the effective volume is much greater at high spring tides than at low neap tides. It is important to consider concentrations of substances in worst case scenarios (usually low neap tides except, for example, when pollutants might be carried further into a sensitive location by spring tides) when calculating appropriate discharge consent conditions. Stratification can reduce the effective volume of the receiving water by reducing vertical mixing and constraining the effluent to either the upper or lower layers of the water column.

The process of dilution can be separated into initial dilution and secondary mixing.

For many discharges from pipes, the effluent is principally freshwater, containing a mixture of pollutants and the discharge point is generally located below Mean Low Water Springs (MLWS) such that the effluent is released under seawater. Initial dilution occurs as the buoyant discharge rises to the surface because of the density differential between the saline receiving water and the freshwater effluent. Under certain circumstances of stratification (see section 6.4) or where the effluent comprises seawater (in a cooling water discharge for instance), the effluent may not rise to the surface but may be trapped in the lower layers of the water column. The design of sewage outfalls including the use of diffusers, can maximise the initial dilution by entraining as much receiving water into the effluent as possible. Guidelines for the amount of initial dilution expected for the design of discharges are set by the competent authorities.

For the many buoyant discharges, the effluent rises to the surface where it can form a ‘boil.’ The plume then forms and spreads and secondary mixing takes place. Eventually, the plume disperses both vertically and horizontally in the water column as the density differential becomes inconsequential and the concentration of pollutants in the water column approaches uniformity. Further dilution occurs as a result of the action of tide, wind and wave driven currents.

6.2.1 Mixing zone

The concept of the mixing zone was developed to allow a sound basis for the derivation of discharge consents which can be readily related to enforceable end of pipe effluent concentrations and outfall design criteria. A mixing zone is an area of sea surface surrounding a surface boil. It comprises an early part of the secondary mixing process and is prescribed to ensure that no significant environmental damage occurs outside its boundaries. An individual mixing zone is only defined with respect to an established EQS for a particular polluting substance. The mixing zone is the area of sea surface within which the EQS will be exceeded (SEPA 1998). The relation of the mixing zone to the location of European Marine site features will be a key consideration for determining the acceptability of dilution criteria.

Dilution within the mixing zone consists of initial dilution (the dilution received as a plume rises from the discharge point to the water surface) and secondary dilution (a slower rate of dilution, occurring between the surface ‘boil’ and the edge of the mixing zone). To ensure that the integrity of a European marine site is not affected, the minimum size of a discharge to be consented (in terms of flow or load) should be assessed on a site-specific basis. This will depend on the substances and/or physico-chemical parameters associated with the discharge, together with the positioning of the discharge in relation to the biotopes(s) or species for which it was designated. The initial dilution of discharges also needs to be considered. For example, an initial dilution of 50 times may be considered appropriate for secondary treated sewage effluent and low toxicity industrial effluents, but highly toxic industrial effluents may require a minimum initial dilution of 100 times (95 %ile).

SEPA (1998) define the maximum size of a mixing zone as 100 m around the centre boil in any direction that the plume may travel, but for European marine sites, more stringent criteria may be applied. Clearly, the flow and concentration of pollutants within the discharge are critical to defining the size of the mixing zone.

Further information on initial dilution and mixing zones and SEPA's policy is provided in SEPA (1998). A further useful introduction to the subject is presented in the Urban Pollution Management Manual (FWR 1998).

6.3 Flushing time

The concept of flushing time (retention or residence time) is important in the consideration of the impact of polluting substances because it is one of the factors determining the exposure period to marine organisms. In relation to estuaries, flushing time is defined as the time required to replace the existing freshwater accumulated in the estuary by the river discharge. Flushing time is influenced primarily by freshwater flow from the river. McLusky (1981) states that the flushing time for the Forth estuary under mean river flow conditions is 12 days, but increases to 10 weeks in Summer with reduced river flow and decreases to 6 days following severe rainfall. Estuaries with shorter flushing times are better able to accept effluents because mixing of fresh and saltwater is greater and dilution of polluting substances is better (McLusky 1981). Models which may be used by the EA in predicting flushing time are usually used to define the retention time of an estuary, but the boundary conditions of the model and the position of the estuary/seawater boundary can make a large difference to the calculated retention time. Models take into account the fact that water is moved progressively out of the estuary over time but may move up and down over shorter distances with the ebb and flow of the tide. Retention times can also be calculated for sea lochs and coastal embayments where the complete turnover of the volume of water within the waterbody can be estimated. Flushing times can be influenced by stratification (see Section 6.4).

The importance of flushing time for non-toxic substances is that shorter flushing times reduce the risk of primary or secondary effects occurring. For example, the risk of deoxygenation of the water column is reduced if the oxygen depleting substances are better mixed in the water column and are washed out of an estuary quickly. Similarly, the risk of the secondary effects of eutrophication are reduced if the phytoplankton are rapidly removed from an estuary and do not die off causing oxygen depletion. For toxic substances, shorter flushing times result in reduced contamination of the water column and sediments and reduced exposure periods for organisms in the waterbody.

When setting consent conditions, it is important that the longest estimated flushing time is used (i.e. in an estuary, during minimum river flow and neap tides) in calculations to maximise the potential for protecting organisms in a European marine site.

In considering the effect of flushing time within a European marine site, it is important that the effect is considered over the entire site, e.g. including its effect on residence time within

offshore/coastal parts of the site (where relevant) and not considering flushing time of the estuary alone.

6.4 Stratification

Stratification occurs as a result of a density differential between two water layers and can arise as a result of the differences in salinity, temperature or a combination of both. Stratification is more likely when the mixing forces of wind and wave action are minimal and this occurs more often in Summer.

In estuaries, the prime reason for stratification is restricted mixing of freshwater river flows and saltwater tidal incursions. In summer, the effects of temperature can reinforce the salinity stratification. In some estuaries, this can divide the water into two distinct layers which do not mix and are kept separate by a sharp change in density.

In stratified estuaries, the lower, saline water is more rapidly replaced, since less dense freshwater inputs (at lower volumes during summer) do not mix but float above the pycnocline. The saline water is more strongly mixed with seawater by tidal flow and so most exchange with the open coast occurs through the bottom layer. In such estuaries, discharge plumes usually rise to the surface and dilution/dispersion occurs primarily in the surface waters which, during stratification, have an increased retention time. This provides an argument for using summer ‘upper layer’ retention times to assess environmental impact, rather than whole estuary or annual mean retention times (see Section 6.3).

In sea lochs with sub-surface sills, the surface layer of water is replaced at a rapid rate by tidal action, while the lower water remains essentially stagnant, physically constrained behind the sills, often with a density barrier (pycnocline) forming between the two layers.

In coastal waters around the UK, stratification is a very transient phenomenon but can occur as a result of high temperatures in periods of calm weather or as a result of very high freshwater flow following severe rainfall.

It is important to know the extent to which stratification occurs in European marine sites comprising coastal waters so that due consideration can be made in the calculation of discharge consent conditions.

6.5 Sediment type

Sediment is present in the marine environment as both suspended and deposited particles and comprises both organic and inorganic components. The extent to which particles are suspended or deposited is a function of their density and the hydrodynamics of the water column.

Suspended sediment influences the effects of some non-toxic substances such as nutrients by reducing light penetration and preventing uptake by primary producers. This allows nutrient concentrations to increase while eutrophication effects are not apparent. Some toxic substances have an affinity for sediments, in particular organic particles, and the presence of suspended sediments can reduce water column concentrations here, but the toxic substance may still be biologically available, e.g. to sediment feeders/dwellers.

Sediment type is critical, not only because of its role in determining the faunal community, but also because of its role in adsorbing pollutants. In general terms, fine mud/silt/clay sediments with high organic content retain more contaminants than relatively coarse sandy sediments. The smaller the particle size, the more likely sediments are to retain contaminants which may subsequently be released back into the water column.

7. Dealing with new proposals and reviews of consents

7.1 Introduction

The procedure for dealing with new plans or projects or reviews of consents or authorisations likely to affect European marine sites is set out in the Conservation (Natural Habitats &c.) Regulations 1994 and in the Conservation (Natural Habitats &c.) Regulations (Northern Ireland 1995). The two main steps in the process prior to deciding to issue the consent (or to revoke or modify it in the case of reviews) are:

1. the judgement as to whether there is likely to be a significant effect on the integrity of the site. If a significant effect is considered likely then

2. the undertaking of an appropriate assessment to demonstrate no adverse impact on the integrity of the site.

Both of these main steps are the subject of existing or developing guidance to advise both competent authority and statutory nature conservation agency staff on the steps in the process. The role of this Section of the guidance manual is to provide background information on how to use this manual when making a judgement of likely significance and undertaking an appropriate assessment. This Section also illustrates by reference to case studies how information on water quality effects may be used to judge whether an effect is likely to be significant or to have an adverse effect.

In the majority of cases, discharges will contain a mixture of toxic and non-toxic substances and the receiving environment is also likely to contain background levels of toxic and non-toxic substances. Consequently, the effects on organisms are likely to be a result of the combined effects of all of these substances. Combined effects comprise interactions between substances that may enhance toxicity (additive or synergistic effects) and cumulative effects where successive additions of substances in space or time may cause progressive deterioration of a system.

When considering new proposals and reviews of consents and authorisations, it is important that consent conditions are set in the context of all inputs to the system, including other point source discharges, diffuse inputs from the land catchment, atmosphere and surrounding coastal waters and background water quality within the European marine site. It is also necessary to appreciate the influence of the hydrodynamic and physical nature of the system (dilution, retention time, stratification and sediment type) on concentrations and exposure times of toxic and non-toxic substances and to ensure that these are taken into consideration when consent conditions are set (see Section 6). The extent to which these considerations have been taken into account by the competent authority in setting consent conditions should be established by the conservation agency.

Where information is not available or is incomplete for any of these above considerations or when the effects of a substance on organisms comprising an interest feature are not known or are uncertain (see section 4 and appendices B and C), a precautionary approach should be adopted. The precautionary principle or approach in relation to the management of European marine sites should be based on that set out in guidance from DETR (1998). It states that:

'All forms of environmental risk should be tested against the precautionary principle. That means that where there are real risks to the site, lack of full scientific certainty should not be used as a reason for postponing measures that are likely to be cost effective in preventing such damage. It does not, however, imply that the suggested cause of such damage must be eradicated unless proved to be harmless and it cannot be used as a licence to invent hypothetical consequences. Moreover, it is important, when considering whether the information available is sufficient, to take account of the associated costs, including environmental costs, and benefits' (DETR 1998 from ABP 1999). A consideration of the degree to which "no adverse effect on integrity" must be determined absolutely is usefully given in the Cairngorm judgement, (opinion of Lord Nimmo-Smith, 27 October 1998, judgement over Judicial Review petition by WWF UK over development proposals affecting Cairngorm SAC). The relevant extract from this judgement reads as follows:

> "There never can be an absolute guarantee about what will happen in the future, and the most that can be expected of a planning authority, as a component authority under the regulations, or of SNH, as the appropriate nature conservation body, is to identify the potential risks, so far as they may be reasonably foreseeable in the light of such information as can reasonably be obtained, and to put in place a legally enforceable framework with a view to preventing these risks from materialising".

7.2 Approach to the consenting process

7.2.1 Reviews of consents

Whilst similar approaches to assessing 'likely significance' and 'no adverse effect' will be required both for new plans or projects and for reviews of consents, there are important differences in procedure between these two. The various stages in the 'review' process are outlined in the joint EA/EN/CCW guidance *Guidance for the Review of Environment Agency Permissions: Determining Relevant Permissions and 'significant effect'* (March 1999), and this should be referred to for guidance on the review process (see also EN Habitat Regulations Guidance Note 1 ('Appropriate Assessment') and CCW guidance on 'Significant Impact').

The reader should note that the legislative requirements for dealing with new proposals and review of consents may be different in Scotland. In determining whether a significant effect is likely during the **review** of consents, conservation officers can use their knowledge of the site's current and past condition in advising whether the consent is likely to have an effect. A flow diagram showing the steps involved in the consultation process for reviews of consents is given in the joint EA/EN/CCW guidance note referred to above.

One of four approaches should be presented to the competent authority when the opinion of the statutory nature conservation body is sought on the likely role of the consented activity in affecting site condition during the review of consents:

A. The designated feature is in favourable condition and there is no evidence to suggest existing consents are currently having a significant effect.

B. The designated feature is in favourable condition but there is concern that a water quality problem caused by a consented discharge may be threatening that condition and/or causing a decline in it..

C. The designated feature is in unfavourable condition, but this can be attributed to a factor unrelated to water quality, e.g. vegetation management, and there is no evidence to suggest relevant consents are currently having a 'significant effect'.

D. The designated feature is in unfavourable condition and poor water quality may be or is likely to be responsible.

As the joint EA/EN/CCW guidance note on judging likely significant effect during reviews of consents points out, there may be circumstances where a discharge consent which is currently not having a significant effect may not be operating at its full capacity. Increasing the discharge up to that level may have an adverse effect and so, although the feature may currently be in good condition, the consent conditions may nevertheless need to be revised. The joint guidance note should be consulted for fuller details of the process currently agreed between the conservation agencies and the EA.

The present guidance document should be used to help to determine whether relevant consents are likely to have a significant effect. The information provided here should help in deciding whether a mechanism exists whereby the conservation feature may be affected by the authorised activity; whether that mechanism is likely to be operating under the particular circumstances being considered; and whether the scale of effect is likely to be significant. The guidance should help in deciding whether further information is needed before a judgement on significant effect can be reached. It should also help at the later stage in the process when judging 'no adverse effect on integrity'. In that case, the guidance should be used to help determine what information is needed during the assessment and what further studies may be needed to help provide that information. If you are in doubt, seek advice from your national specialists as well as from EA conservation staff and specialists.

7.2.2 New plans and projects

When dealing with an authorisation for **new plans and projects** the assessment of site condition ('A' to 'D' above) will play a less significant role, and judgements are likely to depend more upon modelling future impacts, although a decision on the capacity of the site to respond to, e.g. further pollution loadings, will depend upon an understanding of its response to current loadings. In dealing with such situations, this guidance should help in understanding the output from model predictions and in proposing suitable monitoring requirements. Users of this manual should also refer to forthcoming joint EA/EN/CCW guidance on applying the Habitats Regulations to new Agency authorisations and activities (EAS/3100/4/2).

7.3 Case studies

The case studies below illustrate the use of the guidance document in making judgements over the 'likely significance' and 'adverse effect on integrity' in situations involving new authorisations, and those involving reviews of existing consents. These are illustrative of the use of the guidance manual in these processes only, and should **not** be taken as definitive guidance on procedures or of criteria to be used in making judgements. Existing guidance on consent review procedures for assessing ‘likely significant effect’; and forthcoming guidance on ‘new plans and projects’ and assessing ‘adverse effect on integrity’ should be consulted for such definitive advice as exists. It is anticipated that the illustrative examples below will change in response to the experience of users (namely conservation agencies and the EA), and the text should be regarded as provisional at this stage.

Three case studies have been developed to illustrate the use of this guidance manual alongside existing guidance for assessing likely significant effect and undertaking an appropriate assessment of new plans or project and consent reviews. Although the legislative procedures used may not apply in Scotland, the generic principles remain the same.

7.3.1 Case study 1: Kelp Bay

7.3.1.1 Objective

The purpose of this scenario is to introduce the use of the guidance manual and the issues to be considered in a simple situation with a single proposed new discharge consent against a background of good water quality and condition of the interest feature.

7.3.1.2 Scenario

There is a proposal for the construction of a food processing factory which will discharge an effluent having a high BOD and containing high concentrations of nitrogen, phosphorus and suspended solids. It is proposed to discharge the effluent into a sheltered coastal embayment via an outfall. The bay has been selected as a candidate SAC with shallow inlet and bay as the qualifying interest feature. The kelp forest which currently occupies 70% of the seabed in the bay has been identified as a key sub-feature contributing to the maintenance of the ecological integrity of the site. The condition of the kelp forest will be used as a baseline from which to judge the favourable condition of the interest feature. This feature is in good condition and water quality in the bay is considered to be very good, compared to similar types of site elsewhere.

7.3.1.3 Assessment of likely significant effect

Introduction

The construction of a new food processing factory would have already gone through the planning process and the conservation and environment agencies would have been consulted at that stage (see Section 2). Likely water quality issues should have been identified at that early stage during the planning process and staff should encourage an appraisal of such factors as far as is possible during the initial planning stage. To be considering the likely significant effects of the proposed application for consent to discharge, we will assume that planning permission will already have been granted. Food processing is not a prescribed process under IPC (see Section 2) and consequently application for a consent to discharge will be made under the Water Resources Act in England and Wales (Section 3) (NB: food processing is to be brought under the control of the forthcoming Integrated Pollution Prevention and Control Regulations.) The principal components of the discharge are non-toxic but can have primary and secondary effects on interest features (see Section 4). There are no formal standards for the principal polluting substances (see Section 5) and consent conditions for these substances will have to be set such that the concentrations in the receiving water do not have an adverse effect on the integrity of the site.

In considering a consent for this new discharge, the competent authority will have come to a view on the appropriate location for the discharge (in consultation with the conservation agency). Avoiding damage during construction, as well as selecting a location which causes least risk to interest features locally, will be key considerations. This example considers only operational issues, not those arising during construction. The discharge point will be below Mean Low Water Springs (MLWS) and the design of outfall will be suitable to achieve the design guidance for initial dilution. The volume of the discharge under all flow conditions will have been specified and the components of the discharge identified. Consent conditions for polluting substances will also need to be set (as an absolute limit for a non-sewage discharge) such that all other appropriate EC Directives, international obligations, environmental, conservation and aesthetic considerations are met.

In parallel with these considerations, the proposed consent is subject to the Regulation 48 process to establish whether it is likely to have a significant effect on the interest features of the site.

The steps set out in this example are based on forthcoming joint EA/EN/CCW guidance *Applying the Habitats Regulations to New Agency Authorisations and Activities* (EAS/3100/4/2). The initial steps in the process: (a) is the plan or project directly connected with the management of the site for nature conservation, and (b) identify the interest features of the site, have already been completed. The steps below are those now used to determine whether the plan or project is likely to have a significant effect. Three general criteria have been identified:

I. Is there a hazard?
II. Is there a risk of exposure to the hazard?
III. What is the likely scale of any effect?

These are considered in the box below.

Existing *Guidance for the Review of Agency Permissions* (English Nature, Countryside Council for Wales and Environment Agency 1999), sets out four steps in determining whether a discharge is likely to have a significant effect during the process of **reviewing** consents. These are adapted here to the process for considering **new** proposals, but more definitive advice on the steps involved is being developed.

Step I: Are the interest features sensitive to any hazard arising from this process?

Kelp Bay is a large shallow inlet or bay with a submerged reef comprising a kelp bed. The kelp bed is the vulnerable sub-feature present on site because of its sensitivity to light and nutrient regimes (see Table 4.4).

Step II: Is there a mechanism by which the consented discharge(s) is likely to affect the designated features of the site?

In this case, the discharge is directly onto the interest feature.

StepIII: Is the potential scale of any effect likely to be significant?

Since the judgement of ‘likely significance’ is intended as a coarse filter to ensure that all relevant situations are appropriately assessed, any impact which is likely to have a measurable effect onthe feature of interest should be considered potentially of significance (in a similar way a *de minimis* judgement is applied to the area of an interest feature potentially affected by a development, for example).

In helping to reach a judgement over whether the scale of any effect of a change in water quality due to a consented activity is likely to be significant, the following factors should be taken into account:

- Is the area affected likely to be highly localised or more extensive?
- Is the affected area likely to coincide with or impact on the designated feature?
- Is the effect likely to be readily or rapidly reversible during the operation of the consented activity?
- What is the likely contribution from the consented activity relative to other sources (and background levels)?
- Is the designated feature particularly sensitive to the particular water quality change?
- Are cumulative effects likely in association with other consented activities?

Table 4.1 of this guidance manual lists 16 principal activities and the mechanisms by which water quality might be affected. With new discharges, it is important to ascertain what the polluting substances are in the discharge. This information will be contained in the proposed discharge consent. For many polluting substances, there will be a profile in Section 4 of the guidance manual describing the behaviour of that substance, or group of substances, in the environment and the effects on groups of aquatic organisms. This information can be used to determine whether a mechanism exists which links the discharge and the designated features, and also to indicate whether the mechanism is likely to operate in this situation.

In situations such as this, where there are no clearly applicable standards, an understanding of any risks involved may be assisted by a comparison of the predicted state, with the current status of the site.

The guidance manual contains a summary of the water quality monitoring undertaken by the competent authorities in the UK which is co-ordinated at a national level within each country. The sources of information listed should be consulted for available information on a site by site basis. There may local operational monitoring programmes undertaken by the regions of the competent authority and this information may be obtained from regional offices. Alternatively Conservation Officers may have other (including anecdotal) information from a range of sources which suggest that water quality maybe an ongoing issue.

Water quality in Kelp Bay is believed to be good and there are no other discharges likely to affect the bay (although it is worth noting that inputs from the surrounding marine environment are known to be important for several shallow inlet situations in the UK, e.g. Lindisfarne, Budle Bay, Chichester/Langstone Harbours). Available monitoring data were, however, sparse because there has been no history of water quality problems and these areas tend to be monitored less frequently. In this case, therefore, available water quality information is likely to be of little help in determining whether a significant effect is likely, but we can therefore assume that background nutrient levels are unlikely to be affecting the feature adversely.

The conservation agencies may be consulted at this stage to provide information on whether features are in favourable condition. In the case of **new** discharges etc, this information may help to judge whether an additional pollution load is likely to stress the system such that it is unable to maintain its condition. This guidance manual can provide no information on the definition of favourable condition for individual features but can provide some guidance as to what aspects of water quality should be a component of the favourable condition table for each feature.

For the situation in Kelp Bay, the most appropriate response is that the designated feature is in favourable condition and current consents do not appear to be having significant effect.

For the situation in Kelp Bay, the polluting substances are organic particulates (leading to elevated BOD), nitrogen, phosphorus and suspended solids. The kelp bed (with its associated fauna of invertebrates and fish) is used as the sub-feature for helping to judge the site condition. The profiles for the polluting substances are located in Appendix C of the guidance manual.

BOD

Elevated BOD arises from the organic substances in the effluent that undergo aerobic degradation and, therefore, exert an oxygen demand on the water column or the sediments. Much of the organic matter is likely to be in particulate form and, depending on the particle size distribution and the water movements around the outfall, the larger particles would be expected to settle out early in the secondary mixing process and the smaller particles may be carried further afield (see 'suspended solids' below). The oxygen demand on the water column may often be restricted to a small area around the discharge point and probably within the mixing zone. Making such a judgement in a specific case such as this cannot be based on information in this guidance document, instead specialist advice should be sought on the likely behaviour of oxygen demand in the particular circumstances being considered. This effectively will identify a condition where any impact of this factor may be considered trivial and needs not be considered further.

A mechanism exists for BOD lowering the oxygen status of the water column (see Appendix C) which in turn affects the fauna associated with the interest feature. Providing the water is well mixed (and it may be in this case - considering the tidal range and relatively shallow depth of the bay - although this would need to be confirmed by modelling), there will probably be sufficient transfer of oxygen from the atmosphere not to affect any pelagic fauna. However, in the absence of such modelling information, it would be reasonable to conclude that a significant effect is likely in this case due to BOD, and an appropriate assessment is required.

Suspended solids

Larger particles settling out of the water column will be used by filter feeding organisms as a food source and will accumulate initially on the substrate surface if hydrodynamic conditions allow. Water movements within the kelp bed will be reduced compared to the open bay and any particles transported to the kelp bed may be more likely to settle either on the sediment or on the kelp itself. Accumulation of organic particles may result in an oxygen demand on the sediment which can result in a change in the composition of the benthic fauna which could affect associated benthic feeding fish communities (see Section 4 and Appendix C.4).

A mechanism therefore exists whereby suspended solids (comprised principally of organic matter) settle out of suspension and increase the sediment oxygen demand, thereby lowering the oxygen status of lower waters and of the sediment itself. Reduced sediment oxygen status is acknowledged as a major factor determining the infaunal community composition (and to some extent the surface-dwelling faunal community) (see Section 4 and Appendix C.5). The BENOSS model predicts the effects of organic suspended solids on the sediment faunal community and would be an appropriate tool to predict effects during an appropriate assessment. In this case, the existence of a mechanism whereby the interest feature is affected, together with the likely coincidence between area affected and the interest feature lead to a judgement of "likely significant effect" due to change in oxygen status.

Suspended solids also contribute to turbidity and so would decrease light penetration of the water column. The relationship between the lower depth limit of macrophyte colonisation (and thus the total area colonised by macrophytes) and water clarity is well established (see Section 4 and Appendix C.9). Since macrophytes (in this case the kelp beds) form an important sub feature of this site, since also a mechanism exists whereby suspended solids (via effects on light penetration) can affect this sub-feature and since, although we have no information on the area likely to be affected or whether the kelp is in fact light limited in this case, there is likely to be coincidence between the area affected by change in suspended solid levels and the interest feature, a "likely significant effect" due to the effect of suspended solids on light penetration is a reasonable conclusion in this case.

Nutrients

The effects of nutrients on macroalgal communities are extremely difficult to determine. There is some evidence that elevated nutrient levels, up to a maximum concentration, stimulate the rate of growth of macroalgae. However, this maximum concentration is not known. For microalgae (phytoplankton) again there is evidence for N or P limiting growth in certain estuarine situations (see Appendix C1) but the thresholds for this site would probably not be known.

Kelp forests are known to thrive at the nutrient concentrations which typically are likely to occur outside the mixing zone. However, increased nutrient availability could increase the standing crop of epiphytic algae, further reducing light availability to the kelp and thereby reducing the area colonised by the kelp, assuming that light availability is a limiting factor in this case.

For each of the polluting substances, there is a potential mechanism affecting the kelp bed or its associated fauna. For nutrients (this could be nitrogen and/or phosphorus) and suspended solids, there is sufficient evidence to suggest that there may be an effect on the kelp bed or its associated fauna and, without further information, an effect of BOD cannot be ruled out at this stage.

The conclusion for the situation in Kelp Bay is that the proposed consent for the discharge is likely to have a significant effect on the interest feature.

Steps IV: Internal and external consultation

The conclusions of Steps I to III are subject to internal (within the competent authority) and external (with the country conservation agency) consultation to confirm, or otherwise, the judgement of likely significance. The reasons for the judgement of a likely significant effect in this case are:

1. The consent will cause an increase in BOD, suspended solids, turbidity and nutrients, all of which are factors to which the interest feature is considered sensitive.

2. There is insufficient evidence to be able to conclude that these effects are not likely to have a significant effect, specifically:

    - Insufficient evidence that BOD will not be raised locally such as to adversely affect an unacceptably large area of kelp-dominated habitat. Insufficient evidence that the nutrient regime will not adversely affect macro- or planktonic algal development.

    - Insufficient information available to determine where the suspended solids will settle, or to determine whether the sediment will become organically enriched, thereby affecting the sediment oxygen status, altering the particle size composition and potentially changing the infaunal community status.

    - Insufficient information to determine the effect of the discharge on the light climate within the bay (as a result of increased turbidity through the effects of increased suspended solids loading or in response to increased nutrient loading) and light availability to the kelp (as a result of settled particulate matter and potentially increased epiphyte standing crops.

Since the requirement is to establish **likely** effect at this stage for the situation in Kelp Bay, the conclusion is upheld through the consultation steps and the judgement of likely significant effect is confirmed. An “appropriate assessment” is therefore required. An important principle here is that we have erred on the side of caution, in the absence of further information in reaching this judgement. The process of delivering the appropriate assessment is considered briefly below, but more detailed forthcoming guidance (EAS/3100/4/2) should be referred to.

7.3.1.4 Appropriate assessment

The purpose of an appropriate assessment is to gather and assess additional information to demonstrate adequately that a discharge will not affect the integrity of the site. This may involve a range of different activities, including those listed below, although it is important that the assessment remains **appropriate**, the level of assessment needs not be as comprehensive as indicated for all cases. The appropriate assessment may therefore involve:

- A more thorough assessment of available data in terms of compliance with statutory standards (particularly in relation to determining the existing status of the water body).

- Modelling dispersion of the discharge and the concentrations of pollutants within it; then comparing these concentrations with statutory standards (none relevant to this case study).

- Further investigation to determine the concentrations of pollutants within the water column and/or sediment (again relevant to determining current status of the water body).

- Gathering more information on the toxicity of pollutants contained in the discharge (no toxic substances in this case study).

- Undertaking comparative assessments of biotopes within the European marine site with otherwise similar biotopes from tidal water exposed to a range of concentrations of the same pollutants (possibly a useful approach in this case study).

- Ecological modelling to determine the likely effects (short, medium and/or long-term) of non-toxic pollutants contained in the discharge (in this case the BENOSS model would be appropriate for predicting organic carbon impacts).

- Laboratory studies to determine how different pollutants react with each other to affect their potential toxicity in the environment (not relevant to current scenario).

- Investigations of the potential for accumulation of pollutants within the sediment (in this case nutrient dynamics should be assessed).

- Studies to determine bioconcentration factors of discharged chemicals and the potential for bioaccumulation through the food chain (not relevant in this case).

- Collection of hydrodynamic data. Any hydrodynamic models must be validated against real measurements.

The level of assessment, and nature of information required will need to be discussed and agreed in advance with the competent authority and the developers. In this case study, the key issues for the assessment to address (based on the factors previously identified as likely to have a significant effect - see 7.3.1.3) are:

1. To assess likely effect of BOD:

    ! What is predicted size of dilution zone for BOD?

    ! What is its location in relation to the interest features?

    ! What is the duration/timing of maximum BOD loads and their relationship with existing BOD standards (e.g. for dissolved O_2, Section 5.3)?

2. What area is affected by increased suspended solids?

    ! Suspended solids deposition model needed.

    ! Suspended solids water column (light attenuation) model needed.

    This should be compared with background levels (may require sampling) and their variation.

    ! Effect on benthos - location affected and sensitivity of benthos.

    ! Effect on macro-algal growth/distribution.

3. ! Modelling of predicted N and P concentrations at ‘worst case’ situations (time of year, state of tide/wind).

    ! Area affected (timing and duration) by nutrients in relation to sensitivity of features. Must take account of relevant variables: tide, wind, stratification, freshwater flow.

    ! Background nutrient levels and variation.

    ! Relationship of nutrient concentrations with concentrations known to be likely to lead to elevated chlorophyll .

    ! Risk of accumulation in and release from sediments.

If, for example, nutrient concentration elevation is minimal relative to background levels and variation, and there is no other evidence of nutrient disturbance to the site (i.e. the site is not likely to be approaching an irreversible change in nutrient status) then it may be possible to ask for a time-limited consent to enable monitoring of the activity in order to determine:

! how accurate are any model predictions?

! are any (reversible) changes detectable in the most sensitive indicator species?

As with the initial assessment of likely significance, the competent authority is responsible for making the final judgement on whether current or proposed consent conditions will affect the integrity of a European marine site. However, there is a statutory requirement to consult the statutory nature conservation bodies over the results of the appropriate assessment and the conclusions over any effect on the integrity of the site.

It is possible that the results of an appropriate assessment investigation may still leave substantial doubt as to the medium or long-term impact of a discharge on the integrity of a site. The Habitats Regulations require there to be **no** adverse effect on integrity, so where this is the case, staff should employ the precautionary principle and require the proposal to be amended or rejected. In certain cases, e.g. where an adverse effect is clearly going to be reversible (in the short term) it may be acceptable to agree limited consent whilst further monitoring data are collected in order to test model predictions with the scheme in operation. However, even where an appropriate assessment suggests that the integrity of the site will be damaged by current or proposed consent conditions, those consent conditions may still be granted if there are overriding reasons of public interest and alternative solutions are not possible, ultimately a decision on this will be determined by the Secretary of State, and compensatory measures will then be required.

7.3.2 Case study 2: Seal Marsh

7.3.2.1 Scenario

Expansion of an existing organic chemical manufacturing plant which will discharge directly into the mouth of an estuary. The effluent will contain increased quantities of copper (5 mg.l^{-})^{1} and phthalates - principally DNBP (20 mg.l^{-1}), but lower concentrations of other phthalates may also be present.

Instead of the current short outfall, it is proposed to build a longer outfall to discharge closer to the mouth of the estuary where greater mixing is available. Extensive salt marshes are present in the estuary on the opposite side to the chemical works, and *Spartina* (which recently established itself at a number of sites on the intertidal flats) is now expanding in area, leading to locally increased sediment accumulation rates. The outer estuary is used by breeding seals.

The site is designated for Annex I habitat (estuary) and Annex II species (common seal).

The conservation objectives for the site include maintaining the habitat conditions that will maintain seal population and maintaining biodiversity of the upper salt marsh. It is accepted that the area colonised by *Spartina* will increase, and so sediment accumulation rates within the estuary are also likely to increase. The conservation objectives emphasise the importance of protecting salt marsh creeks as nursery areas for fish.

7.3.2.2 Objective

To demonstrate the use of this guidance manual for an amendment to an existing consent (i.e. to be considered as a **new plan or project**) with an effluent containing toxic substances in a situation of greater complexity where background water quality is less good and where there are several interest features to consider.

7.3.2.3 Assessment of likely significant effect

Introduction

The expansion of an existing chemical factory would already have gone through the planning process and the conservation and environment agencies would have been consulted at that stage (see Section 2). The organic chemical industry is a prescribed process under IPC, so a variation to an IPC authorisation will be the mechanism for considering effects on the SAC interest features. The IPC authorisation will cover the release of effluent to air, water and land, requiring that BATNEEC (see Section 2.2.2.1) be applied and so effects of atmospheric discharges, as well as any solid waste disposal on the site, will be considered as well as aquatic discharges. In this case, the principal components of this discharge are toxic aquatic discharges, having direct effects on the interest features (Section 4). Formal standards exist for one of the principal polluting substances (copper), but only for water; not in the sediment. No standards are available for any phthalates (see Section 4, Table 4.3 and Appendix B 49).

The revised outfall discharge point would be below MLWS, the mixing zone would not impinge upon the shoreline and the outfall will be suitable to achieve the design guidance for initial dilution. Discharge conditions will also need to take account of other EC Directive requirements, international obligations and EQSs.

Step I: Are the interest features sensitive to any hazard arising from this process?

Seal Marsh is designated as an estuary. The vulnerable features of interest are the salt marsh and the seal colony (see Section 4, Table 4.3 which describes the sensitivity of marine features to copper and to phthalates).

Step II: Is there a mechanism by which the consented discharge is likely to affect the designated features of the site?

As with the previous example, the discharge is directly into the site.

Step III: Is the potential scale of any effect likely to be deemed significant?

Table 4.1 of the guidance manual lists 16 principal activities and the mechanisms by which water quality might be affected. With applications to vary discharges, it is important to determine what the changes will mean for polluting substances in the discharge. This information for prescribed substances will be contained in the application for variation. For many polluting substances, there will be a profile in Appendix B/C of the guidance manual describing the behaviour of that substance, or group of substances, in the environment and the effects on groups of aquatic organisms. This information can be used to determine whether a mechanism exists which links the discharge and the designated features, and also to indicate whether the mechanism is likely to operate in this situation.

For the situation in Seal Marsh, the polluting substances are copper and phthalates (DNBP) and the designated features are a saltmarsh (with its associated fauna of invertebrates and fish) and seal colony. The profiles for the polluting substances are located in Appendix B, Section 7. (copper) and Appendix B, Section 49 (phthalates) of the guidance manual.

Both copper and phthalates should be regarded as persistent. Bioaccumulation can be a problem for copper, but does not appear to be an issue for phthalates.

When copper in solution comes into contact with the sediment, it may bind. Similarly, it will also be adsorbed onto suspended solids. Suspended sediment which has come into contact with the outfall plume is likely to contain elevated levels of copper, which could be deposited on the saltmarsh, potentially damaging biota. Copper is known to be toxic to vertebrates, invertebrates and algae and higher plants. Limited information is provided in the manual about standards for metals in sediments (see Section 5.4) but this route of exposure would need to be considered for all potentially toxic contaminants.

Biomagnification of copper is not thought to be a problem, and seals are more likely to have lower tissue levels of copper than invertebrates and fish. No data are available on the toxic effects of DNBP on mammals, fish or algae; neither have bioaccumulation studies been undertaken to determine the likely uptake route of DNBP by seals via fish. However, indications from bioaccumulation assessments undertaken for other phthalates do not suggest that this is a cause for concern (see Appendix B 49).

The phthalate group contains some endocrine-disrupting chemicals, with potential consequences for the breeding seal population, as well as possible effects on marine invertebrates and fish. However, little information is available about which phthalates are endocrine disrupters, or the concentrations at which endocrine disruption occurs.

For phthalates, there is a potential mechanism for affecting the seal colony and the saltmarsh invertebrate and fish fauna. For copper there is a potential mechanism for affecting salt marsh fauna and flora. Given that this is a major industry (regulated under IPC), there are initial grounds for assuming that the scale of effect might be significant. For both DNBP and copper, there is sufficient evidence to suggest that a significant effect may be likely.

Available information sources should be consulted for available site-specific information on which the current water quality status of the site may be assessed.

There are a number of different sources of copper in the estuary, largely associated with discharges in the upper reaches. The background copper concentration in the outer estuary mid-channel is usually ~3 mg.l^{-1} but during storm events, levels may exceed 5 mg.l^{-1}. An EQS of 5 mg.l^{-1} (dissolved annual average) exists for copper in water, but no standards exist for copper in sediment (although see guideline values from other countries, summarised in Section 5.4). Concern has been raised that the current EQS may not be protective enough for some fauna (see Section 5 and Table 5.2), but where levels of organic carbon are elevated, a higher EQS may be acceptable.

The term phthalates covers a relatively wide group of chemicals which should be regarded as ubiquitous (see Section Appendix B 49.2). At least some may be adsorbed onto sediments where they can be concentrated to much higher concentrations than found in overlying water. DNBP is likely to be present in both the water column and the sediment (see Appendix B 49.3 and 49.4).

The conservation agencies may be consulted at this stage to provide information on whether the features are in a favourable condition. This approach will be useful in cases such as this where the “new plan or project” is a variation to an existing consent. This guidance manual can provide no information on the definition of favourable condition for individual features but can provide some guidance as to what aspects of water quality should be considered in drawing up condition tables for the site sub-feature.

In the current example, the most appropriate response is that the designated feature is in favourable condition, but there is concern that a water quality problem may be threatening that condition based on the knowledge of occasional breaches of the EQS and uncertainty over effects of the current copper loading.

The conclusion for the situation in Seal Marsh is that the change to the loading of copper may have a likely significant effect on the condition of the saltmarsh. Salt marsh creeks acting as nursery areas for crustaceans and fish may potentially be significantly affected by increased loads and localised high concentrations of DNBP, which may also have an effect on the seal population.

Step IV: Internal and external consultation

The conclusions of Steps I to III are subject to internal (within the competent authority) and external (with the country conservation agency) consultation to confirm, or otherwise, the judgement of likely significance. On the basis of the concentrations above, a judgement that a significant effect is likely seems reasonable. The reasons for this are:

1. Not enough information available on toxicity of DNBP or endocrine disruption of mammals to assess likely significant effect, but a possible mechanism exists for an effect which would not be restricted to the immediate outfall location and may have serious population consequences if realised. Therefore, precautionary approach is required.

2. Background levels of DNBP (and other phthalates) are not known.

3. Copper is already known to exceed EQS outside of a 100 m mixing zone during storm events and this risk is increased if loading increases. The mixing zone would have to made larger to comply with EQS under such circumstances and the consequences of this for the SAC feature would need to be examined.

4. The rate of accumulation in sediment is likely to increase under this scenario. There is a risk of long-term exposure via this route.

For the situation in Seal Marsh, the conclusion is upheld through the consultation steps and the judgement of likely significant effect is confirmed. An appropriate assessment is therefore required.

7.3.2.4 Appropriate assessment

The appropriate assessment for this scenario is likely to require the following:

1. **For DNBP:**

    ! An assessment (from up-to-date sources of information) of endocrine disruptor effects on

        “ invertebrates

        “ fish

        “ aquatic mammals

    with emphasis on pthalates, possible routes of exposure and any information on threshold concentrations.

        “ Modelling of likely phthalate exposure for the most sensitive organisms.

“ There will be a need to adopt a very precautionary approach to areas of uncertainty surrounding this group of pollutants.

2. **For copper:**

! Consideration of the adequacy of the copper EQS in this case (see Table 5.2).

! Modelling of copper mixing zone (where EQS or other threshold selected will be exceeded) in relation to occurrence of features of interest.

! Measurement of current Cu levels in sediment and modelling of Cu accumulation in sediment over time.

7.3.3 Case study 3: Grass Flat Estuary

7.3.3.1 Scenario

To review the consents of three sewage treatment works (PE = 2,000, 3,000 and 4,000) which discharge into a river some 3 km upstream of the tidal limit, together with that of a fourth STW (PE = 20,000) which discharges directly into the upper/middle reaches of the estuary, the lower reaches of which contain submerged *Zostera* beds. There are concerns that intertidal *Enteromorpha* beds have increased in size during recent years on sediment close to the estuarine discharge point. Seasonal dissolved oxygen slumps have caused occasional mortalities of migratory salmonids. The largest treatment works were built to treat the waste from a population of 21,000 people, together with the effluent from two factories which discharged effluent with a high organic content (combined PE = 10,000). However, the use of these factories changed, so that they now produce relatively little liquid effluent, with a low organic content.

The site is designated as both an SAC (as an estuary, with key sub-features against which site condition is assessed being *Zostera* beds and salmon) and an SPA (birds).

The conservation objectives for the site include allowing anadromous/catadromous fish passage through the estuary, and maintenance of the distribution of estuarine species throughout the whole estuary. In addition, the colonisation of intertidal sediments by *Enteromorpha* should not be allowed to expand , the current status of the bird community should be maintained and any reduction in the area/density of *Zostera* should be prevented.

7.3.3.2 Objective

To demonstrate the process for a **review** of consents in a situation where there are combined effects from several discharges and where the interest feature is currently in unfavourable condition due to a water quality problem.

7.3.3.3 Assessment of likely significant effect

Introduction

The four sewage treatment works which discharge into this site have consent conditions which were issued some years ago. The industrial inputs from the factories are not such as to require

IPC authorisation, and the current consents are based solely on the sanitary determinands (suspended solids, ammonia and BOD), although the works also discharge dissolved nutrients (nitrogen, phosphorus) and more slowly biodegradable organic matter.

The current outfall discharge point into the European marine site lies below MLWS, but the mixing zone impinges upon the shoreline and the outfall will be suitable to achieve the design guidance for initial dilution. All discharge conditions have been set as 95%iles.

The steps in this process follow those in joint EA/EN/CCW *Guidance for the Review of Environment Agency Permissions: Determining Relevant Permissions* and *Significant Effect* (EA, EN and CCW, 1999), outlined in Section 7.2.1.

Step I: Are vulnerable features present on the site?

Grass Estuary is designated as an estuary. The features vulnerable to water quality are the *Zostera* beds and the sand/shingle flats which are used by the bird community (avocet and tern spp) as a feeding area. Salmon (an anadromous fish) is listed under Habitats Directive Annex II and uses the estuary on passage and is also sensitive to the water quality effects here (Section 4.2.4 and Appendix C 5).

Step II: Is there a known water quality problem?

Available information sources should be consulted for available site-specific information.

Dissolved oxygen slumps occur on a seasonal basis in the upper estuary.

The growth of *Enteromorpha* close to the estuary discharge is indicative of nutrient enrichment. TIN levels are relatively low compared to levels in many other estuaries with extensive intertidal flats that do not suffer from ‘green tides’, but the role of nitrogen mineralisation within the sediment as a nutrient source for (see Appendix C 1, Table C 2) *Enteromorpha/Ulva* growth is now well established and so measurements of TIN alone are a poor indicator of the risk of eutrophication effects such as *Enteromorpha* spread (see Appendix C 1).

Step III: Are features in a favourable condition?

The *Zostera* reef has decreased in area during recent years and the salmon population suffers mortalities due to dissolved oxygen slumps. The bird population is believed to be in favourable condition, but there is concern that a water quality-related problem may threaten that condition (the expansion of *Enteromorpha* would reduce food availability in the intertidal flats for wading birds) (see Appendix C). In terms of its SAC designation, the designated features are in an unfavourable condition and poor water quality is likely to be responsible. In terms of its SPA designation, the designated feature is in favourable condition, but there is concern that a water quality problem may be threatening that condition. Overall, the most appropriate response appears to be that poor water quality is contributing to the unfavourable condition of the feature(s) (i.e. response ‘D’ in Section 7.2.1).

Step IV: Do any consents meet the criteria for significance?

The response at Step IV for this estuary depends on the general criteria for ‘likely to have a significant effect’ being met.

I: Are the interest features sensitive to any hazard arising from the consented discharges?

The SPA features and the *Zostera* beds may be affected by the discharges.

II:. Is there a mechanism by which the consented discharge is likely to affect the designated features of the site?

The discharges enter the site so there is a potential route of exposure.

III. Is the potential scale of any effect potentially significant?

A clear relationship exists between water column dissolved oxygen status, BOD and sediment oxygen demand (SOD) (see Appendix C 5). SOD is related to the settlement of suspended solids with a high organic content (as is the case for suspended solids discharged in STW effluent). The effluent in the three river discharges may therefore be linked to the poor oxygen status of the water in the upper estuary. The estuarine discharge may also contribute to the low dissolved oxygen status, but this is unknown at present - modelling would be required to determine this.

Suspended solids in the estuarine discharge plume contribute to turbidity of the waters overlying the *Zostera* reef. Thus, the estuarine discharge is likely to have decreased the maximum depth of *Zostera* colonisation and, therefore, reduced the area colonised. However, such reductions are likely to have happened within a year or two of outfall operation, so this is unlikely to be the mechanism for damage in recent years. However, steady organic enrichment of the reef sediment could have led to progressive changes in the associated benthic invertebrate community.

A link exists between accumulation of organic nitrogen in intertidal sediments and *Enteromorpha* colonisation/higher standing crops (see Table 4.4 and Appendix C 4). However, organic N enrichment is rarely measured in sediments, neither is the mineralisation rate, particularly during late Spring, which is the best prediction of *Enteromorpha* standing crop during late Summer in such situations. A substantial proportion of the organic N present in sediment close to the estuary discharge point may be derived from the outfall - tracing studies would be required to assess this. Thus, although there is a known mechanism linking *Enteromorpha* growth to the discharge, further work is required to determine whether the discharges (specifically the estuarine discharge) is the source of the problem.

Step V: Internal and external consultation

The conclusions of Steps I to IV are subject to internal (within the competent authority) and external (with the country conservation agency) consultation to confirm, or otherwise, the judgement of likely significance. The conservation body stance on the proposed consent is that there is a likely significant effect. Moreover, only limited further assessment is needed in order to recommend need for action to remedy/prevent problem. The reasons for this are:

1. There is an acknowledged water quality problem in terms of oxygen status associated with the turbidity maximum. This is ascribed to the high organic loading from the four works, but notably to the organic load from the three upstream works.

2. Organic enrichment of the *Zostera* reef could be causing a gradual change in the invertebrate community (unless historic records are available for comparison with recently collected samples, as part of an appropriate assessment, it will be very difficult to provide evidence to support this hypothesis).

3. *Enteromorpha* beds are thought to be expanding due to mineralisation of organic nitrogen deposited around the estuary outfall. Further work is required to determine whether this is the case.

For the situation in Grass Flat Estuary, the conclusion is upheld through the consultation steps and the judgement of likely significant effect is confirmed. An appropriate assessment is therefore required.

7.3.3.4 Appropriate assessment

In this case the adverse effect due to O_2 status, organic-N and suspended solid loading is quite clear cut. A fuller assessment would be needed to support proposals for mitigation or amendment of consent conditions, and would need to consider the following:

! A clear examination of the timing and extent of the oxygen, say in relation to salmon migration, and known requirements for oxygen saturation.

! Modelling of oxygen and organic-C loading and distribution in relation to sources.

! Comparison of *Zostera* depth distribution with expected, and modelling of SS distribution and deposition rates.

! Predictive modelling of organic-N mineralisation rates and dissolved N concentrations.

! Information is needed on any other contaminants arising from the factory discharges which may affect the features of interest.

A potential solution to the problems would be to close down the three smaller STWs, pipe their sewage to the larger in-estuary works (which has the spare capacity to cope with this extra load) and construct a longer outfall so that the mixing zone does not impinge upon the shore. This would enable greater mixing and minimise deposition of organic nitrogen on sediments around the outfall. An appropriate assessment would be required for this proposal, to model the distribution of N, organic-N and SS within the SAC under this scenario.

References

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DETR. 1998. *European Marine Sites in England and Wales - A Guide to the Conservation (Natural Habitats etc.) Regulations 1994 and to the Preparation and Application of Management Schemes.*

ENVIRONMENT AGENCY, ENGLISH NATURE & COUNTRYSIDE COUNCIL FOR WALES. 1999. *Guidance for the Review of Environment Agency Permissions: Determining Relevant Permissions and 'Significant Effect'.* Version 1.0. Implementation date 31 March 1999.

Glossary

AchE	Acetylcholinesterase
ADRIS	Association of Directors and River Inspectors in Scotland
AOX	Assimilable Organic Halogens
BAT	Best Available Techniques
BATNEEC	Best Available Technology Not Entailing Excessive Cost
BCF	Bioconcentration Factor
BEP	Best Environmental Practice
BPEO	Best Practicable Environmental Option
COD	Chemical Oxygen Demand
CP	Chlorophenols
CSO	Combined Sewer Overflow
DCP	Dichlorophenols
DIN	Dissolved Inorganic Nitrogen
DOsags	Dissolved oxygen sags
DTA	Direct Toxicity Assessment
EA-SIS	Environment Agency - Substance Information System
EC50	Concentration which causes the required effect (e.g. reduced growth) in 50% of the test organisms
EINECS	European Inventory of Existing Chemical Substances
EQSs	Environmental Quality Standards
GQA	General Quality Assessment
hexavalent	Term used to describe the oxidation state of an element (e.g. Chromium)
HNDA	High Natural Dispersion Area
in vitro	tests on cultures of specially bred cell lines or tissue taken from living organisms
in vivo	tests on living animals
IPC	Integrated Pollution Control
IPPC	Integrated Pollution Prevention and Control
LAAPC	Local Authority Air Pollution Control

LC0	Concentration which causes no mortality in the test organisms
LC100	Concentration which causes mortality in 100% of the test organisms
LC50s	Concentration which causes mortality in 50% of the test organisms
LOD	Limit of detection
LOEC	Lowest observed effect concentration
log Koc	Term for the partition coefficient of a substance between water and organic carbon
log Kow	Term for the partition coefficient of a substance between octanol and water
MAC	Maximum Allowable Concentration
MATC	Maximum Acceptable Toxic Concentration
MHWS	Mean High Water Springs
MLWS	Mean Low Water Springs
NMP	National Monitoring Programme
NOEC	No Observable Effect Concentration
non-synthetic	Term used to describe substances not manufactured by Man
SERAD	Scottish Executive Rural Affairs Department
PCSDs	Polychloro chloromethyl sulphanomido diphenyl esters
PELs	Probable Effect Levels
Pt/l	Concentration of platinum (Pt) determined photometrically on the Platinum/Cobalt scale as a measure of colour in water
NVZ	Nitrate Vulnerable Zone
synthetic	Term used to describe substances manufactured by Man
TCA	Trichloroacetic acid
TEC50	Concentration in the tissue which causes the required effect (e.g. reduced growth) in 50% of the test organisms
TELs	Threshold Effects Levels
THM	Trihalomethanes
TIN	Total Inorganic Nitrogen
TOC	Total Organic Carbon
UES	Uniform Emission Standards

UWWT	Urban Waste Water Treatment
VROM	Dutch acronym for the Ministry of Housing Spatial Planning and the Environment in the Netherlands
WEC50	Concentration in the water which causes the required effect (e.g. reduced growth) in 50% of the test organisms
xenobiotic	Term used to describe substances that are not naturally found in the environment

Appendices

Appendix A. Toxic substances formally identified as potentially harmful to aquatic life

A1. Introduction

Various studies carried out for the Nature Conservancy Council and English Nature have highlighted and investigated areas of concern with regard to the marine environment. Nixon *et al* (1992) highlight a variety of toxic contaminants of concern based on List I and List II substances (from the Dangerous Substances Directive 76/464/EEC) and Red List substances. Subsequently, other studies have conducted more in-depth analysis of some of the issues raised by Nixon *et al*.

In addition to the issues raised by Nixon *et al* (1992), contaminants of importance to marine waters can be identified and are reflected in the legislation controlling discharges to estuarine, coastal and marine waters. Priority lists have been drawn up by various authorities and conferences related to the protection of marine waters.

Those considered of relevance are the Dangerous Substances Directive (Section A2), The Convention on the Protection of the Marine Environment of the North-East Atlantic (Section A3) and the Ministerial Conferences on the Protection of the North Sea (Section A4).

A2. The Dangerous Substances Directive

In 1976, the EU Council of Ministers adopted the Dangerous Substances Directive (76/464/EEC) to control pollution caused by certain dangerous substances discharged into the environment. The Directive established two lists of compounds:

- List I dealing with substances regarded as being particularly dangerous because of their toxicity, persistence and bioaccumulation. Pollution by List I substances must be eliminated; and

- List II containing substances which are less dangerous but which nevertheless have a deleterious effect on the aquatic environment. Pollution by List II substances must be reduced.

In the last two years, the UK has added a number of new chemicals to List II. The two lists as they currently stand are given in Tables A2.1 and A2.2.

Table A2.1 Agreed List I substances

Cadmium	Mercury	Lindane (hexachlorocyclohexane)
Pentachlorophenol	DDT	Carbon tetrachloride
Chloroform	Hexachlorobenzene	Hexachlorobutadiene
Dieldrin	Aldrin	Isodrin
Endrin	1,2-dichloroethane	Trichloroethylene
Perchloroethylene	Trichlorobenzene	

In addition to the chemicals adopted as List II substances (Table A2.2), Department of the Environment, Transport and the Regions (DETR) and Environment Agency have been conducting programmes for deriving EQSs for the protection of aquatic life (including marine organisms). Although not adopted into legislation, these EQSs may be used as guidance for consenting discharges. Those chemicals for which EQSs have been agreed (and are not adopted into legislation) are given below.

List II substances for which EQSs have been adopted by the UK

Arsenic	Boron
Chromium	Copper
Iron	Lead
Mothproofers	Nickel
Organotins	pH
Vanadium	Zinc

List II substances for which EQSs have recently been adopted

Arsenic	Atrazine
Azinphos-methyl	Benzene
Biphenyl	4-chloro-3-methyl phenol
Chloronitrotoluenes	2-chlorophenol
2,4-dichlorophenol	Dichlorvos
Dimethoate	Endosulfan
Fenitrothion	2,4-D
Bentazone	Demeton
Linuron	Mecoprop
Naphthalene	Omethoate
Simazine	Trifluralin
Trichloroethanes	Triazophos
Toluene	Xylenes

Table A2.3 Chemicals for which EQSs for the protection of saltwater life have been agreed (but not adopted into legislation)

Aluminium	Ammonia	Abamectin
Ivermectin	Doramectin	Bromine
Bromoxynil	Carbendazim	Chlorine
Chlorine dioxide	Chlorothalonil	Chlorotoluron
Chlorpropham	Cobalt	Cyanide
Dichlorobenzenes	Dichlorphen	Diflubenzuron
EDTA	Ethofumesate	Fluoride
Flusilazole	Formaldehyde	Imazethypyr
Inorganic tin	Ioxynil	Isoproturon
Maneb	Macozeb	Manganese
Malachite green	Mevinphos	NTA
Nonylphenol	Octylphenol	Oxolinic acid
Oxytetracycline	Pendimethalin	Phthlates
Pirimiphos-methyl	Phenol	Propyzamide
Pirimicarb	Prochloraz	Silver
Styrene		

A.3 Convention on the Protection of the Marine Environment of the North East Atlantic

The Convention on the protection of the marine environment of the North-East Atlantic replaces the 1972 Oslo Convention on Waste Dumping at Sea and the 1974 Paris Convention on pollution of the North Sea and Adjacent Areas from Land-Based Sources. The new Convention requires signatory countries to prevent and, where possible, eliminate pollution of the marine environment. Previous Conventions merely required a reduction in pollution.

The Convention places particular emphasis on preventing pollution from diffuse sources. To this end, a list of substances that contribute to diffuse pollution has been drawn up.

Table A3.1 Priority substances identified under the North Atlantic Marine Convention as contributing to diffuse pollution

Brominated flame retardants
Chlorinated paraffins
Metals (Cd, Hg, Cu, Zn, Pb, As, Cr, Ni)
Nonyl phenol ethoxylates
Organotin compounds
Polyaromatic hydrocarbons
PCBs and PCB substitutes
Polybrominated naphthalenes
Timber treatment chemicals
Triazine herbicides

A.4 Ministerial Conferences on the Protection of the North Sea

Concern about the quality of the North Sea has resulted in a series of Conferences of the Environment Ministers of countries bordering the North Sea. Decisions reached at these Conferences have had a significant impact on the development of policy and legislation for the protection of the aquatic environment in Western Europe. The first Conference was held in Bremen in 1985, subsequent meetings have been held in London and the Hague and the latest Conference was held in Esjberg in June 1995.

A4.1 Second Ministerial Conference

Countries meeting at the Second Ministerial Conference on the Protection of the North Sea held in London in November 1987 agreed to reduce the inputs of potentially dangerous substances to the North Sea by approximately 50% and also to restrict the inputs of nutrients to vulnerable zones by about 50%. The Conference also agreed to eliminate the incineration of dangerous waste and disposal of sewage sludge at sea.

A4.1.1 The UK Red List initiative

In response to the Conference, the UK agreed in a Ministerial Declaration to apply a dual approach to the control of certain particularly dangerous substances - The Red List. The dual approach consists of applying EQSs or limit values, whichever are the more stringent, to the control of the Red List substances (Table A4.1).

Table A4.1 Control of Red List Substances

Proposals for environmental quality standards (EQSs) have been prepared for the DETR (then the DoE) for those substances for which EQS values had not yet been adopted.

The UK Red List Substances

	Substance	List I status[(1)]
	Mercury	+
	Cadmium	+
*	Gamma hexachlorocyclohexane (lindane)	+
*	DDT	+
*	Pentachlorophenol (PCP)	+
	Hexachlorobenzene (HCB)	+
	Hexachlorobutadiene (HCBD)	+
*	Aldrin	+
*	Dieldrin	+
*	Endrin	+
*	PCB (Polychlorinated biphenyls)	
*	Tributyltin compounds	
*	Triphenyltin compounds	
*	Dichlorvos	
*	Trifluralin	
	1,2 Dichloroethane	+
	Trichlorobenzene	+
*	Azinphos-methyl	
*	Fenitrothion	
*	Malathion	
*	Endosulfan	
*	Atrazine	
*	Simazine	

Notes:

1 Chloroform has List I status but is not included in the UK Red List

* Substances which enter the environment predominantly from diffuse sources

A4.2 Third Ministerial Conference

At the Third Ministerial Conference held in the Hague in March 1990, a common list of substances was agreed for which inputs via rivers and estuaries to the North Sea should be reduced by 50% by 1995 using 1985 as baseline. The list of “priority hazardous substances” includes all the UK Red List substances, except PCBs (for which separate measures have been agreed). Equal reductions are to be made in atmospheric emission by 1999 for the substances arising predominantly from diffuse sources, provided that the application of Best Available Technology (BAT) (including the use of strict emission standards) enables such reductions to be made.

A list of additional substances has also been identified which should be assessed for future priority action (Table A4.2).

Table A4.2. List of 'priority hazardous substances' agreed at the Third North Sea Conference

Mercury	Cadmium	Copper	Zinc
Lead	Arsenic	Chromium	Nickel
Drins	HCH	DDT	Pentachloro-phenol
Hexachloro-benzene	Hexachlorobutadiene	Carbon tetrachloride	Chloroform
Trifluralin	Endosulfan	Simazine	Atrazine
Tributyltin-compounds	Triphenyltin-compounds	Azinphos-ethyl	Azinphos-methyl
Parathion	Parathion-methyl	Dichlorvos	Trichloro-ethylene
Tetrachloro-ethylene	Trichloro-benzene	Dichloroethane	1,2-Trichloro-ethane
Dioxins	Fenitrothion	Fenthion	Malathion

In addition, a number of agreements were reached at the Third North Sea Conference, including a commitment to make substantial reductions in the quantities of pesticides reaching the North Sea with special attention to phasing out those pesticides which are the most persistent, toxic and liable to bioaccumulate (Table A4.3).

Table. A4.3 Pesticides that are to be restricted or banned

Aldrin	Atrazine
Carbon tetrachloride	Chlordane
Chlorpicrin	1,2-Dibromoethane
1,2-Dichloroethane	Dieldrin
Endrin	Fluoroacetic acid and its derivatives
Heptachlor	Hexachlorobenzene
Hexachlorocyclohexane(a and b isomers)	Mercury compounds
Pentachlorophenol	Nitrofen
Quintozene	Polychlorinated terpenes

There are a number of substances that would have been restrictedor banned but are not currently used as pesticides (Table A4.4).

Substances which would have been included in Table above but which are not currently in use as pesticides

Acrylonitrile	Aramite
Lead compounds	Cadmium compounds
Captafol	Chlordecone (Kepone)
Chlordimeform	Chloroform
Crimidine	Isobenzan
Isodrin	Kelevan
Morfamquat	Toxaphene
Selenium compounds	2,4,5-T

A4.2.1 The Fourth North Sea Conference

The Fourth North Sea Conference was held in Esjberg, Denmark on 8/9 June 1995. The nine countries discharging to the North Sea Catchment (Belgium, Denmark, France, Germany, the Netherlands, Norway, Sweden, Switzerland and the UK) were represented, together with the European Commission.

The topics discussed included:

- protection of species and habitats in coastal and offshore areas;
- fisheries;
- prevention of pollution by hazardous substances;
- further reduction of nutrient inputs to the North Sea;
- the prevention of pollution from ships;
- the prevention of pollution from off-shore installations; and
- radioactivity.

Several areas of contention at the Conference arose at the Conference, including the proposed dumping of the Brent Spar oil platform in the North Sea, overfishing in the North Sea and the discharge of toxic chemicals.

References

NIXON, S.C., SMITH, I.N.H. AND PARR, W. 1992. *Water quality criteria for nature conservation in estuaries.* Report to English Nature.

Appendix B Toxic substances profiles

Introduction

Care should be taken when using the toxic substances profiles to help in decision-making, to take into account the **full** relevant text. The brief summaries of potential effects on interest features of European marine sites do not generally include the appropriate caveats about adopting EQS values, for example, and these should not be adopted where there is a risk to Natura 2000 features without checking the main text, and if necessary consulting the further literature cited or English Nature specialists.

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B49. PHTHALATES
B50. POLYBROMINATED NAPHTHALENES
B51. OILS AND PETROCHEMICALS
B52. SURFACTANTS
B53. TOLUENE
B54. XYLENES
B55. RADIOACTIVE SUBSTANCES
B56. ALGAL TOXINS AND ALGAE-RELATED FISH KILLS
B57. MICROBIAL PATHOGENS AND TOXINS

B1. Ammonia

B1.1 Entry to the marine environment

Ammonia is present in all natural waters, even if only at very low concentrations. It is derived either from the breakdown of organic nitrogen (mineralisation) or by the reduction of nitrate (a process known as denitrification). Ammonia also represents an intermediate stage in nitrogen fixation - the conversion of atmospheric N_2 to fixed nitrogen and subsequent incorporation into microbial proteins, etc. However, this remains a relatively unimportant source of ammonia compared to mineralisation. A substantial proportion of atmospheric nitrogen deposition is in the form of ammonia (Review Group on Acid Rain 1997), although this too is a relatively minor source.

However, although ammonia is produced in the nitrogen cycle, anthropogenic sources are more important, notably sewage treatment effluent and, in some situations, run-off from agricultural land (Seager *et al* 1988). In tidal waters, the primary source of ammonia is direct discharge from Secondary Treatment Work (STW) outfalls.

B1.2 Levels reported in the marine environment

Total ammonia is most often measured in discrete samples. However, the need for continuous monitors to properly record the variability in levels has been addressed in a number of UK estuaries, such as the Forth, Humber and Thames. The following values are annual mean total ammonia levels recorded at continuous monitoring sites (Nixon *et al* 1995) measured as mg/ln:

Estuary	10%ile	Annual mean	90%ile	Year(s)
Forth @ Alloa	3.28-4.28	6.14-7.16	9.58-10.79	89-92
Humber @ Blacktoft	2.33	6.51	2.78	92
Humber @ Cawood	10.81	11.69	0.70	92
Humber @ Corporation	3.52	5.44	1.55	92
Humber @ Long Drax	1.92	7.84	3.70	92
Humber @ Upper Whitton	4.67	7.36	1.78	92
Langstone Harbour	8.84	9.36	10.06	94
Thames @ Cadogan	3.77-5.60	6.42-8.25	9.25-11.00	89-93
Thames @ Greenwich	3.35-5.70	5.80-7.43	7.20-9.73	89-93
Thames @ Hammersmith	4.10-7.30	.5.66-9.11	7.05-11.60	90-93
Thames @ Kew	3.68-6.35	7.04-9.36	10.20-11.70	89-93
Thames @ Purfleet	2.63-4.00	4.32-6.25	5.93-8.00	89-93
Thames @ Putney	3.47-5.60	6.52-8.58	9.55-11.40	89-93
Thames @ Wapping	3.80-4.90	6.03-8.02	8.08-10.70	89-93
Thames @ Crossness	2.30-3.37	3.74-5.55	1.51-2.31	89-93
Tywi @ Green Castle	7.02	8.19	9.41	90
Tywi @ School Pool	7.21	8.76	10.10	90

Seager *et al* (1988) presented some older data for UK estuaries, with mean total ammonium values ranging between 0.017 mg N l^{-1} in the Tay at Perth (at the tidal limit) to 2.094 mg N l^{-1} in the Clyde at Glasgow. Much higher values were presented for two sites in the Tees Estuary, but these appear to be based on a single sample each.

The proposed GQA classification scheme for ammonia in the estuaries of England and Wales (Nixon *et al* 1995) consisted of a four tier system, with class boundaries at 0.86 mg N l^{-1} (Class A/B); 4.7 mg N l^{-1} (Class B/C) and 8.6 mg N l^{-1} (Class C/D) using the upper 90%ile as the classification statistic. These boundary values were derived from a review of toxicity data. This scheme has not been implemented in England and Wales so far.

B1.3 Fate and behaviour in the marine environment

Total ammonia in aqueous solution comprises two principal forms: the ionised ammonium ion (NH_4^+) and un-ionised ammonia (NH_3). There are technical difficulties in measuring the unionised form. However, total ammonium is usually monitored instead, despite the fact that the proposed EQS of 0.021 mg NH_3-N l^{-1} for the protection of saltwater fish and shellfish is presented in terms of unionised ammonia. However, the proportion of ionised and un-ionised ammonia can be calculated from total ammonia, the relative proportions depending on salinity, temperature and pH. The proportion of unionised ammonia increases with increasing temperature and pH, but decreases with increasing salinity (Seager *et al* 1988). Of these three factors, salinity appears to be relatively unimportant, but at pH 8.5, the proportion of un-ionised ammonia is approximately 10 times that at pH 7.5. For every 9°C increase in temperature, the proportion of unionised ammonia approximately doubles.

B1.4 Effects in the marine environment

B1.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of ammonia to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Seager *et al* 1988 and Nixon *et al* 1995). The most sensitive groups of organisms have been identified.

The toxicity of ammonia to marine organisms has not received the same level of study as freshwater organisms but there is sufficient information to indicate that the principal groups of organisms affected by ammonia toxicity in the marine environment are invertebrates and fish.

The un-ionised form of the ammonium ion (NH_3) is the most toxic. The toxicity of ammonia to aquatic life is affected by the following physico-chemical parameters: temperature, pH, dissolved oxygen and salinity. In general, ammonia toxicity is greater, the higher the temperature and pH and the lower the levels of dissolved oxygen and salinity.

Concerns about the toxicity of ammonia should be greatest in estuarine European marine sites and close to sewage outfalls in coastal waters.

Invertebrates

A review of the effects of ammonium on estuarine and marine benthic organisms is given in Nixon *et al* (1995). Toxicity data are presented for shrimps, mysids and lobsters (in which ammonia appears to interfere with lobsters' ability to adjust to different salinities). Allan *et al* (1990) estimated 96 hour LC50s for juvenile school prawns *Metapenaeus macleayi* and leader prawns *Penaeus monodon* to be 1.39 and 1.69 mg un-ionised ammonia NH3-N/l (26.3 mg and 37.4 mg total ammonia-N/l respectively). Williams and Brown (1992) estimated a 96 hour LC50 of 0.787 mg NH_3-N/l (24.6 mg NH_4-H/l) for the nauplius of the marine copepod *Tisbe battagliai* and a No Observed Effect Concentration (NOEC) of 0.106 mg NH_3-N/l (3.34 mg NH_4-N/l) for a study comprising tests on several life stages. For invertebrates, toxicity appears to increase as salinity decreases (Miller *et al* 1990, Chen and Lin 1991), although too few data exist to indicate whether this pattern is typical for all or most invertebrates (Nixon *et al* 1995). Several studies indicate that ammonia toxicity is greatest to early life stages of invertebrates.

Fish

Acute toxicity of ammonia to fish increases with low dissolved oxygen concentrations. This has been shown in both fresh and marine water environments (Seager *et al* 1988, Nixon *et al* 1995). For this reason, the proposed GQA scheme for ammonia in estuaries was combined in a proposed joint scheme for dissolved oxygen and ammonia (Nixon *et al* 1995).

The majority of ammonium toxicity data relates to fish, although most of the species tested are freshwater species, with many coarse fish appearing to be as sensitive to ammonia as salmonids (Mallet *et al* 1992). Nevertheless, data are available for sole, turbot and larval inland silversides. Eddy and Twitchen (1990) suggested that high environmental sodium concentrations can decrease toxicity to fish.

In the Mersey Estuary at a mean unionised ammonia concentration of 0.008 mg NH_3-N/l, a diverse invertebrate population was present, and this region was passable by flounder and salmonids. For fish, ammonium toxicity appears to be less at lower salinity levels, gradually decreasing until it reaches a point similar to that found in freshwaters (Seager *et al* 1998, Miller *et al* 1990). This may be of relevance, especially in estuaries where DO sags occur at low salinities.

Sediment dwelling organisms

Ammonia exerts toxic effects in the water column and does not accumulate in the sediments. However, sediment dwelling organisms that use water in the boundary layer between the sediment and the water column (molluscs, crustacea and most annelids) for feeding or respiration could be at risk.

B1.5 Bioaccumulation

Ammonia does not bioaccumulate.

B1.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxicity to invertebrates and fish associated with Annex I habitat sub-features at concentrations above the EQS of 0.021 mg NH_3-N l^{-1} in the water column;

! increased toxicity to these groups of animals with decreasing dissolved oxygen and salinity. These conditions are more likely in estuaries;

! Annex II species (other than anadromous fish) and birds are unlikely to be affected directly by ammonia toxicity. However, in estuaries, in particular, ammonia toxicity is a component of the effects of organic pollution which can degrade bird feeding habitats.

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B2. Cadmium

B2.1 Entry to the marine environment

Cadmium is widely distributed in the Earth's crust at an average concentration of about 0.1 mg kg^{-1} and is commonly found in association with zinc. Higher levels are present in sedimentary rocks: marine phosphates often contain about 15 mg kg^{-1} (GESAMP, 1984). Weathering and erosion result in the transport by rivers of large quantities of cadmium to the world's oceans and this represents a major flux of the global cadmium cycle; an annual gross input of 15,000 tonnes has been estimated (GESAMP, 1987). Volcanic activity is also a major natural source of atmospheric cadmium release. The global annual flux from this source has been estimated to be 100-500 tonnes (WHO 1992b).

The principal applications of cadmium fall into five categories:

- protective plating on steel;
- stabilizers for PVC;
- pigments in plastics and glass;
- electrode material in nickel-cadmium batteries; and
- as a component of various alloys (Wilson, 1988).

The relative importance of the major applications has changed considerably over the last 25 years. The use of cadmium for electroplating represented has decreased, with its share in 1985 less than 25% (Wilson, 1988). In contrast, the use of cadmium in batteries has grown considerably in recent years from only 8% of the total market in 1970 to 37% by 1985.

Non-ferrous metal mines represent a major source of cadmium to the aquatic environment. Contamination can arise from mine drainage water, waste water from the processing of ores, overflow from the tailings pond, and rainwater run-off from the general mine area. The release of these effluents to local watercourses can lead to extensive contamination downstream of the mining operation. Disused mines can also be a source of water contamination (Johnson and Eaton, 1980).

At the global level, the smelting of non-ferrous metal ores has been estimated to be the largest human source of cadmium release to the aquatic environment (Nriagu and Pacyna, 1988). Discharges to fresh and coastal waters arise from liquid effluents produced by air pollution control (gas scrubbing), together with the site drainage waters.

The manufacture of phosphate fertilizer results in a redistribution of the cadmium present in the rock phosphates between the phosphoric acid product and gypsum waste. In many cases, the gypsum is disposed of by dumping in coastal waters, which leads to considerable cadmium inputs. The atmospheric fall-out of cadmium to fresh and marine waters also represents a major input of cadmium at the global level (Nriagu and Pacyna, 1988). A GESAMP study of the Mediterranean Sea indicated that this source was comparable in magnitude to the total river inputs of cadmium to the region (GESAMP, 1985). Similarly, large cadmium inputs to the North

Sea (110-430 tonnes/year) have also been estimated, based on the extrapolation from measurements of cadmium deposition along the coast (van Alst *et al.*, 1983a,b). However, another approach based on model simulation yielded a modest annual cadmium input of 14 tonnes (Krell and Roeckner, 1988).

B2.2 Recorded levels in the marine environment

The average cadmium content of sea water has been given as about 0.1 µg l^{-1} or less (Korte, 1983). WHO (1992) reported that current measurements of dissolved cadmium in surface waters of the open oceans gave values of < 5 ng l^{-1}. The vertical distribution of dissolved cadmium in ocean waters is characterized by a surface depletion and deep water enrichment, which corresponds to the pattern of nutrient concentrations in these areas (Boyle *et al.*, 1976). This distribution is considered to result from the absorption of cadmium by phytoplankton in surface waters and its transport to the depths, incorporation to biological debris, and subsequent release. In contrast, cadmium is enriched in the surface waters of areas of upwelling and this also leads to elevated levels in plankton unconnected with human activity (Martin and Broenkow, 1975; Boyle *et al*, 1976). Oceanic sediments underlying these areas of high productivity can contain markedly elevated cadmium levels as a result of inputs associated with biological debris (Simpson, 1981). Cadmium levels of up to 5 mg kg^{-1} have been reported in river and lake sediments and from 0.03 to 1 mg kg^{-1} in marine sediments (Korte 1983).

Concentrations of cadmium have been measured in water, sediments and biota as part of the National Monitoring Programme at sites throughout the UK in estuaries and coastal waters (MPMMG 1998). The results of the National Monitoring Programme are summarised in Appendix D. MPMMG 1998 should consulted for further details.

The available data suggest that, although sometimes elevated, in general, concentrations of cadmium in UK coastal and estuarine waters, sediments and biota do not appear to exceed relevant quality standards derived for the protection of saltwater life.

As an example of the recorded levels of dissolved cadmium in the marine environment, the following concentrations have been reported by DETR (1998) for some English estuaries (Tables B2.1 to B2.3).

Table B2.1 Minimum concentration (ng l^{-1}) of dissolved cadmium in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	0.0	50.0	0.0	0.0	0.0
Wear	100.0	0.0	0.0	0.0	0.0
Tees	0.0	0.0	0.0	0.0	0.0
Ouse		0.0	0.0	0.0	0.0
Wash		0.0	0.0	0.0	0.0
Thames	0.0	0.0	0.0	110.0	0.0
Tamar	0.0	0.0	0.0	0.0	0.0

Table B2.2 Average concentration (ng l^{-1}) of dissolved cadmium in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	382.7	725.5	433.0	254.8	49.1
Wear	1333.3	1190.0	52.0	174.5	0.0
Tees	366.9	240.8	24.6	158.2	24.6
Ouse		132.0	0.0	0.0	0.0
Wash		0.0	0.0	0.0	48.8
Thames	163.2	147.1	95.4	435.0	85.0
Tamar	42.5	101.8	0.0	23.3	43.9

Table B2.3 Maximum concentration (ng l^{-1}) of dissolved cadmium in the water column of some English estuaries (from DETR 1998)

	1991	**1992**	**1993**	**1994**	**1995**
Tyne	700.0	2500.0	3400.0	1120.0	240.0
Wear	4700.0	6200.0	195.0	1380.0	0.0
Tees	2200.0	2900.0	85.0	974.0	390.0
Ouse		1000.0	0.0	0.0	0.0
Wash		0.0	0.0	0.0	439.0
Thames	290.0	380.0	400.0	760.0	160.0
Tamar	120.0	450.0	0.0	70.0	130.0

B2.3 Fate and behaviour in the marine environment

Cadmium does not break down in the environment, but may be affected by physical and chemical processes that modify its mobility, bioavailability, and residence time in different environmental media. The mobility and bioavailability of cadmium in aquatic environments are enhanced under conditions of low pH, low hardness, low suspended matter levels, high redox potential, and low salinity.

The speciation of cadmium in the environment is of importance in evaluating the potential hazard. Some cadmium salts, such as the sulphide, carbonate, and oxide, are practically insoluble in water; these can be converted to water-soluble salts in nature. The sulphate, nitrate, and halides are soluble in water. In addition, cadmium is strongly adsorbed onto sediments.

B2.4 Effects on the marine environment

B2.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of cadmium to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (WHO 1992b). The most sensitive groups of organisms have been identified.

Cadmium uptake from water by aquatic organisms is extremely variable and depends on the species and various environmental conditions, such as water hardness (notably the calcium ion and zinc concentration), salinity, temperature, pH, and organic matter content.

The majority of chelating agents decrease cadmium uptake but some, such as dithiocarbamates and xanthates, increase uptake. Increasing temperature increases the uptake and toxic impact, whereas increasing salinity or water hardness decreases them.

Acute lethal effects for marine organisms have been noted as low as 16 µg l^{-1} (WHO 1992b). Cadmium is toxic to a wide range of micro-organisms. However, the presence of sediment, high concentrations of dissolved salts or organic matter all reduce the toxic impact. The main effect is on growth and replication.

Zinc increases the toxicity of cadmium to aquatic invertebrates. Sub-lethal effects have been reported on the growth and reproduction of aquatic invertebrates; there are structural effects on invertebrate gills. There is evidence of the selection of resistant strains of aquatic invertebrates after exposure to cadmium in the field.

An increase in toxicity as temperature increases and salinity decreases has been noted. This implies that the same cadmium concentration may have the potential to cause greater toxicity to estuarine rather than to marine species. For example, Rosenberg and Costlow (1976) reported increased cadmium toxicity during larval development of two estuarine crab species as salinity decreased and increased toxicity as temperature increased.

Invertebrates

O'Hara (1973) investigated the effects of temperature and salinity on the toxicity of cadmium to adult male and female fiddler crabs *Uca pugilator*. Mortality was greatest at high temperatures and low salinities in tests lasting 240 h. LC50 values varied from 2.9 mg l^{-1} for the lowest salinity (10%) and highest temperature (30 °C) to 47.0 mg l^{-1} for the highest salinity (30%) and lowest temperature (10 °C). Frank and Robertson (1979) exposed the blue crab *Callinectes sapidus* to cadmium chloride at salinities of 1, 15, and 35%. Like O'Hara, they found a decrease in cadmium toxicity with increase in salinity. For example, 96-h LC50 values were 0.32, 4.7, and 11.6 mg cadmium l^{-1} for the three salinities respectively.

Voyer and Modica (1990) found the same pattern with the mysid shrimp *Mysidopsis bahia*. For salinities of 10 and 30%, the 96-h LC50 values ranged from 15.5 to 28 µg cadmium l^{-1} at a temperature of 25 °C and from 47 to 84 µg l^{-1} at a temperature of 20 °C. At 30 °C, the 96-h LC50 was < 11 µg l^{-1} at both salinities. However, when Robert and His (1985) exposed embryos and larvae of the Japanese oyster *Crassostrea gigas* to cadmium concentrations of up to 50 µg l^{-1} at various salinities (20 to 35%), decreasing the salinity severely affected the development of the oysters but cadmium had no effect. At temperatures higher than 11 °C, the combined effect of temperature and cadmium caused a heavy stress to the copepod *Tisbe holothuriae* so that the effects of salinity were masked (Verriopoulos and Moraitou-Apostolopoulou, 1981).

Fish

At low concentrations (10 µg cadmium l^{-1}), cadmium inhibits ion transport systems and induces metallothionein synthesis (< 1 µg cadmium l^{-1}) in freshwater fish.

Cadmium toxicity has been found to be variable in fish, with salmonids being particularly susceptible to cadmium. Sub-lethal effects in fish, notably malformation of the spine, have been reported. The most susceptible life-stages are the embryo and early larva, while eggs are the least susceptible. There is no consistent interaction between cadmium and zinc in fish (WHO 1992b).

Seabirds

Cadmium has been found to affect the kidney of sea-birds. However, it is not always thought to have been as a result of exposure to cadmium as an industrial pollutant since the individuals most affected come from areas where there is no industrial effluent. Such effects appear therefore to be a response to naturally occurring cadmium presumed to derive from the oceans (WHO 1992b).

However, these effects do not appear to affect survival or breeding success. No damage resulting from exposure to strictly anthropogenically derived cadmium appears to have been reported on the same scale as that from exposure to naturally occurring cadmium (WHO 1992b).

Nicholson *et al* (1983) compared the kidneys of seabirds contaminated with cadmium in the wild, seabirds from uncontaminated colonies, starlings dosed with cadmium in the laboratory, and control starlings. The authors found damage to kidney cells to be comparable between wild seabirds and dosed starlings having kidney cadmium levels of 60-480 and 95-240 mg kg^{-1} respectively. Nicholson and Osborn (1983) reported kidney lesions in several different species of seabird caught in contaminated areas, although other pollutant metals, such as mercury, were also present in the tissues.

B2.5 Bioaccumulation

Cadmium bioaccumulates in organisms with the main uptake routes being dissolved cadmium from the water column and cadmium associated with prey items.

Muller *et al* (1993) reported bioconcentration factors of 5,000 in natural samples of *Enteromorpha intestinalis* in the Weser estuary and these increased to between 7,000 and 10,000 for plants transplanted from a clean source.

B2.6 Potential effects on interest features of European marine sites

The potential effects include:

- acute toxicity of dissolved cadmium to invertebrates and fish at concentrations above the EQS of 2.5 Fg l^{-1} (annual average) in the water column;

- accumulation of cadmium in sediments and a potential risk to sediment dwelling organisms at concentrations greater than 0.7 mg kg^{-1}, according to Canadian interim marine sediment quality guidelines (see Section 5.5);

- bioaccumulation of cadmium in organisms and a potential threat to some invertebrates, fish, birds and Annex II mammals.

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B3. Mercury

B3.1 Entry into the marine environment

Mercury is a metal which is liquid at normal temperatures and pressures. It forms salts in two ionic states mercury (I) and mercury (II). Mercury (II), or mercuric, salts are very much more common than mercury (I) salts. Mercury also forms organometallic compounds, some of which have found industrial and agricultural use. These organometallic compounds are stable, although some are readily broken down by living organisms, while others are not readily biodegraded.

A number of reviews (e.g. WHO 1989 and 1991 and CCME 1992, US EPA 1984) reviewed the environmental fate and behaviour and aquatic toxicity of mercury. These are discussed below. The reader is referred to the above reports for a more comprehensive assessment.

Natural mercury arises from the degassing of the Earth's crust through volcanic gases and, probably, by evaporation from the oceans. Local levels in water derived from mercury ores may also be high (up to 80 µg l^{-1}). Atmospheric pollution from industrial production is probably low, but pollution of water by mine tailings is significant. The burning of fossil fuels is a source of mercury. The chloralkali industry and, previously, the wood pulping industry, also released significant amounts of mercury. Although the use of mercury is decreasing, high concentrations of the metal are still present in sediments associated with the industrial applications of mercury. Some mercury compounds have been used in agriculture, principally as fungicides.

B3.2 Recorded levels in the marine environment

WHO (1989) stated that for the open ocean and for coastal sea-water, concentrations of dissolved mercury in the range of 0.5 - 3 ng l^{-1} and 2 - 15 ng l^{-1} respectively could be considered to be representative.

However, local variations from these values are considerable, especially in coastal sea water and in lakes and rivers where mercury associated with suspended material may also contribute to the total load or where near to anthropogenic sources, e.g. in the vicinity of mining sites and chloralkali plants for the industrial extraction of mercury. However, the majority of mercury in the environment can be considered to be natural rather than the result of human activities.

WHO (1989) estimated concentrations in ocean sediments probably lie in the range between 20 and 100 µg kg^{-1}.

Concentrations of mercury have been measured in water, sediments and biota as part of the National Monitoring Programme at sites throughout the UK in estuaries and coastal waters (MPMMG 1998). The results of the National Monitoring Programme are summarised in Appendix D. MPMMG 1998 should be consulted for further details.

These show elevated levels in some sediments. However, with regard to the water column, the available data suggest that concentrations of mercury in UK coastal and estuarine waters appear unlikely to exceed relevant quality standards derived for the protection of saltwater life.

As an example of the recorded levels of dissolved mercury in the marine environment, the following concentrations have been reported by DETR (1998) for some English estuaries (Tables B3.1 to B3.3).

Table B3.1 Minimum concentration (ng l^{-1}) of dissolved mercury in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	105.0	0.0	0.0	0.0	0.0
Wear		24.0	0.0	0.0	0.0
Tees		0.0	0.0	0.0	0.0
Ouse	0.0	0.0	0.0	0.0	0.0
Wash	0.0	0.0	0.0	0.0	0.0
Thames	0.0	0.0			
Tamar	0.0	0.0	0.0	0.0	0.0

Table B3.2 Average concentration (ng l^{-1}) of dissolved mercury in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	105.0	59.8	87.9	0.0	24.2
Wear		26.5	139.3	0.0	14.6
Tees		63.8	19.9	0.0	16.2
Ouse	33.3	28.2	7.6	21.4	5.0
Wash	0.0	0.0	0.0	6.4	91.0
Thames	12.1	21.0			
Tamar	36.6	3.9	0.0	0.0	0.0

Table B3.3 Maximum concentration (ng l^{-1}) of dissolved mercury in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	105.0	130.0	185.0	0.0	80.0
Wear		31.0	565.0	0.0	60.0
Tees		160.0	130.0	0.0	60.0
Ouse	136.0	148.0	79.0	200.0	20.0
Wash	0.0	0.0	0.0	24.0	430.0
Thames	53.0	110.0			
Tamar	249.0	39.0	0.0	0.0	0.0

B3.3 Fate and behaviour in the marine environment

Dissolved mercury has a strong affinity for organic matter and suspended sediment and so can be expected to be bound to these particles in the water column and subsequently to accumulate in sediments. Campbell *et al* 1986 reported a well defined increase in dissolved mercury concentrations in a seaward direction from the Mersey estuary. Within the estuary where suspended material concentrations are greater, concentrations of dissolved mercury decrease away from a point source but increase again towards Liverpool Bay.

Once deposited in sediments, mercury can undergo methylation to produce methylmercury. This form of mercury is bioavailable and is a hazard to aquatic life.

B3.4 Effects on the marine environment

B3.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of mercury to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (WHO 1989, 1991, CCME 1992 and US EPA 1994)). The most sensitive groups of organisms have been identified.

The organic forms of mercury are generally more toxic to aquatic organisms than the inorganic forms.

Macrophytes

Aquatic plants are affected by mercury in the water at concentrations approaching 1 mg l^{-1} for inorganic mercury but at much lower concentrations of organic mercury.

Invertebrates

Aquatic invertebrates vary greatly in their susceptibility to mercury, with the concentration and species of mercury, the developmental stage of the organisms, and the temperature, salinity, water hardness, and flow rate all affecting the sensitivity. Methylmercury is more toxic than aryl or inorganic mercury. The larval stage is apparently the most sensitive stage of the organism's life cycle. Mercury toxicity increases with temperature and decreases with water hardness. Toxicity appears to be higher in flow-through systems than in static systems. This effect is probably due mostly to the actual concentration of mercury available to the organism, which is lower in static systems.

Levels of 1 to 10 µg l^{-1} normally cause acute toxicity for the most sensitive developmental stage of many different species of aquatic invertebrates.

Fish

Inorganic mercury is toxic to fish at low concentrations. 96-h LC50s as low as 30 µg l^{-1} have been reported. Organic mercury compounds are more toxic. Toxicity is affected by temperature, salinity, dissolved oxygen, and water hardness. A wide variety of physiological and biochemical abnormalities have been reported after exposure of fish to sub-lethal concentrations of mercury, although the environmental significance of these effects is difficult to assess. Reproduction is also adversely affected by mercury.

Seabirds

Fatalities and severe poisonings in birds have been reported in association with outbreaks of human poisoning. Methylmercury levels in fish in Japan have caused a major problem for human health. During these incidents, there were also reports of direct effects of mercury on wildlife in the area. Fish carrying methylmercury were found dead or showed symptoms of mercury poisoning. Fish-eating and scavenging birds were also killed (Harada, 1978). Birds found dead in the area showed characteristic pathological changes in the central nervous system of Minamata disease, but no measurement of mercury content was made (Takeuchi *et al.* 1957).

Birds, particularly coastal species or those eating prey that feed in estuaries, have been affected by mercury contamination. It has adversely affected breeding and may have influenced population stability.

Merlins sampled in Scotland contained organochlorines along with mercury in their eggs. Statistical analysis of the data showed a clear inverse relationship between mercury content of eggs and brood size; the higher the mercury content, the less likelihood of successful breeding. Productivity fell markedly when mercury residues in eggs exceeded 3 mg kg^{-1}. Productivity (i.e. the number of young successfully reared) showed no statistically significant relationship with residues of other chemicals present in the eggs. Levels of mercury were highest in birds sampled in Orkney and Shetland, but the relationship between mercury residue and productivity remained when these, particularly high, residue levels were excluded from the analysis (Newton and Haas, 1988).

The merlins were feeding on wading birds in estuaries and this was presumed to be the source of the mercury. A similar, but not quite significant, relationship was found in peregrine falcons breeding near the coast.

Sea mammals

There is some limited information on the effects marine mammals.

Ronald *et al* (1977) fed harp seals on herring dosed with methylmercuric chloride. Two animals were used as controls, two were fed 0.25 mg kg^{-1} body weight per day and two fed 25.0 mg kg^{-1} body weight per day. Various blood parameters were monitored and found to be unaffected by the lower dose. The two animals on the higher dose died after 20 and 26 days of dosing. Prior to death, these animals exhibited toxic hepatitis, uremia, and renal failure.

B3.5 Bioaccumulation

Although environmental levels can be considered to be low, the high capacity of organisms to accumulate mercury means that the metal is found widely in aquatic animals and plants.

Inorganic mercury can be methylated in the environment and the resultant methylmercury is taken up into organisms more readily than inorganic mercury. The speciation of mercury is of great importance in determining the uptake of the metal from water and soil. Much of the mercury in natural waters is strongly bound to sediment or organic material and is unavailable to organisms.

Aquatic invertebrates accumulate mercury to high concentrations. Fish also take up the metal and retain it in tissues, principally as methylmercury. Although most of the environmental mercury to which they are exposed is inorganic, there is a strong indication that bacterial action leads to methylation in aquatic systems. Elimination of methylmercury is slow from fish (with half times in the order of months or years) and from other aquatic organisms. Loss of inorganic mercury is more rapid and so most of the mercury in fish is retained in the form of methylmercury.

Langston *et al* (1996) reported levels of methylmercury bioaccumulated by a range of estuarine algae and invertebrates in the Mersey estuary in 1995 to be between 10 (*Fucus vesiculosus*) and 100 (*Mytilus edulis*) times higher than sediment concentrations at the sites they were collected from. Correlations between sediment and tissue levels of methylmercury in the invertebrates suggest that sediments are the prime source of the contaminant for these animals.

Seabirds and those feeding in estuaries have also been found to be contaminated. The form of retained mercury in birds is more variable and depends on species, organ, and geographical site.

B3.6 Potential effects on interest features of European marine sites

Potential effects include:

! acute toxicity in the water column to interest features comprising macrophytes, invertebrates and fish at concentrations of dissolved mercury above the EQS of 0.3 Fg l^{-1} (annual average). Toxic effects below this concentration may occur if methylmercury is present;

! inorganic mercury accumulates in sediments and may be a hazard to sediment-dwelling organisms at concentrations above 0.13 mg kg^{-1}, according to Canadian interim marine sediment quality guidelines (see Section 5.5). Toxic effects below this concentration may occur if methylmercury is present;

! methylmercury bioaccumulates in the food chain and poses a hazard to fish, birds and Annex II sea mammals.

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B4. Lead

B4.1 Entry into the marine environment

Lead is a bluish or silvery-grey soft metal. With the exception of the nitrate, chlorate, and, to a much lesser degree, chloride, the salts of lead are poorly soluble in water. Lead also forms stable organic compounds. Tetraethyllead and tetramethyllead are used extensively as fuel additives. Both are volatile and poorly soluble in water. Trialkyllead compounds are formed in the environment by the breakdown of tetraalkylleads. These trialkyl compounds are less volatile and more readily soluble in water. Lead is mined, most usually as the sulfide, "galena".

Hence, entry into the aquatic environment occurs through releases (directly or through atmospheric deposition) from the smelting and refining of lead, the burning of petroleum fuels containing lead additives and, to a lesser extent, the smelting of other metals and the burning of coal and oil. Metallic lead deriving from shotgun cartridges or used as fishing weights is lost in the environment and often remains available to organisms (WHO 1995).

B4.2 Recorded levels in the marine environment

Concentrations of lead have been measured in water, sediments and biota as part of the National Monitoring Programme at sites throughout the UK in estuaries and coastal waters (MPMMG 1998). The results of the National Monitoring Programme are summarised in Appendix D. MPMMG 1998 should be consulted for further details.

Grimwood and Dixon (1997) compiled monitoring data for lead in water, sediments and biota for marine sites of nature conservation importance in England.

As an example of the recorded levels of dissolved lead in the marine environment, the following concentrations have been reported by DETR (1998) for some English estuaries (Tables B4.1 to B4.3).

Table B4.1 Minimum concentration (Fg l^{-1}) of dissolved lead in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	0.0	0.0	0.0	1.7	0.0
Wear	16.0	0.0	0.0	0.0	0.0
Tees	0.0	0.0	0.0	0.0	0.0
Ouse		0.0	0.0	0.0	0.0
Wash		0.0	0.0	0.0	0.0
Thames	0.0	0.0	0.0	0.2	0.1
Tamar	0.0	0.0	0.0	0.2	0.0

Table B4.2 Average concentrations (Fg l^{-1}) of dissolved lead in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	18.0	3.8	1.4	4.1	2.5
Wear	31.0	2.1	0.4	0.6	2.0
Tees	13.8	1.8	1.2	2.2	1.0
Ouse		0.3	0.8	0.0	0.0
Wash		0.0	0.0	0.0	0.0
Thames	6.7	1.2	0.9	0.6	0.5
Tamar	0.5	0.7	0.2	0.5	0.2

Table B4.3 Maximum concentrations (Fg l^{-1}) of dissolved lead in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	64.0	10.5	2.9	12.7	4.0
Wear	72.0	6.0	2.0	3.3	9.0
Tees	70.5	10.5	2.6	15.3	4.0
Ouse		3.0	5.6	0.0	0.0
Wash		0.0	0.0	0.0	0.0
Thames	23.6	7.0	2.1	1.1	1.2
Tamar	1.7	3.4	0.8	2.2	0.5

B4.3 Fate and behaviour in the marine environment

The fate and behaviour of lead in the marine environment is complex because of the many compounds of lead that can be found and the natural variability of natural systems.

Much of the lead in the marine environment is strongly adsorbed onto sediment and suspended particles, reducing its availability to organisms. The transport of lead in estuaries and coastal waters is therefore closely linked with the movement of particles. The sediments form a sink for lead in the marine environment.

Lead in true solution may be present as the hydrated Pb^{2+} ion or may be complexed. However, in view of the low solubility of most of its salts, lead tends to precipitate out of complex solutions.

B4.4 Effects on the marine environment

B4.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of lead to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Brown *et al* 1984, WHO 1995, Grimwood and Dixon 1997). The most sensitive groups of organisms have been identified.

In the form of simple salts, lead is acutely above 2.5 and >500 mg l^{-1} for marine organisms (WHO 1995).

Lead salts are poorly soluble in water, with the presence of other salts reducing the availability of lead to organisms because of precipitation. Results of toxicity tests should be treated with caution unless dissolved lead is measured.

In 1984, Brown *et* al reviewed data on the toxicity of lead to marine organisms and proposed an EQS (for the protection of saltwater life) of 25 µg l^{-1}, (expressed as a dissolved annual average concentration), a value currently adopted in UK legislation (HMSO 1989). The EQS was proposed at this level as, at the time of writing (1984), adverse effects had not been observed in any saltwater organisms following exposure to concentrations below 100 µg l^{-1}. However, following a review of more recent toxicity data in 1992, Young (1992) proposed a more stringent EQS of 10 µg l^{-1}. This value (also expressed a dissolved annual average) was derived by applying an arbitrary safety factor of around 2 to the lowest, most reliable No-Observed Effect Concentration (NOEC) for mysid shrimp.

An additional review by Grimwood and Dixon in 1997 of data on the saltwater toxicity of lead available since the EQS of 10 µg l^{-1} was proposed, found that only one study had been reported that perhaps indicated higher toxicity to saltwater organisms. Fernandez-Leborans and Novillo (1992) reported that lead concentrations ranging from 1 to 50 µg l^{-1} caused significant effects on the division and biomass of ciliate communities in laboratory microcosms. However, the magnitude of effects at the 1 µg l^{-1} exposure level was not distinguished from the effects that occurred following exposure to 50 µg l^{-1}. Moreover, it is difficult to assess the relevance of these laboratory sub-lethal (growth) data in predicting wider ecosystem effects under field conditions. Grimwood and Dixon (1997) concluded that no other relevant ecotoxicity data had been reported that suggested a need to revise to the latest proposed EQS value.

The authors recommended that the revised EQS of 10 µg l^{-1} (dissolved annual average) proposed to DETR was appropriate for the protection of all saltwater life in the majority of cases. However, where there is concern that the health of communities at sites of nature conservation interest may be compromised as a result of the presence of particularly sensitive algal or ciliate species, a lower value may be used as a Guideline. For instance, a value of 0.5 µg l^{-1} may be used where necessary by applying arbitrary factors of 10 and 2 to the lowest algal EC50 and the lowest ciliate effect concentration respectively. In the absence of any reliable supporting data, it was not possible to confirm the precision of this value.

Algae

In one laboratory study, a 12 day EC50 (growth) as low as 5 µg l^{-1} was reported for the diatom *Skeletonema costatum* although the reliability of this result is questionable due to uncertainties in measurements and apparent medium-dependent effects. All other algal data were higher than the NOEC reported for the mysid shrimp. Nevertheless, Young (1992) still concluded that, on the basis of the potential higher sensitivity of some algae, a more stringent standard may be required where lead-sensitive algal species were important primary producers in a saltwater ecosystem. Further research into algal sensitivity was recommended.

Invertebrates

In aquatic invertebrates communities, some populations are more sensitive than others and community structure may be adversely affected by lead contamination. However, invertebrate populations from polluted areas can show more tolerance to lead than those from non-polluted areas. In other aquatic invertebrates, adaptation to hypoxic conditions can be hindered by high lead concentrations (WHO 1995).

Young (1992) reported a No Observed Effect Concentration (NOEC) of 17 Fg l^{-1}, for the mysid shrimp *Mysidopsis bahia* following 44 days exposure.

Fish

Young stages of fish are more susceptible to lead than adults or eggs. Typical symptoms of lead toxicity include spinal deformity and blackening of the caudal region. The maximum acceptable toxicant limit (MATC) for inorganic lead has been determined for several species under different conditions and results range from 0.04 mg l^{-1} to 0.198 mg l^{-1}. The acute toxicity of lead is highly dependent on the presence of other ions in solution, and the measurement of dissolved lead in toxicity tests is essential for a realistic result. Organic compounds of lead are more toxic to fish than inorganic lead salts (WHO 1995).

Sediment dwelling organisms

Lead accumulates in sediments and can pose a hazard to sediment-dwelling organisms at concentrations above 30.2 mg kg^{-1}, according to Canadian interim marine sediment quality guidelines (see Section 5.5).

B4.5 Bioaccumulation

In aquatic ecosystems, uptake by primary producers and consumers seems to be determined by the bioavailability of the lead. The uptake and accumulation of lead by aquatic organisms from water and sediment are influenced by various environmental factors, such as temperature, salinity, and pH, as well as humic and alginic acid content.

In many organisms, it is unclear whether lead is adsorbed onto the organism or actually taken up. Consumers take up lead from their contaminated food, often to high concentrations, but without biomagnification (WHO 1995).

Lead uptake by fish reaches equilibrium only after a number of weeks of exposure. Lead is accumulated mostly in gill, liver, kidney, and bone. Fish eggs show increasing lead levels with increased exposure concentration, and there are indications that lead is present on the egg surface but not accumulated in the embryo. In contrast to inorganic lead compounds, tetraalkyllead is rapidly taken up by fish and rapidly eliminated after the end of the exposure (WHO 1995). Alkyllead was identified as the cause of a major bird kill in the Mersey estuary in 1979/80 (NRA 1995). Approximately 2,500 birds from 20 species were killed and alkyl lead was found in analyses of bird tissue and in a common bivalve *Macoma balthica*. The source of the pollution was traced to an industrial discharge from a manufacturer of tetraalkyllead.

In shellfish, lead concentrations are higher in the calcium-rich shell than in the soft tissue; they relate to the concentrations in sediment. Lead concentrations in some marine fish are higher in gills and skin than in other tissues, but this may be largely due to adsorption. Liver levels increase significantly with age (WHO 1995).

In dolphins, lead is transferred from mothers to offspring during fetal development and lactation. This might be related to the calcium metabolism. In studies on the common porpoise *Phocoena phocoena* from the east coast of Scotland, Falconer *et al* (1983) found that lead residues were below detectable limits (0.5 mg kg^{-1}). The sampled animals had died after becoming entangled in cod nets. The tissues analysed were the brain, liver, kidney, heart, and spleen. Honda *et al* (1986) sampled striped dolphin *Stenella coeruleoalba* and found significant accumulation of lead in the bone of offspring during the suckling period. Significantly more lead was found in adult males than females. The authors suggested that lead was removed from the mother via the milk and as the result of parturition. Lead levels ranged between 0.09 and 0.74 mg kg^{-1} wet weight.

B4.6 Potential effects on interest features of European marine sites

The potential effects include:

! acute toxicity to algae, invertebrates and fish at concentrations of dissolved lead above the proposed EQS of 10 Fg l^{-1} (annual average) in the water column. A lower guideline value of 0.5 Fg l^{-1} of dissolved lead has been suggested by Grimwood and Dixon (1997) for sites of nature conservation importance where particularly sensitive algal species are to be protected;

! accumulation in sediments and can pose a hazard to sediment-dwelling organisms at concentrations above 30.2 mg kg^{-1}, according to Canadian interim marine sediment quality guidelines (see Section 5.5);

! bioaccumulation in the food chain posing a hazard to fish, birds and Annex II sea mammals.

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B5. Chromium

B5.1 Entry into the marine environment

Chromium occurs ubiquitously in nature with natural levels in uncontaminated waters ranging from fractions of 1 µg to a few µg l^{-1}. Sea water contains less than 1 µg chromium l^{-1} (US NAS, 1974), but the exact chemical forms in which chromium is present in the ocean, and surface water is unclear. Theoretically, chromium can persist in the hexavalent state (Cr IV) in water with a low organic matter content. In the trivalent form (Cr III), chromium will form insoluble compounds at the natural pH of water, unless protected by complex formation. The exact distribution between the trivalent and hexavalent state is unknown

Almost all the hexavalent chromium in the environment arises from human activities. Chromium compounds are used in ferrochrome production, electroplating, pigment production, and tanning. These industries, the burning of fossil fuels, and waste incineration are sources of chromium in air and water. In the hexavalent oxidation state, chromium is relatively stable in air and pure water, but is reduced to the trivalent state when it comes into contact with organic matter in biota, soil, and water. There is an environmental cycle for chromium, from rocks and soils to water, biota, air, and back to the soil. However, a substantial amount (estimated at 6.7×10^6 kg per year) is diverted from this cycle by discharge into streams, and by run-off and dumping into the sea. The ultimate repository is ocean sediment (WHO 1988).

It appears that the zero-, di-, tri-, and hexavalent oxidation states have biological importance. The effects of the last two oxidation states are so fundamentally different that they must always be considered separately. The trivalent form is an essential nutrient for Man, in amounts of 50 - 200 µg day^{-1} (WHO 1988) .

B5.2 Recorded levels in the marine environment

Concentrations of chromium have been measured in water and sediments as part of the National Monitoring Programme at sites throughout the UK in estuaries and coastal waters (MPMMG 1998). The results of the National Monitoring Programme have been summarised in Appendix D. MPMMG (1998) should be consulted for further details.

Grimwood and Dixon (1997) compiled available monitoring data for chromium in water, sediments and biota for marine sites of nature conservation importance in England.

As an example of the recorded levels of dissolved chromium in the marine environment, the following concentrations have been reported by DETR (1998) for some English estuaries (Tables B5.1 to B5.3).

B5.3 Fate and behaviour in the marine environment

The solubility of trivalent chromium in sea water varies with salinity and depends strongly on the complexes actually present. The loss of Cr III from solution by precipitation is unlikely to occur to any great extent and the main removal process is adsorption to suspended particles. Chromium in the oxidised form (Cr IV) is very soluble and is not adsorbed strongly to suspended particles in natural waters (Mance *et al* 1984).

Table B5.1 Minimum concentration (Fg $^{l-1}$) of dissolved chromium in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	0.0	0.0	0.0	1.0	0.0
Wear	6.0	0.0	0.0	1.1	0.0
Tees	0.0	0.0	0.0	1.0	0.0
Ouse				0.0	0.0
Wash				0.0	0.0
Thames	0.0	0.0	0.0	0.0	0.0
Tamar	0.0	0.0			0.0

Table B5.2 Average concentration (Fg $^{l-1}$) of dissolved chromium in the water column of some English estuaries (from DETR 1998)

	1991	**1992**	**1993**	**1994**	**1995**
Tyne	14.0	1.6	0.4	1.9	2.5
Wear	17.7	0.7	0.6	8.2	0.8
Tees	10.5	4.3	1.0	8.6	2.0
Ouse				0.4	0.0
Wash				0.0	0.0
Thames	2.9	0.6	0.2	0.3	0.3
Tamar	6.6	0.0			0.1

Table B5.3 Maximum concentration (Fg l^{-1}) of dissolved chromium in the water column of some English estuaries (from DETR 1998)

	1991	**1992**	**1993**	**1994**	**1995**
Tyne	66.0	11.0	2.2	5.2	9.0
Wear	44.0	4.0	1.6	19.0	3.0
Tees	53.0	37.0	2.3	23.1	16.0
Ouse				4.7	0.0
Wash				0.0	0.0
Thames	17.0	1.8	0.8	1.2	0.8
Tamar	30.0	0.0			1.0

B5.4 Effects on the marine environment

B5.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of chromium to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Mance *et al* 1984, Hunt and Hedgecott 1992, Grimwood and Dixon 1997). The most sensitive groups of organisms have been identified.

In 1984, Mance *et al* reviewed data on the toxicity of chromium to saltwater organisms. The authors found acute toxicity to be extremely variable. Fish appeared to be considerably less sensitive than invertebrates, although the data on fish larvae indicated that these forms were particularly sensitive to chromium contamination.

Mance *et al* (1984) proposed an EQS for the protection of saltwater organisms of 15 μg l^{-1}, expressed as a dissolved annual average concentration. (this is currently adopted in UK legislation (HMSO 1989)). The EQS was established by applying an arbitrary factor of 2 to the lowest chronic effects (unspecified) concentration of 30 μg l^{-1} reported at that time for the polychaete worm *Neanthes arenaceodentata*. However, following a review of more recent toxicity data by Hunt and Hedgecott (1992), a more stringent EQS of 5 μg l^{-1} was proposed. This value (also expressed a dissolved annual average) is based on effect concentrations of 10 - 30 μg l^{-1} reported for a range of organisms tested in the laboratory and corresponds to the application of a factor of 2 to the lower end of this range.

A further review of data on the toxicity of chromium to saltwater organisms (since the report by Hunt and Hedgecott 1992) has been undertaken by Grimwood and Dixon (1997). The authors found no reliable toxicity data that indicated higher sensitivity of saltwater organisms than that previously reported. They recommended that the revised EQS of 5 μg l^{-1} (dissolved annual average) was appropriate for the protection of all saltwater life, although where there is concern that the health of communities in sites of nature conservation importance may be compromised as a result of the presence of particularly sensitive species, a lower value may be used as a guideline. However, in the absence of any new toxicity data, it was not possible to make any recommendations for such a value.

Sediment-dwelling organisms

Chromium is found in sediments and can pose a hazard to sediment dwelling organisms at concentrations above 52.3 mg kg^{-1} according to Canadian interim marine sediment quality guidelines (see Section 5.5).

B5.5 Bioaccumulation

Hunt and Hedgecott (1992) reported some information on the bioaccumulation of Cr IV. Laboratory experiments on annelids, crustaceans and molluscs have resulted in bioconcentration factors (BCFs) in the range 158 to 596 for annelids and 383 to 620 (based on dry weights) for molluscs and crustaceans in the laboratory. Much lower BCFs have been calculated in the field: 0.46 to 15 for annelids and <1 for molluscs and crustaceans. These BCFs indicate that chromium is not expected to bioaccumulate under field conditions.

B5.6 Potential effects on interest features of European marine sites

Potential effects include:

! acute toxicity to invertebrates and fish at concentrations of dissolved chromium above the EQS of 5 Fg l^{-1} (annual average) in the water column;

! toxic effects to sediment dwelling-organisms at concentrations above 52.3 mg kg^{-1} according to Canadian interim marine sediment quality guidelines (see Section 5.5).

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B6. Zinc

B6.1 Entry into the marine environment

Zinc is used in coating to protect iron and steel, in alloys for die casting, in brass, in strips for dry batteries, in roofing and in some print processes. It may enter the aquatic environment through natural or anthropogenic sources, including sewage and industrial discharges.

B6.2 Recorded levels in the environment

Concentrations of zinc have been measured in water, sediments and biota as part of the National Monitoring Programme at sites throughout the UK in estuaries and coastal waters (MPMMG 1998). The results of the National Monitoring Programme are summarised in Appendix D. MPMMG should be consulted for further details.

Grimwood and Dixon (1997) compiled available monitoring data for zinc in water, sediments and biota for marine sites of nature conservation importance in England.

As an example of the recorded levels of dissolved zinc in the marine environment, the following concentrations have been reported by DETR (1998) for some English estuaries (Tables B6.1 to B6.3).

Table B6.1 Minimum concentration (μg l^{-1}) of dissolved zinc in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	22.0	8.4	9.2	20.0	0.0
Wear	32.0	5.1	7.9	18.1	0.0
Tees	2.7	0.0	7.7	5.0	0.0
Ouse		5.3	5.5	0.0	0.0
Wash		0.0	36.0	7.7	0.0
Thames	0.0	8.0	7.0	10.9	14.6
Tamar	0.0			4.7	2.7

Table B6.2 Average concentration (Fg l^{-1}) of dissolved zinc in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	161.8	29.9	28.0	88.0	28.6
Wear	92.3	18.9	17.1	67.7	5.1
Tees	50.9	26.9	14.4	74.2	50.6
Ouse		28.7	15.7	19.1	0.0
Wash		0.0	36.0	28.0	0.0
Thames	41.0	22.1	19.0	26.1	30.6
Tamar	12.4			8.2	7.4

Table B6.3 Maximum concentration (Fg l^{-1}) of dissolved zinc in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	478.0	64.0	44.5	296.0	50.0
Wear	203.0	42.0	22.0	346.0	16.0
Tees	212.0	220.0	23.0	397.0	417.0
Ouse		103.0	36.0	112.0	0.0
Wash		0.0	36.0	67.9	0.0
Thames	85.0	43.0	30.0	52.1	71.3
Tamar	110.0			18.2	19.5

B6.3 Fate and behaviour in the marine environment

Zinc is one of the most ubiquitous and mobile of the heavy metals and is transported in natural waters in both dissolved forms and associated with suspended particles (Mance and Yates 1984) In river water, zinc is predominantly present in the dissolved form. In estuaries, where concentrations of suspended particles are greater, a greater proportion of the zinc is adsorbed to suspended particles (CCREM 1987). In low salinity areas of estuaries, zinc can be mobilised from particles by microbial degradation of organic matter and displacement by calcium and magnesium. In the turbidity maximum, zinc associated with suspended sediment will be deposited with flocculated particles where it can accumulate particularly in anaerobic sediments. In seawater, much of the zinc is found is dissolved form as inorganic and organic complexes.

B6.4 Effects on the marine environment

B6.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of zinc to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Mance and Yates 1984, Hunt and Hedgecott 1992 and Grimwood and Dixon 1997). The most sensitive groups of organisms have been identified.

Mance and Yates (1984) reviewed data on the toxicity of zinc to marine organisms. The authors found invertebrates to be generally more sensitive than the fish species studies, while, effects on marine macro and microalgae were noted at concentrations slightly lower than reported for invertebrates. They also reported a complicating factor was the apparent development of increased tolerance. Hunt and Hedgecott (1992) reported the toxicity and bioaccumulation of zinc to be greater at lower salinity.

Mance and Yates (1984) proposed an EQS (for the protection of saltwater life) of 40 Fg l^{-1} (expressed as a dissolved annual average concentration), which is currently adopted in UK legislation (HMSO 1989). The EQS was established by applying an arbitrary factor of 4 to a 96 hour LC50 of 166 Fg l^{-1} reported at that time for the mysid shrimp *Mysidopsis bahia*. However, following a review of more recent toxicity data, Hunt and Hedgecott (1992) proposed a more stringent EQS to DoE of 10 Fg l^{-1}. This value (also expressed a dissolved annual average) was based on the lowest, most reliable NOECs reported for a range of organisms (7 - 20 Fg l^{-1}).

Grimwood and Dixon (1997) reviewed data on the saltwater toxicity of zinc following the Hunt and Hedgecott review and found only one study had been reported that perhaps indicated higher toxicity to saltwater organisms. Exposing the calanoid copepod *Temora stylifera* to zinc chloride, Nipper *et al* (1993) reported 48 hour LC50s ranging from 30 - 40 Fg l^{-1}, following exposure in saltwater of salinity 28 - 32 ppt. In addition, an LC50 as low as 4 Fg l^{-1} was reported on exposure in saltwater of 23 ppt salinity. However, the authors concluded that this value should be treated with caution as there was also an unacceptable level of mortality in the control organisms. NOECs were not determined, although since the LC50s are lower than those reported for any other copepod species, it is conceivable that the NOECs may also be lower.

While the above data gave cause for concern, Grimwood and Dixon concluded that in the absence of a measured NOEC (the above are nominal concentrations), it was difficult to assess the implications of these values for the existing EQS. Furthermore, *Temora stylifera* is not indigenous to the UK. Moreover, any decrease in the revised EQS of 10 Fg l^{-1} would lead to a value below "background" levels of zinc in saltwaters.

Grimwood and Dixon recommended that the revised EQS of 10 Fg l^{-1} (dissolved annual average) proposed to DoE is appropriate for the protection of all saltwater life, although where there was concern that the health of communities in sites of nature conservation importance may be compromised as a result of the presence of particularly sensitive species (e.g. mollusc communities and sensitive copepods), a lower value may be used as a guideline. However, in the absence of a suitable toxicity dataset, it was not possible to make any recommendations on such a value. This is particularly pertinent considering that if the EQS is lowered any further, the value would be at a level below background concentrations.

Sediment-dwelling organisms

Zinc accumulates in sediments and can pose a hazard to sediment dwelling organisms at concentrations above 124 mg kg^{-1}, according to Canadian interim marine sediment quality guidelines (see Section 5.5).

B6.5 Bioaccumulation

Zinc is an essential element for many marine organisms and, as such, is readily bioaccumulated. Several species of crustacean are able to regulate the uptake of zinc but, at higher concentrations, this process appears to breakdown leading to an influx of zinc. These issues complicate the calculation of bioconcentration factors which can be misleading. Organisms can take up zinc which is reflected in the BCF but the concentrations in the tissues are of no toxicological significance. Highest concentrations of zinc reported by Hunt and Hedgecott (1992) were: 300 - 9700 Fg g^{-1} (dry weight) in *Fucus vesiculosus*; 605 - 619 Fg g^{-1} in *Littorina littorea*; 16460 Fg g^{-1} in *Elminius modestus* and 2800 Fg g^{-1} in dogfish.

B6.6 Potential effects on interest features of European marine sites

Potential effects include:

! acute toxicity to algae, invertebrates and fish above the proposed EQS of 10 Fg l^{-1} (annual average) for dissolved zinc;

! accumulation in sediments and can pose a hazard to sediment-dwelling organisms at concentrations above 124 mg kg^{-1}, according to Canadian interim marine sediment quality guidelines (see Section 5.5);

! bioaccumulation in marine organisms posing a potential threat to fish, birds and Annex II sea mammals.

References

CCREM (Canadian Council of Resource and Environmental Ministers). 1987. Canadian Water Quality Guidelines. Inland Waters Directorate, Environmental Canada, Ottawa.

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B7. Copper

B7.1 Entry into the marine environment

Uses of copper include electrical wiring and electroplating, the production of alloys, copper piping, photography, antifouling paints and pesticide formulations. Major industrial sources include mining, smelting, refining and coal-burning industries. Certain of these anthropogenic sources may led to significant concentrations entering the aquatic environment (either directly via sewage or industrial discharges or through atmospheric deposition) but copper will also enter the aquatic environment through natural sources, e.g. from the weathering of or the solution of copper minerals (CCREM 1987).

B7.2 Recorded levels in the marine environment

The ambient levels of copper in seawater remote from source of pollution is estimated to be in the order of 1 Fg l^{-1} (Mance *et al* 1984).

Concentrations of copper have been measured in water and sediments as part of the National Monitoring Programme at sites throughout the UK in estuaries and coastal waters (MPMMG 1998). The results of the National Monitoring Programme are summarised in Appendix D. MPMMG (1998) should be consulted for further details.

Grimwood and Dixon (1997) compiled available monitoring data for copper in water, sediments and biota for marine sites of nature conservation importance in England.

As an example of the recorded levels of dissolved copper in the marine environment, the following concentrations have been reported by DETR (1998) for some English estuaries (Tables B7.1 to B7.3) .

Table B7.1 Minimum concentration (Fg l^{-1}) of dissolved copper in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	0.0	2.5	1.0		0.0
Wear	0.0	1.4	0.0		0.0
Tees	0.0	0.0	1.0		0.0
Ouse	0.0	1.4	0.0	0.0	0.0
Wash		0.0	3.3	0.0	0.0
Thames	3.1	0.0	0.0	0.7	2.1
Tamar	2.0			2.0	0.0

Table B7.2 Average concentration (Fg l^{-1}) of dissolved copper in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	0.6	8.8	3.6		4.9
Wear	6.4	7.4	1.6		3.0
Tees	2.9	36.1	2.5		1.0
Ouse	0.0	5.6	2.7	3.0	0.0
Wash		0.0	3.3	4.4	0.0
Thames	13.9	4.7	4.0	4.6	7.0
Tamar	9.7			3.3	2.5

Table B7.3 Maximum concentration (Fg l^{-1}) of dissolved copper in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	2.0	18.0	9.7		29.0
Wear	32.0	18.0	2.9		5.0
Tees	11.0	505.0	4.0		3.0
Ouse	0.0	12.0	6.0	12.3	0.0
Wash		0.0	3.3	10.3	0.0
Thames	30.4	12.0	7.1	9.3	18.8
Tamar	50.0			6.1	3.9

B7.3 Fate and behaviour in the marine environment

Copper may exist in a natural water system, either in the dissolved form as the cupric (Cu^{2+}) ion or complexed with inorganic anions or organic ligands or as suspended particles when present as a precipitate or absorbed to organic matter (Mance *et al* 1984). It can also be adsorbed to bottom sediments or exist as settled precipitates. The concentration of each of these forms depends on the complex interaction of many variables, including the concentration of copper and hardness, alkalinity, salinity, pH and concentration of bicarbonate, carbonate, sulphide, phosphate, organic ligands and other metal ions. Some of these variables are more relevant to freshwaters (e.g. hardness, alkalinity and pH) than for saltwaters. Complexes formed by copper with natural organic compounds are generally more stable than other metals such as cadmium, lead and zinc.

The high concentrations of particulate matter in most estuaries will facilitate the removal of copper from solution by adsorption to suspended particles which in turn may be deposited and accumulate in sediments. Estuarine sediments are thought to be the most important depositional site for particulate copper transported from rivers, although remobilisation may occur when sediment is disturbed. The remaining dissolved copper in the water column is likely to be present either as an organic complex or as the cupric ion. Copper in the form of the cupric ion is the most bioavailable.

B7.4 Effects on the marine environment

B7.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of copper to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Mance *et al* 1984, Smith 1993 and Grimwood and Dixon 1997). The most sensitive groups of organisms have been identified.

Mance *et al* (1984) reviewed data on the toxicity of copper to saltwater organisms. They found that invertebrates exhibited slightly greater sensitivity to divalent copper than fish species tested. There were also indications of the moderation of toxicity in the presence of organic and inorganic ligands. Mance *et al* (1984) proposed an EQS (for the protection of saltwater organisms) of 5 μg l^{-1} (expressed as a dissolved annual average concentration), although higher concentrations may be acceptable where high levels of dissolved organic carbon may reduce the potential for toxicity. This EQS is currently adopted in UK legislation (HMSO 1989). The EQS was established by applying an arbitrary factor of 10 to an effect concentration of 54 μg l^{-1} reported in a life-cycle study conducted on the mysid shrimp *Mysidopsis bahia*.

A review of toxicity data by Smith in 1993 found no evidence to suggest that the EQS should be revised. In this later review, the lowest most reliable data were LOECs of 9 - 10 μg l^{-1}, reported for growth reduction in the amphipod *Allorchestes compressa* following 4 weeks exposure. Smith (1993) also reported some effect concentrations below the EQS, although for various reasons (e.g. nominal concentrations, poor controls) these were considered unreliable. Nevertheless, in light of these uncertainties, further research was recommended to validate the proposed EQS.

A more recent review by Grimwood and Dixon (1997) found no reliable toxicity data that indicated higher sensitivity of saltwater organisms had been reported for copper. The authors recommended that the EQS of 5 μg l^{-1} (dissolved annual average) was appropriate for the protection of all saltwater life, although where there was concern that the health of communities at sites of nature conservation importance may be compromised as a result of the presence of particularly sensitive species, a lower value may be used as a guideline. However, in the absence of a suitable toxicity dataset, it was not possible to make any recommendations on such a value. This is particularly pertinent considering that if the EQS is lowered any further, the value would be at a level close to background concentrations.

Sediment-dwelling organisms

Copper accumulates in sediments and can pose a hazard at concentrations above 18.7 mg kg^{-1} according to Canadian interim marine sediment quality guidelines (see Section 5.5).

B7.5 Bioaccumulation

As an essential element, copper is readily accumulated by plants and animals. Bioconcentration factors ranging from 100 to 26,000 have been recorded for various aquatic species. However, whole-body concentrations tend to decrease with increasing trophic level. It is believed copper is regulated or immobilised in many species and is not biomagnified in food chains to any significant extent (CCREM 1987).

B7.6 Potential effects on interest features of European marine sites

Potential effects include:

! acute toxicity to invertebrates, and to a lesser extent fish, at concentrations of dissolved copper above the EQS of 5 Fg l^{-1} (annual average) in the water column;

! accumulation in sediments and can pose a hazard at concentrations above 18.7 mg kg^{-1} according to Canadian interim marine sediment quality guidelines (see Section 5.5).

! bioaccumulation in organisms posing a potential hazard to marine organisms, including fish, birds and Annex II sea mammals.

References

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B8 Nickel

B8.1 Entry into the marine environment

Nickel is a ubiquitous trace metal and occurs in soil, water, air, and in the biosphere. The average content in the Earth's crust is about 0.008%. Levels in natural waters have been found to range from 2 to 10 µg l^{-1} (fresh water) and from 0.2 to 0.7 µg l^{-1} (marine). The prevalent ionic form is nickel (II) (WHO 1991).

Most nickel is used for the production of stainless steel and other nickel alloys with high corrosion and temperature resistance. Nickel alloys and nickel platings are used in vehicles, processing machinery, armaments, tools, electrical equipment, household appliances, and coinage. Nickel compounds are also used as catalysts, pigments, and in batteries. The primary sources of nickel emissions into the ambient air are the combustion of coal and oil for heat or power generation, the incineration of waste and sewage sludge, nickel mining and primary production, steel manufacture, electroplating, and miscellaneous sources, such as cement manufacturing. Nickel from various industrial processes and other sources finally reaches waste water. Residues from waste-water treatment are disposed of by deep well injection, ocean dumping, land treatment, and incineration (WHO 1991).

Entry into the aquatic environment is by removal from the atmosphere, by surface run-off, by discharge of industrial and municipal waste, and also following natural erosion of soils and rocks. In rivers, nickel is mainly transported in the form of a precipitated coating on particles and in association with organic matter.

B8.2 Recorded levels in the marine environment

Concentrations of nickel have been measured in water and sediments as part of the National Monitoring Programme at sites throughout the UK in estuaries and coastal waters (MPMMG 1998). The results of the National Monitoring Programme are summarised in Appendix D. MPMMG (1998) should be consulted for more details.

Grimwood and Dixon (1997) compiled monitoring data for nickel in water, sediments and biota for marine sites of nature conservation importance in England.

As an example of the levels of dissolved nickel in the marine environment, the following concentrations have been reported by DETR (1998) for some English estuaries (Tables B8.1 to B8.3).

B8.3 Fate and behaviour in the marine environment

Nickel occurs in aquatic systems as soluble salts adsorbed on clay particles or organic matter (detritus, algae, bacteria), or associated with organic particles, such as humic and fulvic acids and proteins. Absorption processes may be reversed leading to release of nickel from the sediment (WHO 1991).

Table B8.1 Minimum concentration (Fg l^{-1}) of nickel in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	0.0	3.2	1.8	1.5	0.0
Wear	0.0	4.0	1.2	5.0	0.0
Tees	0.0	0.0	0.0	2.0	0.0
Ouse		0.0	0.0	0.0	0.0
Wash		0.0	9.5	0.9	0.0
Thames	0.0	0.0	1.3	1.4	0.9
Tamar	0.0	0.0	0.0	0.5	0.0

Table B8.2 Average concentration (Fg l^{-1}) of nickel in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	3.6	43.0	2.5	6.4	2.5
Wear	23.8	44.3	2.8	11.4	3.8
Tees	6.6	16.5	2.0	10.8	2.1
Ouse		4.1	5.8	2.3	0.0
Wash		0.0	9.5	1.4	0.0
Thames	10.2	8.2	4.1	3.5	3.5
Tamar	0.6	2.6	1.0	1.1	1.1

Table B8.3 Maximum concentration (Fg l^{-1}) of nickel in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Tyne	17.0	70.0	3.6	17.9	11.0
Wear	130.0	70.0	4.8	19.1	7.0
Tees	29.0	77.0	3.5	21.7	14.0
Ouse		9.6	14.0	3.6	0.0
Wash		0.0	9.5	2.1	0.0
Thames	16.9	19.6	6.7	4.6	5.5
Tamar	2.1	5.6	1.8	1.9	2.2

The fate of nickel in freshwater and sea water is affected by several factors including pH, pE, ionic strength, type and concentration of organic and inorganic ligands, and the presence of solid surfaces for adsorption.

B8.4 Effects on the marine environment

B8.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of nickel to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Mance and Yates 1984, Hunt and Hedgecott 1992 and Grimwood and Dixon 1997). The most sensitive groups of organisms have been identified.

Nickel toxicity in aquatic invertebrates varies considerably according to species and abiotic factors. Mance and Yates (1984) reviewed data on the toxicity of nickel to saltwater organisms and found considerable variation of the sensitivity of marine fauna.

The authors proposed an EQS (for the protection of saltwater life) of 30 Fg l^{-1} (expressed as a dissolved annual average concentration) which is currently adopted in UK legislation (HMSO 1989). The EQS was established by applying an arbitrary factor of 5 to a chronic effect concentration of 141 Fg l^{-1} found to cause significant effects on spawning in the mysid shrimp *Mysidopsis bahia*. However, following a review of more recent toxicity data, Hunt and Hedgecott (1992) proposed a more stringent EQS to DoE of 15 Fg l^{-1}. This value (also expressed as a dissolved annual average) was derived by applying a safety factor of around 10 to the same data as that used by Mance and Yates (1984).

Hunt and Hedgecott (1992) also reported effect concentrations ranging from 0.6 - 9 and 10 - 20 Fg l^{-1} for certain sensitive species of algae and molluscs. However, the studies from which these data were taken were considered to be too unreliable for EQS derivation. Nevertheless, further research into algal and mollusc sensitivity was recommended.

A further review by Grimwood and Dixon (1997) on the toxicity data following the study by Hunt and Hedgecott (1992) found no reliable toxicity data that indicated higher sensitivity of saltwater organisms had been reported for nickel. Grimwood and Dixon recommended that the revised EQS of 15 Fg l^{-1} (dissolved annual average) proposed by Hunt and Hedgecott was appropriate for the protection of all saltwater life in the majority of cases. However, as suggested by Hunt and Hedgecott (1992), they stated that where there was concern that the health of communities in sites of nature conservation importance may be compromised as a result of the presence of particularly sensitive algal or mollusc species, a lower value may be used as a guideline. However, in the absence of any new toxicity data, it was not possible to make any recommendations on such a value. This is particularly pertinent considering that if the EQS is decreased further, the value would be at a level close to background concentrations.

Nickel is known to accumulate in sediments but no Canadian interim marine sediment quality guideline was set for nickel in 1999 (see Section 5.5).

B8.5 Bioaccumulation

Laboratory studies have shown that nickel had little capacity for accumulation in all the fish studied. In uncontaminated waters, the range of concentrations reported in whole fish (on a wet-weight basis) ranged from 0.02 to 2 mg kg^{-1}. These values could be up to 10 times higher in fish from contaminated waters. In wildlife, nickel is found in many organs and tissues due to dietary uptake by herbivorous animals and their carnivorous predators. However, accumulation factors in different trophic levels of aquatic food chains suggest that biomagnification of nickel along the food chain, at least in aquatic ecosystems, does not occur (WHO 1991).

B8.6 Potential effects on interest features of European marine sites

Potential effects include:

! acute toxicity to algae and invertebrates (in particular molluscs) at concentrations in the water column of dissolved nickel above the proposed EQS of 15 Fg l^{-1} (annual average) of dissolved nickel.

References

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B9. Arsenic

B9.1 Entry into the marine environment

Arsenic is a ubiquitous element with metalloid properties. Its chemistry is complex and there are many different compounds of both inorganic and organic arsenic. In nature, it is widely distributed in a number of minerals, mainly as the arsenides of copper, nickel, and iron, or as arsenic sulfide or oxide. In water, arsenic is usually found in the form of arsenate or arsenite. Methylated arsenic compounds occur naturally in the environment as the result of biological activity. The most important commercial compound, arsenic (III) oxide, is produced as a by-product in the smelting of copper and lead ores. Arsenic compounds are also used in wood preservatives (see Section B33).

Arsenic enters the marine environment from natural diffuse sources and from anthropogenic point and diffuse sources.

B9.2 Recorded levels in the marine environment

The ambient level of arsenic in the marine environment is generally accepted as being in the range 2 - 3 Fg l^{-1} (Mance *et al* 1984).

Concentrations of arsenic have been measured in sediments and fish muscle as part of the National Monitoring Programme at sites throughout the UK in estuaries and coastal waters (MPMMG 1998). The results of the National Monitoring Programme are summarised in Appendix D. MPMMG (1998) should be consulted for further details.

Grimwood and Dixon (1997) compiled monitoring data for arsenic in water, sediments and biota for marine sites of nature conservation importance in England.

As an example of the recorded levels of dissolved arsenic in the marine environment, the following concentrations have been reported by DETR (1998) for some English estuaries (Tables B9.1 to B9.2).

Table B9.1 Minimum concentration (Fg l^{-1}) of dissolved arsenic in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Ouse	0.0	0.8	1.1	0.0	0.0
Wash	3.6	1.1	1.8	0.0	0.0
Thames	0.0	0.0	0.0		
Tamar	3.0	0.0	1.3	2.0	0.0

Table B9.2 Average concentration (Fg l^{-1}) of dissolved arsenic in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Ouse	3.5	2.2	1.9	0.6	0.0
Wash	3.7	1.4	1.8	0.0	0.0
Thames	0.0	0.0	0.0		
Tamar	3.0	2.2	4.0	3.9	0.0

Table B9.3 Maximum concentration (Fg l^{-1}) of dissolved arsenic in the water column of some English estuaries (from DETR 1998)

	1991	1992	1993	1994	1995
Ouse	7.9	3.7	3.0	3.0	0.0
Wash	3.9	1.7	1.8	0.0	0.0
Thames	0.0	0.0	0.0		
Tamar	3.0	7.1	9.0	8.4	0.0

B9.3 Fate and behaviour in the marine environment

Sedimentation of arsenic in association with iron and aluminium may sometimes be considerable. In oxygenated water, arsenic usually occurs as arsenate, but under reducing conditions, for instance, in deep well waters, arsenite predominates. Methylation of inorganic arsenic to methyl- and dimethylarsenic acids is associated with biological activity in water. Some marine organisms have been shown to transform inorganic arsenic into more complex organic compounds, such as arsenobetaine, arsenocholine, and arsoniumphospholipids.

B9.4 Effects on the marine environment

B9.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of arsenic to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Mance *et al* 1984, Smith and Edwards 1992 and Grimwood and Dixon 1997). The most sensitive groups of organisms have been identified.

Mance *et al* (1984) reviewed information on the aquatic toxicity of arsenic to saltwater organisms, in order to derive an EQS for the protection of marine organisms. A value of 25 Fg l^{-1}, (expressed as a dissolved annual average concentration) was proposed and this is currently adopted in UK legislation (HMSO 1989).

Mance *et al* (1984) found limited data on the toxicity of arsenic to marine organisms. However, the authors concluded that invertebrate species appeared more sensitive than vertebrate species and it is likely that larval stages may be more susceptible. The limited data on algae suggested that they may exhibit a sensitivity similar to that exhibited by the more sensitive invertebrates species. The EQS was established by applying an arbitrary factor of 20 to the lowest 96 hour LC50 of 508 µg l^{-1} reported at that time for the copepod (*Arcatia clarsi*).

Following a review of more recent toxicity data, Smith and Edwards (1992) proposed that the EQS should remain unchanged. The EQS of 25 µg l^{-1} was confirmed by applying a safety factor of around 10 to the lowest, most reliable 96 hour LC50 of 232 µg l^{-1}, reported for zoae of the Dungeness crab *Cancer magister*. Given the high sensitivity of this life-stage and the low acute-to-chronic ratios for arsenic, a reduced safety factor of 10 was considered suitable.

Smith and Edwards (1992) reported that concentrations as low as 7 µg l^{-1} caused significant inhibition of growth of the alga *Fucus vesiculosus*. However, the data were considered insufficiently reliable to influence the EQS. Moreover, the corresponding concentration causing complete inhibition was much higher at 75 µg l^{-1}. Nevertheless, Smith and Edwards concluded that where sensitive algal species such as *F.vesiculosus* are important primary producers in a saltwater ecosystem, a more stringent EQS may be required. They recommended that further research into algal sensitivity be undertaken.

In 1997, a further review of available data on the saltwater toxicity of arsenic was carried out by Grimwood and Dixon (1997). They found no reliable toxicity data that indicated higher sensitivity of saltwater organisms had been reported for arsenic. They recommended that the EQS of 25 µg l^{-1} (dissolved annual average) was appropriate for the protection of all saltwater life in the majority of cases. However, as suggested by Smith and Edwards (1992), where there was concern that the health of communities in sites of nature conservation importance may be compromised as a result of the presence of particularly sensitive algal species, a lower value may be used as a guideline. For instance, a value of 7 µg l^{-1} may be used where necessary by taking into account potential effects on growth of the sensitive species *Fucus vesiculosus*. In the absence of any reliable supporting data, it was not possible to confirm the precision of this value.

Sediment-dwelling organisms

Arsenic is found in sediments and can pose a hazard to sediment dwelling organisms at concentrations above 7.24 mg kg^{-1} according to Canadian interim marine sediment quality guidelines (see Section 5.5).

B9.5 Bioaccumulation

A range of marine organisms have been found to accumulate arsenic from sediments and the water column, including the bivalve molluscs *Scrobicularia plana*, *Cerastoderma* spp. and *Mytilus edulis*, the flatworm *Planaria* and the algae *Fucus vesiculosus*, *Ectocarpus siliculosus*, *Cladophora glomerata* and *Enteromorpha intestinalis. S. plana* and *M. edulis* were considered to take up sorbed arsenic from suspended or surficial sediments and *F. vesiculosus* from dissolved arsenic from the water column. While these species appear to accumulate arsenic to quite high levels, a large proportion may be present as arsenobetaine which is a water soluble compound that poses little hazard to the organism or its consumer (Smith and Edwards 1992). Arsenic is bioconcentrated in organisms but is not biomagnified in food chains and so bioaccumulation is unlikely to be a problem in marine organisms.

B9.6 Potential effects on interest features of European marine sites

Potential effects include:

- acute toxicity to algae and invertebrates at concentrations above the EQS of 25 μg l^{-1} (annual average) of dissolved arsenic in the water column;
- sediment concentrations above 7.24 mg kg^{-1} according to Canadian interim marine sediment quality guidelines (see Section 5.5) can pose a hazard to sediment dwelling organisms.

References

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B10. Vanadium

B10.1 Entry into the marine environment

Vanadium (V) is a greyish metal that occurs in the form of two natural isotopes 50V and 51V. It forms oxidation states of -1, 0, +2, +3, +4, and +5, the oxidation states +3, +4, and +5 being the most common. Oxidation state +4 is the most stable.

Metallic vanadium does not occur in nature. Over 70 vanadium minerals are known, carnatite and vanadinite being the most important from the point of view of mining. Vanadium is mainly (75 - 85%) used in ferrous metallurgy as an alloy additive in various types of steel. Its use in non-ferrous metals is important for the atomic energy industry, aircraft construction, and space technology. Vanadium is also widely used as a catalyst in the chemical industry, where vanadium pentoxide and metavanadates are especially important for the production of sulfuric acid and plastics. Small quantities of vanadium are used in a variety of other applications (WHO 1988).

Power- and heat-producing plants using fossil fuels (petroleum, coal, oil) cause the most widespread discharge of vanadium into the environment. Burning of coal wastes or dumps of coal dust in mining areas are other sources of vanadium discharge into the atmosphere. In the distillation and purification of crude oil, most of the vanadium remains in the residues. Burning of distilled petroleum fuels contributes less vanadium to the atmosphere (WHO 1988).

B10.2 Recorded levels in the marine environment

Vanadium is not commonly monitored for in UK marine waters and was not included in the National Monitoring Programme (MPMMG 1998). Grimwood and Dixon (1997) reported some values for total vanadium at two sites in the North East region of the Environment Agency (ranging from an annual average of 1 Fg l^{-1} to <20 Fg l^{-1}).

B10.3 Fate and behaviour in the marine environment

Most of the vanadium entering sea water is in suspension or adsorbed on colloids. It does not react chemically with sea water but passes mechanically through it. This is reflected in its distribution on the sea bed in the form of silt. Only about 10% of the vanadium is present in a soluble form. The very low concentrations of vanadium in sea water indicate that vanadium is continuously removed from sea water, but the actual mechanisms are largely unknown. Vanadium that accumulates in ascidians, holothurians, and in marine algae will end up in the silt (WHO 1988).

B10.4 Effects on the marine environment

B10.5 Toxicity to marine organisms

An exhaustive literature review on the toxicity of vanadium to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Mance *et al* 1984 and Grimwood and Dixon 1997). The most sensitive groups of organisms have been identified.

The current EQS adopted in UK legislation (HMSO 1989) is a value of 100 μg l^{-1}, expressed as a total annual average concentration which Mance *et al* proposed in 1988. They found few data and these only related to acute toxicity. Too few data were available to assess which group of organisms exhibited greatest sensitivity. The EQS was derived by applying a safety factor of 100 to the lowest, most reliable LC50 of 10,000 μg l^{-1}, reported for the annelid *Nereis diversicolor* following 9 days exposure. It was recommended that the EQS should be reviewed once a larger dataset became available.

More recently, Grimwood and Dixon (1997) reviewed data on the saltwater toxicity of vanadium since the report by Mance *et al* (1984). They found no reliable toxicity data that indicated higher sensitivity of saltwater organisms had been reported for vanadium. They recommended that the EQS of 100 μg l^{-1} (total annual average) was appropriate for the protection of all saltwater life, although where there was concern that the health of communities in sites of nature conservation importance may be compromised as a result of the presence of particularly sensitive species, a lower value may be used as a guideline. However, in the absence of any new toxicity data, it was not possible to make any recommendations on such a value.

B10.5 Bioaccumulation

Mance *et al* (1988) reviewed the limited information on the bioaccumulation of vanadium and reported the majority of BCFs below 100, indicating that bioaccumulation of vanadium is not likely to be a problem.

B10.6 Potential effects on European marine sites

Potential effects include:

- acute toxic effects on marine organisms at concentrations above the EQS of 100 μg l^{-1} (annual average) of dissolved vanadium in the water column.

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B11. Boron

B11.1 Entry into the marine environment

Boron is used in fire retardants, as a component of enamels, in the photographic, cosmetic, leather, paint, textile and wood-processing industries. Borax, a major boron compound, is used as a cleaning compound and may occur in domestic and/or industrial effluents. Because of its wide variety of industrial uses, there are many potential pathways for entering the aquatic environment.

B11.2 Recorded levels in the marine environment

Boron is not commonly monitored for in UK marine waters. Grimwood and Dixon (1997) report some values for total boron at two sites in the North-East region of the Environment Agency (ranging from an annual average of 700 Fg l^{-1} to 4,627 Fg l^{-1}).

B11.3 Fate and behaviour in the marine environment

Boron, with oxidation states of 0 and +3, may form various boranes (hydrides) and organoboron compounds. The environmental chemistry of boron in water is not well understood, but the predominant boron species in seawater is boric acid (76%) while the borate anion ($B(OH)^{-}$) accounts for approximately 13% (CCREM 1987).

B11.4 Effects on the marine environment

B11.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of boron to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Mance *et al* 1988, and Grimwood and Dixon 1997). The most sensitive groups of organisms have been identified.

Mance *et al* (1988) reviewed the toxicity of boron to saltwater organisms. They found only limited data, which made it difficult to determine whether any group of organisms exhibited greater sensitivity. The authors proposed an EQS (for the protection of saltwater life) of 7,000 Fg l^{-1} (expressed as a total annual average concentration) which is currently adopted in UK legislation (HMSO 1989). Due to a lack of data, it was deemed that the derivation of an objective EQS was not possible. However, a tentative EQS of 7,000 Fg l^{-1} was derived by applying an arbitrary factor of 10 to the lowest, most reliable 96 hour LC50 of 74,000 Fg l^{-1}, reported for the dab *Limanda limanda*. The derivation of a lower standard by using a larger safety factor was considered unnecessary as the tentative EQS is proposed at a level approximating normal ambient concentrations of boron in seawater. Nevertheless, it was recommended that the EQS should be reviewed once a larger dataset became available.

Grimwood and Dixon (1997) reviewed data on the saltwater toxicity of boron since the review by Mance *et* al. They found no reliable toxicity data that indicated higher sensitivity of saltwater organisms had been reported for boron. The authors recommended that the tentative EQS of 7,000 Fg l^{-1} (total annual average) proposed by Mance *et al* was probably appropriate for the protection of all saltwater life. However, the lack of toxicity data should be taken into account and this recommendation reviewed in the light of any new data.

B11.5 Bioaccumulation

There is some evidence that boron accumulates in marine zooplankton, algae and seaweeds, although tissue levels are generally low (BCF <50) (CCREM 1987).

B11.6 Potential effects on interest features of European marine sites

Potential effects include:

! acute toxic effects to marine organisms at concentrations above the EQS of 7,000 Fg l^{-1} (annual average) in the water column;

! bioaccumulation in marine zooplankton and algae.

References

CCREM (Canadian Council of Resource and Environmental Ministers). 1987. Canadian Water Quality Guidelines. Inland Waters Directorate, Environmental Canada, Ottawa.

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B12. Iron

B12.1 Entry into the marine environment

Iron is the fourth most abundant element in the Earth's crust. While it is naturally released into the environment from weathering, it may also be released into the aquatic environment through human activities, such as burning of coke and coal, acid mine drainage, mineral processing, sewage, iron related industries and the corrosion of iron and steel (CCREM 1987).

B12.2 Recorded levels in the marine environment

Concentrations of iron were not measured as part of the National Monitoring Programme (MPMMG 1998). Grimwood and Dixon (1997) compiled available monitoring data for iron in water, sediments and biota for marine sites of nature conservation importance in England.

In unpolluted oceanic seawater, concentrations of iron between 2.8-29 ng l^{-1} and 224-1,228 ng l^{-1} have been reported, although higher concentrations may be found in estuarine waters (Whitehouse *et al* 1998).

Iron concentrations in saltmarsh sediments are frequently much higher than those occurring in the overlying waters. Mean concentrations as high as 20,800 mg kg^{-1} appear to be tolerated in coastal saltmarshes which are designated as 'healthy.' It has been shown that iron concentrations are higher in the immediate vicinity of saltmarsh plant roots and in the burrow walls produced by organisms, such as *Arenicola.*

B12.3 Fate and behaviour in the marine environment

On reaching saltwater, suspended iron oxyhydroxides are rapidly precipitated such that at salinities of 10 ppt or greater, the vast majority of the iron present occurs in particulate form and is effectively removed from solution. In anoxic marine waters, ferrous iron is mobilised from sediments and diffuses into the water column.

B12.4 Effects on the marine environment

B12.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of iron to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Mance and Campbell 1988, Grimwood and Dixon 1997 and Whitehouse *et al* 1998). The most sensitive groups of organisms have been identified.

Mance and Campbell (1988) reviewed data on the toxicity of iron to saltwater species and proposed EQSs (for the protection of saltwater life) of 10,000 and 25,000 Fg l^{-1} for total iron in less turbulent seawaters and more turbulent estuaries with high suspended solids content, respectively (as annual averages). These are adopted in UK legislation (HMSO 1989). In addition, an EQS of 1,000 Fg l^{-1} expressed as a dissolved annual average concentration has also been adopted. Due to a lack of data, the derivation of an objective EQS based on iron toxicity was not considered possible. Therefore, the above values are based on observations of general water quality at various estuarine and marine sites. A review of these EQSs was recommended once direct observations of biological quality associated with these concentrations became available.

Grimwood and Dixon (1997) reviewed data on the saltwater toxicity of iron and found no reliable toxicity data that indicate higher sensitivity of saltwater organisms had been reported for iron. The authors recommended that the EQSs of 1,000, 10,000 and 25,000 Fg l^{-1}, expressed as dissolved, total and total annual averages, respectively, were appropriate for the protection of all saltwater life. The latter value should only be adopted in estuaries of considerable tidal energy and containing a high level of suspended solids.

A further review in 1998 (Whitehouse *et al*) also found that, against a background of a very wide range of sensitivities for different species and a relatively sparse dataset for saltwater organisms, that there was little evidence to suggest that saltwater organisms were more or less sensitive than freshwater organisms and that toxicity data reported since Mance *et al* (1988) do not indicate any greater sensitivity. Based on their findings, Whitehouse *et al* proposed no change to the current annual average of 1,000 Fg l^{-1}.

B12.5 Bioaccumulation

Marine organisms accumulate iron but also rapidly excrete iron in clean water conditions. Normally, tissue concentrations of iron are related to the water and sediment concentrations, but there is considerable variability. Tissue concentrations vary seasonally, being lower in winter and spring than in summer and autumn and furthermore tissue and shell concentrations increase with increasing salinity (Mance and Campbell 1988). The bioaccumulation of iron by marine organisms does not appear to pose a hazard to higher trophic levels.

B12.6 Potential effects on interest features of European marine sites

Potential effects include:

! acute toxicity to marine organisms at concentrations above the EQS of 1,000, 10,000 and 25,000 Fg l^{-1}, expressed as dissolved, total and total annual averages, respectively, in the water column.

References

CCREM (Canadian Council of Resource and Environmental Ministers). 1987. Canadian Water Quality Guidelines. Inland Waters Directorate, Environmental Canada, Ottawa.

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B13. Triazine herbicides (atrazine and SIMAZINE)

B13.1 Entry into the marine environment

Atrazine and simazine are systemic herbicides, transported within plants via the xylem, and accumulated in apical meristems and leaves. They act primarily by binding to specific proteins in the thylakoid membranes of chloroplasts, where they inhibit the Hill reaction (photolysis of water) and thus block photosynthesis. Atrazine also disrupts other enzymic processes. Simazine is absorbed via roots, and atrazine is absorbed via roots and leaves. Both herbicides have many applications in both agricultural and non-agricultural situations, where they may be used selectively or non-selectively.

Concern over the increasing occurrence of atrazine in groundwater in many EC States have led to restrictions on its use in a number of countries.

In the absence of relevant data, it is assumed that only a small part of the atrazine and simazine produced is released to the environment in industrial effluents, via spillage or dumping, and following direct application to water (which is not approved in the UK). The main input is probably associated with diffuse sources, including surface run-off; soil leaching and drainage; drifting of sprays and cleaning of spray equipment.

B13.2 Recorded levels in the marine environment

Hedgecott (1996) concluded that concentrations of atrazine and simazine in the marine environment were likely to be lower because their entry is restricted to river inputs, sewage and industrial discharges, and direct losses from application at coastal sites.

In the UK, atrazine was detected in 5 out of 11 estuaries with a maximum concentration of 0.38 µg l^{-1}, whilst simazine was detected in 6 of the estuaries with a maximum concentration of 0.39 µg l^{-1} (SAC Scientific 1987).

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. No water column concentration was found to exceed the EQS value (see Appendix D). Monitoring data were not available for sediments or biota.

The available data suggest that concentrations of atrazine and simazine in UK coastal and estuarine waters do not exceed relevant quality standards derived for the protection of saltwater life.

B13.3 Fate and behaviour in the marine environment

Hedgecott (1996) reviewed data on the fate and behaviour of atrazine and simazine and concluded that both are stable in the aquatic environment. Their aquatic fate is strongly influenced by their moderate solubilities (33 mg l^{-1} for atrazine and 5 mg l^{-1} for simazine) and their persistence. Neither compound is volatile and losses to the atmosphere are therefore likely to be minimal (although aerosol losses may result from spraying).

The main routes of removal of atrazine and simazine from water are photo-enhanced hydrolysis to 2-hydroxy derivatives, adsorption onto sediments and degradation by micro-organisms. Adsorption to suspended and sedimented clay and organic particles can remove significant amounts of atrazine and simazine from solution. Correll and Wu (1982) found that, in an estuarine system at equilibrium, about 12% of atrazine was adsorbed on sediments, but suggested that this underestimated adsorption in real estuaries. However, other studies have shown sorption is both rapid and reversible.

Atrazine and simazine are stable in pure solution, with an estimated half-life for hydrolysis of atrazine in sterile, neutral water of 1,800 years (Armstrong and Chesters 1968). In the environment, degradation is enhanced by light and by the presence of organic matter or minerals, in particular humic and fulvic acids. For example, Mansour *et al* (1985) recorded a half-life of 340 days for the photo-reaction of atrazine with hydroxyl radicals in clean water.

Clearly persistence of triazines in water is dependent upon the local conditions. Atrazine (and probably simazine) appears to be more rapidly removed from saline water than from fresh water. In all waters, simazine appears to be slightly more persistent than atrazine.

In laboratory microcosms with estuarine waters, Jones *et al* (1982) recorded a much shorter half-life for removal of atrazine in solution of 3 to 12 days. However, in this test, sediment was included and most of the removal was by adsorption, which was increased by the high sediment content and by sediment resuspension when sampling. Atrazine's half-life in the sediment was 15 to 20 days.

B13.4 Effects on the marine environment

B13.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of atrazine and simazine to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Hedgecott 1996). The most sensitive groups of organisms have been identified.

Hedgecott (1996) found few data for saltwater invertebrates or fish. However, based on the information available, animals are much less sensitive than algae or plants. Most of the available data are for estuarine species. For simazine fewer studies are available, but it is likely that its toxicity will be similar to that of atrazine.

As atrazine and simazine are very similar compounds and share a common toxic action in photosynthesising organisms, it is probable that their combined effects will be additive (although this has not been investigated experimentally).

Atrazine

Hedgecott (1996) found acute sub-lethal EC50s of approximately 60 to 100 µg l^{-1} atrazine for a number of saltwater algae (Walsh 1972, Hollister and Walsh 1973), with `lowest observed effect concentrations' as low as 50 µg l^{-1} (Tchan and Chiou 1977). The effects usually studied are inhibition of photosynthesis, growth or reproduction. Plants show a similar level of sensitivity to atrazine, with acute EC50s in the range 75 to 104 µg l^{-1} for inhibition of photosynthesis or growth of many species (Correll and Wu 1982, Jones and Winchell 1984, Jones *et al* 1986), and a lower concentration of 10 µg l^{-1} disrupting metabolism in *Zostera marina* (Delistraty and Hershner 1984).

In chronic tests, significant growth suppression in the macro-alga *Laminaria* was caused by 10 µg l^{-1} or more of atrazine (Hopkin and Kain 1978) and reproduction of the unicellular algae *Nannochloris* and *Phaeodactylum* was significantly reduced by 15 to 50 µg l^{-1} (Mayasich *et al* 1986, 1987). For higher plants, chronic EC50s of 30 and 55 µg l^{-1} have been reported for growth and photosynthesis of P*otamogeton perfoliatus*, respectively (Kemp *et al* 1985), and a chronic LC50 of 100 µg l^{-1} has been estimated for *Zostera marina* (Delistraty and Hershner 1984). A concentration of 12 µg l^{-1} atrazine caused about 50% mortality in the warm-water species *Vallisneria americana* over 47 days (control mortality 10%; no effect at 1.3 µg l^{-1}) (Correll and Wu 1982).

In laboratory micro-ecosystems designed to simulate conditions in a tidal saltmarsh, a treatment with 2.2 mg l^{-1} atrazine for five days resulted in significant decreases in primary productivity (from 191 to 29 mg C/m² hour in one test and from 283 to 30 mg C/m² hour in the second). Measurements of the chlorophyll content of edaphic diatoms on the sediment surface and in the top 5 mm showed that, although there were some significant reductions at certain depths, these were not consistent between the test. There were no obvious changes in species diversity and, although there were some changes in community structure, these were neither consistent nor statistically significant. Attempts to conduct similar studies in the field were unsuccessful as the plastic tubs used to enclose small areas of saltmarsh were found to have more effects than atrazine at the concentrations used.

Effects on saltwater fish and invertebrates are not normally observed at concentrations below the mg l^{-1} level for atrazine. However, two particularly low values have been reported: a 96 hour LC50 of 94 µg l^{-1}(nominal) for the copepod *Acartia tonsa*; and significantly reduced survival in mysid shrimps chronically exposed to 190 µg l^{-1} (measured) (Ward and Ballantine 1985).

Simazine

Although Hedgecott (1996) found data for simazine more limited than for atrazine, toxicity to saltwater organisms is probably similar to that of atrazine. The most sensitive organisms appear to be algae, with Tchan and Chiou (1977) reporting a `LOEC' of 100 µg l^{-1} for photosynthesis of *Dunaliella teriolecta*. No other adverse responses have been reported at concentrations below 100 µg l^{-1}.

The only data on the toxicity of simazine toward saltwater animals was information on 48 hour LC50s for adult brown shrimps *Crangon crangon*, shore crabs *Carcinus maenas* and cockles *Cardium edule* in static systems. All above 100 mg l^{-1}, the maximum test concentration used.

B13.4.2 Sediment-dwelling organisms

Simazine and atrazine have only low to moderate persistence in sediments and no data on the effects on sediment dwelling organisms could be located.

B13.5 Bioaccumulation

Atrazine's and simazine's relatively high solubilities (33 and 5 mg l^{-1}) and relatively low octanol-water partition coefficients (log Kow 2.7 and 2.3) suggest that they will have only low-to-moderate tendencies to accumulate in saltwater biota. Hedgecott (1996) concluded that there were insufficient experimental data to confirm this assertion, with only two studies reported for atrazine and none for simazine.

Jones *et al* (1986) found that the uptake of atrazine from water by the estuarine plant *Potamogeton perfoliatus* was a rapid process, reaching equilibrium after about 15 minutes when exposed to 20 to 100 µg l^{-1}. Depuration when placed in uncontaminated water was also rapid, with 45% released after 2 hours and another 20% removed by two subsequent washes, after which the rate of release declined and a portion remained bound to the plant material. A separate series of tests showed that the highest atrazine concentrations were associated with the shoots rather than the roots with, for example, respective dry weight bioconcentration factors (BCFs) of 85 and 19 when exposed to 10 µg l^{-1}.

Pillai *et al* (1979) fed box crabs *Sesarma cinereum* on cordgrass *Spartina alterniflora* that had been grown for two days in 0.2 mg l^{-1} radio-labelled atrazine followed by three days in clean water. The crabs ingested on average 15 µg atrazine/kg^{-1} bodyweight/day^{-1} and 46 µg metabolites kg^{-1} bodyweight/day^{-1}, and were fed for 10 days. No behavioural or physiological effects were noted. A total of 0.61 mg atrazine and metabolites kg^{-1} bodyweight was consumed, 0.21 mg kg^{-1} was egested in the faeces and homogenised crabs at the end of the test contained 0.4 mg kg^{-1} (measured as radioactivity). However, the proportion of radioactivity as atrazine (rather than its metabolites) was 24% in the ingested plant matter but only 1.2% in crab tissue and 0.5% in faeces, indicating that the crabs had metabolised much of the atrazine.

The ability of certain plants and animals - particularly crustaceans - to metabolise atrazine suggests that biomagnification of atrazine up food chains is not likely to be extensive, although it may occur in food webs that do not include such `resistant' organisms.

B13.6 Potential effects on interest features of European marine sites

Potential effects include:

- toxic effects to algae and macrophytes at concentrations above the EQS of 2 Fg l^{-1} (annual average) and 10 Fg l^{-1} (maximum allowable concentration) in the water column;

- atrazine has been identified as an endocrine disrupting substance and a precautionary approach should be adopted in the control of this substance.

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B14. Diuron and Linuron

B14.1 Entry into the marine environment

Diuron and linuron are herbicides which are members of what is usually known as the phenylurea group. Diruon is also increasingly being used as a booster biocide in antifoulant paints (see Section B32). Because of their similar mode of action, a consideration of the effects to the marine environment of both linuron and diuron is discussed here.

These compounds are stable to hydrolysis in the normal pH range and exist as the undissociated form in natural waters. The vapour pressures at about 20 °C indicate negligible losses through vaporisation in the environment, and sunlight-induced photochemical decomposition is of relatively minor importance.

Phenylurea herbicides are easily taken up from soil solution by the root systems of plants and rapidly translocated into stems and leaves by the transpiration system, moving primarily via the xylem. Linuron and isoproturon, and to a lesser extent other phenylurea derivatives, can also be taken up through application to the leaves, especially in the presence of surfactants.

The principal mode of action of these substances is through disruption of photosynthesis, probably by inhibition of an enzyme involved in the Hill reaction.

Lewis and Gardiner (1996) have reviewed data on the use and fate and behaviour of these herbicides.

Diuron is used extensively on industrial land and to a limited extent in agriculture. A major user of diuron in the UK was British Rail to control weed growth on railway tracks. Its 32,000 km of track is sprayed annually, with 22 tonnes of diuron used in 1991. This amount probably increased as the triazine herbicides, atrazine and simazine, were banned from August 1993 for non-agricultural uses. Lewis and Gardiner (1996) were unable to estimate the total amount of diuron used on industrial land and around domestic buildings in the UK.

Little information is available on the quantities of linuron used. However, Lewis and Gardiner (1996) estimated that approximately 100 tonnes were used on crops in 1992.

Linuron is mainly used as an agricultural herbicide and, therefore, its main routes of entry into the aquatic environment are likely to be run-off, leaching, spray drift during application, washing down of machinery used during application and accidental spillage.

B14.2 Recorded levels in the marine environment

Monitoring data from the National Rivers Authority (NRA) and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D Monitoring data for diuron and linuron were only available for the NRA survey. No water column concentration was found to exceed the EQS value (see Appendix D). Monitoring data were not available for sediments or biota.

The available data suggest that concentrations of diuron and linuron in UK coastal and estuarine water do not exceed relevant quality standards derived for the protection of saltwater life.

B14.3 Fate and behaviour in the marine environment

Lewis and Gardiner (1996) found few data on the fate and behaviour of these herbicides in water. However, based on the information available, the authors concluded that removal from water was likely to be by biodegradation and adsorption, with half-lives in the range of a few weeks to a few months reported.

B14.4 Effects on the marine environment

B14.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of diuron and linuron to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Lewis and Gardiner 1996). The most sensitive groups of organisms have been identified.

Lewis and Gardiner (1996) reviewed the limited data on the toxicity of linuron and diuron to saltwater organisms. The authors concluded (although only acute toxicity data were available) that the results of Mayer (1987) for diuron and Kemp *et al* (1985) for linuron suggested that these herbicides may have similar toxicities to saltwater organisms.

In freshwaters, algae and macrophytes appear to be the species most sensitive to these herbicides. The lowest effect concentrations reported for these species are approximately 20 µg l^{-1} and higher for all four herbicides.

Based on data for freshwater organisms, Lewis and Gardiner (1996) concluded that because of a similar mode of action, and because it is likely that they could occur together in the aquatic environment, it was possible that they could exert an additive toxic effect on aquatic life when present together.

B14.4.2 Sediment dwelling organisms

No data could be located.

B14.5 Bioaccumulation

Lewis and Gardiner (1996) found no data on the bioaccumulation of these herbicides in saltwater organisms. However, data for freshwater organisms suggest bioaccumulation is unlikely to be significant (reliable reported BCFs were <100), and therefore likely to be the same for saltwater organisms.

B14.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxic effects on algae and macrophytes at concentrations above the EQS of 2 Fg l^{-1} in the water column.

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B15. Trifluralin

B15.1 Entry into the marine environment

Trifluralin is applied as a herbicide for pre-emergent control of annual grasses and some broad leaved weeds in a wide variety of vegetables and some fruit. It is usually directly incorporated into soils, although some trifluralin mixtures may be sprayed.

Trifluralin may enter the aquatic environment predominantly via diffuse sources resulting from its recommended use, e.g. in agricultural run-off bound mainly to soil particles. Industrial discharges, accidental spillages during transport, storage and use are potential point sources of trifluralin contamination.

B15.2 Recorded levels in the marine environment

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. No water column concentration was found to exceed the EQS value (see Appendix D). Monitoring data were not available for sediments or biota.

The available data suggest that concentrations of trifluralin in UK coastal and estuarine waters do not exceed relevant quality standards derived for the protection of saltwater life.

B15.3 Fate and behaviour in the marine environment

Jones (1996) reviewed the fate and behaviour and aquatic toxicity of trifluralin. Trifluralin is readily adsorbed on solid surfaces. The solubility and log Kow are also expected to be pH dependent. A realistic value for solubility is likely to be below 1 mg l^{-1} and for log Kow greater than 4. The low vapour pressure indicates that loss from the water phase by volatilisation will be slow.

Kearney *et al* (1977) studied the degradation of trifluralin in model aquatic ecosystems containing a variety of organic matter. The addition of 100 g loam containing 1 µg g^{-1} of labelled trifluralin to a 4 litre aquarium filled with water resulted in a maximum water concentration after 30 days of 7.5 µg l^{-1} based on 14C measurement. After 33 days, only degradation products were isolated from the water and no trifluralin was detected in fish placed in the tank for the last 3 days of the test. As the experiment was carried out in daylight, photolysis was probably the major degradation process.

In the environment, biodegradation is not thought to be an important pathway for the removal of trifluralin from water or soils (Shuker and Hutton 1986). Photodecomposition is the major degradation process for trifluralin released into the aquatic environment (Helling 1976). Kosinski (1984) added trifluralin to artificial streams and calculated a half-life of less than one hour. The rapid loss of chemical was attributed to photodecomposition.

However, trifluralin present in the aquatic environment is likely to be readily degraded by photolysis and adsorbed onto sediments.

B15.4 Effects on the marine environment

B15.5.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of trifluralin to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Jones 1996). The most sensitive groups of organisms have been identified.

Jones (1996) reviewed the aquatic toxicity of trifluralin. Data for marine organisms were found to be limited. Jones (1996) concluded that elevated trifluralin concentrations in the marine environment were likely to occur only in estuaries receiving significant freshwater inputs contaminated with run-off from agricultural land. Most of the trifluralin entering marine waters is therefore likely to be adsorbed on suspended solids and may therefore not be readily bioavailable. Invertebrates and fish were found to exhibit the greatest sensitivity.

Algae

Walsh (1972) reported that 2.5 mg l^{-1} of trifluralin reduced the growth of four marine phytoplankton species by 50%. No other data were found for marine algae.

Invertebrates

Liu and Lee (1975) exposed adults and larvae of the mussel *Mytilus edulis* to trifluralin. Larval growth was inhibited at 90 µg l^{-1} and 100 µg l^{-1} affected the ability of adults to attach to glass. The corresponding LC50 for adults was 240 µg l^{-1}.

The effects of a technical mixture of trifluralin (93% active ingredient) on eggs, larvae, juveniles and adults of *Cancer magister* (Dungeness crab) were investigated by Caldwell *et al* (1979). Exposure to 590 µg l^{-1} for 24 hours in static water did not affect egg hatching success or first stage zoeal motility. In a further long-term continuous flow test with larvae, juveniles and adults 220 µg l^{-1} produced 100% mortality of zoea after 8 days, whereas exposure to 26 µg l^{-1} for 50 days produced no significant effects on survival but significantly delayed the first molt. The survival of juveniles exposed for 80 days to 590 µg l^{-1} and of adults exposed to 300 µg l^{-1} for 85 days was not affected. Based on the results for the larval stages the MATC for the crab was estimated to be 326 and <220 µg l^{-1}.

Fish

Trifluralin was found to be very toxic to sheepshead minnows *Cyprinodon variegatus* (Couch *et al* 1979). Exposure to 5.5-31 µg l^{-1} for the initial 28 days of life resulted in acute vertebral dysplasia which was thought to be a direct result of the effect of trifluralin on the hormonal control of calcium metabolism. High calcium levels were found in the blood serum of adult sheepshead minnows exposed to 16.6 µg l^{-1}. Wells and Cowan (1982) also reported spinal deformities in minnows exposed to 16 µg l^{-1} for 51 days.

Parrish *et al* (1978) studied sheepshead minnows exposed to trifluralin over a full life cycle (166 days). Exposure to 17.7 µg l^{-1} caused significant mortality of adult fish, whereas 9.6 and 4.8 µg resulted in significantly reduced growth and fecundity of adult fish, respectively. In addition, significantly reduced hatching success of embryos spawned by parent fish and survival and growth of the second generation fish were observed on exposure to 9.6 µg l^{-1}. From the results, an MATC of >1.3 and <4.8 µg l^{-1} was estimated for the sheepshead minnow.

Sediment-dwelling organisms

Trifluralin is likely to be absorbed to sediment but no data could be located on the toxic effects to sediment-dwelling organisms.

B15.5 Bioaccumulation

No data on the bioaccumulation of trifluralin in marine organisms could be located. However, it has been demonstrated by Garnas (1976) that marine invertebrates metabolise trifluralin via oxidative, reductive, hydrolytic and conjugative pathways. High BCF (>1,000 for algae and fish) and slow depuration (generally in the order of weeks) have been reported for freshwater organisms. Therefore, there is potential for bioaccumulation, although trifluralin is likely to be adsorbed to sediment and therefore its bioavailability is uncertain.

B15.6 Potential effects on interest features of European marine sites

Potential effects include:

- toxic effects to algae, invertebrates and fish at concentrations above the EQS of 0.1 µg l^{-1} (annual average) and 20 µg l^{-1} (maximum allowable concentration) in the water column;

- accumulation in sediments but there is no evidence of effects on sediment-dwelling organisms;

- potential to bioaccumulate but there is no evidence of bioaccumulation in marine organisms, including fish, birds and Annex II sea mammals;

- trifluralin has been identified as an endocrine disrupting substance and a precautionary approach should be adopted in its control.

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B16. Bentazone

B16.1 Entry into the marine environment

Bentazone is a contact herbicide absorbed by the leaves and is used to control broad leafed weeds in winter and spring cereals. In 1992, 85 tonnes of bentazone were used in Great Britain, which declined to 73 tonnes in 1994. In 1994, it was the 40th most commonly used active substance on arable crops (PSD Data, Pers. Comm., Dr Marsden, DoE 1996).

The main mode of action of bentazone is by inhibition of photosynthesis, causing depletion of carbohydrate reserves and loss of chloroplast membrane integrity (Fletcher and Kirkwood 1982).

The major diffuse sources of bentazone into the aquatic environment are likely to be run-off from soils or accidental over-spray as a result of its use on agricultural land. Bentazone has a low affinity for particulate or organic carbon material, log Kow of 0.35, (RSC 1991); log Koc of 2.42 (Donigian and Carsel 1987).

B16.2 Recorded levels in the marine environment

Murgatroyd *et al* (1996) reported that no exceedances to the EQS were measured in estuarine or coastal waters by the NRA in 1993. In other parts of Western Europe, up to 1 µg l^{-1} (Leistra and Boestsen 1989) of bentazone has been recorded. However, in estuarine and coastal waters, bentazone concentrations are generally below detection limits (Readman *et al.* 1993).

The available data suggest that concentrations of bentazone in UK coastal and estuarine waters are unlikely to exceed relevant quality standards derived for the protection of saltwater life.

B16.3 Fate and behaviour in the marine environment

Murgatroyd *et al* (1996) reviewed the fate and behaviour and aquatic toxicity of bentazone. However, little information was available.

Photolysis appears to be the main abiotic degradation process for bentazone (80% degradation of bentazone in a 24 hour period when exposed to artificial sunlight, Nilles and Zabik 1975), as in water, no hydrolysis of 1 mg l^{-1} of bentazone was observed after 122 days at 22 °C (US EPA 1987).

B16.4 Effects on the marine environment

B16.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of bentazone to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Murgatroyd *et al* 1996). The most sensitive groups of organisms have been identified.

Murgatroyd *et al* (1996) found no reliable data on the toxicity of bentazone to marine organisms, but concluded that bentazone was of low to moderate toxicity to freshwater organisms, with acute effects ranging from 10-6,232 mg l^{-1} (saltwater organisms are likely to exhibit similar sensitivity).

Algae appear to be the most sensitive species. Bentazone affects algae through inhibition of photosynthesis and, although no data are available, aquatic macrophytes are likely to be of equal or greater sensitivity. The majority of reliable toxicity data indicates that invertebrates and fish are much less sensitive to bentazone than algae.

B16.4.2 Sediment dwelling organisms

No data could be located.

B16.5 Bioaccumulation

Murgatroyd *et al* (1996) found no data on bioaccumulation in marine organisms, but concluded, based on evidence for freshwater organisms, that the bioaccumulation potential for bentazone was low.

B16.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxic effects on algae and macrophytes at concentrations above the EQS of 500 Fg l^{-1} (annual average) and 5,000 Fg l^{-1} (maximum allowable concentration) in the water column.

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B17. Organochlorine pesticides (aldrin, ddt, dieldrin, endrin and isodrin)

Organochlorine pesticides have been widely used in the past, but aldrin, DDT, dieldrin and endrin have been banned from use as a pesticide in the UK (PSD/HSE 1998). However, the continued persistence and wide distribution of these substances in the marine environment remain a concern. They are List I and Red List (except isodrin) substances. Two other organochlorine pesticides remain in use: lindane (see Section B18) and endosulfan (see Section B19).

B17.1 Entry into the marine environment

Aldrin, DDT, dieldrin and endrin, have been widely used and therefore are found widely distributed in the environment.

B17.2 Recorded levels in the marine environment

Concentrations of aldrin, DDT (and its metabolites: pp-TDE and pp-DDE), dieldrin, endrin and isodrin have been measured in water, sediments and biota as part of the National Monitoring Programme at sites in estuaries and coastal waters throughout the UK. DDT compounds and dieldrin were also monitored in estuarine and coastal waters of England and Wales by the NRA. These results are summarised in Appendix D.

Dieldrin and DDT compounds were detected in the flesh of *Mytilus edulis* at a small number of sites. Dieldrin, endrin and DDT compounds were detected in fish livers. In sediments, dieldrin and DDT compounds were found at estuarine and intermediate sites. The NRA survey found DDT compounds and dieldrin at concentrations greater than 0.1 Fg l^{-1} in very few (0.1%) of estuarine and coastal water samples. In general, concentrations are very low and in many cases are considered to be close to background.

B17.3 Fate and behaviour in the marine environment

In general, these compounds have a low water solubilities, high log Kows and log Kocs. They tend to be persistent and sorb strongly to suspended solids and sediments.

B17.4 Effects on the marine environment

B17.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of these organochlorine pesticides has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents and directed towards particular areas of concern.

In general, these organochlorine pesticides are highly toxic to aquatic organisms but the bans on their use and their fate and behaviour suggest that water column concentrations are of low concern. This is reflected in low observed water column concentrations. EQSs in the water column exist for total DDT, pp-DDT, total ‘drins’, aldrin, dieldrin, endrin and isodrin. The standstill provision applies for these substances such that concentrations in sediments and/or shellfish and/or fish must not increase significantly with time (see Section 5.5 and Table B5.1).

The majority of the remaining environmental burden of these substances appears to be in the sediment and in marine organisms.

In Canada, interim marine sediment quality guidelines (ISQGs) have recently been set for dieldrin, endrin, DDT and its metabolites (see Section 5.5). ISQGs for these compounds are: 0.71 Fg kg^{-1} (dry weight) for dieldrin, 2.673 Fg kg^{-1} (dry weight) for endrin, 1.19 Fg kg^{-1} (dry weight) for DDT (sum of all isomers), 2.07 Fg kg^{-1} (dry weight) for DDE (sum of all isomers) and 1.22 Fg kg^{-1} (dry weight) for DDD (sum of all isomers). The ISQGs represent the lower end of the range of concentrations at which biological effects are occasionally observed on the native fauna of Canada. They represent only an indication of the concentrations that may occasionally cause effects in the UK.

Organochlorine pesticides (dieldrin, DDT and its compounds, aldrin) have been identified as endocrine disrupting substances (see Section 4.2.3). The presence of high concentrations of organochlorine pesticides (and PCBs (see Section B48)) or their residues in marine mammals have been suggested as the cause of (or contributing towards) pathological changes and reproductive failures in Baltic seals (Helle *et al* 1976) sealions, seals and beluga whales (Addison 1989); immunity suppression (and hence the possibility of being more susceptible to disease) in harbour porpoises (Kuiken *et al* 1994) and seals (Reijnders 1986; Swart *et al*, 1994); changes in the development stability of the Baltic grey seal (Zakharov and Yablokox 1990); and premature pupping in California sea lions (Delong *et al* 1973).

B17.5 Bioaccumulation

In general, organochlorine pesticides tend to be highly bioaccumulated by aquatic organisms (with different degrees of biomagnification reported).

B17.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxicity of organochlorine pesticides to aquatic life at concentrations above the appropriate EQS in the water column (see Table 5.1);

! accumulation in sediments and a potential hazard to sediment dwelling fauna at concentrations similar to those indicated by Canadian interim marine sediment quality guidelines (see Table 5.6);

! bioaccumulation in marine organisms and biomagnification in food chains posing a threat to fish, sea birds and Annex II sea mammals;

! endocrine disruption in fish, sea birds and Annex II sea mammals.

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B18. Lindane (gamma isomer of Hexachlorocyclohexane)

B18.1 Entry into the marine environment

Lindane is the gamma isomer of hexachlorocyclohexane and possesses the significant insecticidal activity. A number of studies (e.g. US EPA 1980, WHO 1991, CCME 1992) have reviewed the environmental fate and behaviour and aquatic toxicity of lindane to which the reader is referred for a more comprehensive assessment. An outline of the fate and behaviour, aquatic toxicity and bioaccumulative potential is presented below.

Direct and indirect application of lindane, agricultural run-off and industrial discharges are the principal sources of lindane in surface waters.

B18.2 Recorded levels in the marine environment

Data on concentrations of lindane reported in the marine environment are presented in Appendix D.

B18.3 Fate and behaviour in the marine environment

Lindane appears to be relatively stable in the water environment with some adsorption to sediment occurring (CCME 1992) . Abiotic degradation and volatilisation are not thought to be major removal processes. However, some biodegradation has been found to occur, with half-lives in the range of several days to a year reported in water and aquatic sediments

B18.4 Effects on the marine environment

B18.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of lindane to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (US EPA 1980, WHO 1991 and CCME 1992). The most sensitive groups of organisms have been identified.

Lindane can be considered to be highly toxic to both fish and aquatic invertebrates with acute effect concentrations generally occurring at concentrations > 1 µg l^{-1}. The EQS for all isomers of hexachlorocyclohexane, including lindane, is 0.02 µg l^{-1} (annual average) in the water column. The standstill provision applies such that concentrations in sediments and/or shellfish and/or fish must not increase significantly with time (see Section 5.5 and Table 5.1).

Lindane has also been identified as an endocrine disrupting substance in *in vivo* assessments (see Section 4.2.3).

Lindane accumulates and persists in sediments and can pose a hazard to sediment dwelling organisms at concentrations above 0.32 µg kg^{-1} according to Canadian interim marine sediment quality guidelines (see Section 5.5).

B18.5 Bioaccumulation

Lindane may be bioaccumulated in aquatic organisms (calculated log Kow of 3.72) and bioconcentration factors of 10^2 for aquatic invertebrates and fish have been reported. However, lindane appears to be rapidly eliminated once continuous exposure ceases and therefore biomagnification is not expected. For example, a half-life of less than 2 days was found for lindane depuration by bluegill sunfish (CCME 1992).

B18.6 Potential effects on interest features of European marine sites

Potential effects include:

- toxic effects to invertebrates and fish at concentrations of all isomers of hexachlorocyclohexane, including lindane above the EQS of 0.02 Fg l^{-1} (annual average) in the water column;

- accumulation and persistence in sediments and can pose a hazard to sediment dwelling organisms at concentrations greater than 0.32 Fg kg^{-1} according to Canadian interim marine sediment quality guidelines (see Section 5.5);

- identification as an endocrine disrupting substance which may affect fish, birds or Annex II sea mammals.

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B19. Endosulfan

B19.1 Entry into the marine environment

Endosulfan is a broad spectrum, non-systemic, contact and stomach acting insecticide and acaricide. It is sometimes seen as a replacement for other more persistent organochlorine insecticides (e.g. DDT, drins) but it is not widely used in agriculture.

The technical endosulfan product (typically 96% active ingredient (a.i.)) is a mixture of two isomers, known as a (or A or I) and b (or B or II), in the ratio of 70-80% a to 30-20% b.

In 1984, Dequinze *et al* (1984) estimated EC production capacity was 6,700 tonnes/year (t/y). World production was estimated at approximately 10,000 t/y (WHO 1984).

The main route of entry into the aquatic environment in the UK is from diffuse sources associated with its use as a pesticide, such as run-off from land and spray-drift.

B19.2 Recorded levels in the marine environment

A survey of 80 UK surface water sites involving 160 samples during the winter of 1988/89 (SAC 1989) revealed only two samples with positive, i.e. >10 ng/l, results for endosulfan: 11 ng l^{-1} on the River Torridge and 14 ng l^{-1} in the Forth estuary. In both samples, only a-endosulfan was detected. Both sites were sampled twice but only one positive result was obtained at each site.

Additional data on concentrations reported in the marine environment are presented in Appendix D.

B19.3 Fate and behaviour in the marine environment

Information summarised by Crane and Jones (1991) suggests that removal of endosulfan from the aqueous environment may occur by photolysis, hydrolysis, oxidation, volatilisation, biodegradation and sorption under certain conditions. However, the relative importance of the different processes is likely to be difficult to predict for a particular circumstance.

Sorption is an important fate for endosulfan in aquatic systems. Greve and Wit (1971) found that more than 75% of the endosulfan in the River Rhine was associated with particulate matter (mud or silt).

The degradation of endosulfan in marine microcosms was investigated by Cotham and Bidleman (1989). The results seemed to indicate virtually no degradation under the non-sterile conditions. Degradation in unsterilised sediment-water mixtures was also studied. Sediment was taken from a creek on the South Carolina coast where a number of fish kills had occurred. The half-lives of the two isomers were 22 days for the alpha and 8.3 days for the beta forms. The system was spiked by adding the pesticide to the overlying water and it was not until day 4 that the majority of the substance was found adsorbed in the sediment layer. The greater volatility of the a-isomer was demonstrated with most of the remaining a-endosulfan being found in the polyurethane plug used to seal the flasks by day 20 of the experiment. Endosulfan diol was the only metabolite identified in these studies.

B19.4 Effects on the marine environment

B19.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of endosulfan to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Crane and Jones 1991). The most sensitive groups of organisms have been identified.

Crane and Jones (1991) summarised information on the aquatic toxicity of endosulfan and the more significant data are presented below.

Algae

Thursby *et al* (1985) conducted experiments to determine the effects of technical endosulfan on the growth and reproduction of the marine red macroalga (seaweed) *Champia parvula*. Growth of female and tetrasporophyte structures was significantly reduced after 14 days exposure to 47 µg l^{-1} (lowest concentration tested) and 130 µg l^{-1}, respectively.

Invertebrates

For molluscs, effects of endosulfan at concentrations of less than 100 µg l^{-1} were only observed in the test on the inhibition of shell growth in the eastern oyster *Crassostrea virginica* reported by Butler (1964). However, this test was performed at 28 °C, which is above the recommended (US EPA 1982) temperature range for the species. At 19 °C, the EC50 for shell growth was six times larger at 380 µg l^{-1}. The effect was temporary with recovery periods in clean water of seven weeks at 19 °C and two weeks at 28 °C.

The toxicity of the a- and b-isomers of endosulfan to the common mussel *Mytilus edulis* was assessed by Roberts (1975) who measured the effects of the chemicals on the development of the byssal threads used by bivalves to anchor themselves. The b-isomer was found to be more toxic than the a-isomer with reductions in byssal thread attachment after 48 hours exposure to 200 µg l^{-1} of 85% for b and 35% for a-. In experiments with an emulsifiable formulation of endosulfan, the toxicity was greater for smaller mussels and at higher temperatures.

Short-term LC50s for a variety of species of shrimp vary between 0.04 and 17 µg l^{-1}.

The lowest 96-hour LC50 for a crustacean species is 0.04 µg l^{-1} for *Pennies duorarum* (Schimmel *et al* 1977). *Crangon septemspinosa* had an LC50 value of 0.2 µg l^{-1} (McLeese and Metcalfe 1980), whereas the LC50s for all other crustaceans were greater than 0.4 µg l^{-1}. The lowest fish LC50s were 0.09 µg l^{-1} for *Leistomus xanthurus* (Schimmel *et al* 1977) and 0.1 µg l^{-1} for *Morone saxatilis* (Korn and Earnest 1974). The chronic values for the shrimp *Mysidopsis bahia* and the sheepshead minnow *Cyprinodon variegatus* are higher than the acute LC50s cited above.

B19.4.2 Sediment-dwelling animals

The results of a six-laboratory ring-test on the toxicity of technical endosulfan to the polychaete worm *Neanthes arenaceodentata* were reported by Pesch and Hoffman (1983). The worms were exposed in flow-through systems and sand was provided as a sediment in which they could burrow. After exposure for 96 hours, 10 days and 28 days LC50 values were 195 µg l^{-1}, 158 µg l^{-1} and 106 µg l^{-1}, respectively. Values for EC50s, based on the numbers of test animals which did not burrow, were almost identical to the corresponding LC50s.

In another experiment with a polychaete worm, McLeese *et al* (1982) investigated the toxicity of endosulfan to the ragworm *Nereis virens* with and without sediment in the test vessel. The preparation of the test solutions and dosed sediments was unusual in that solutions of the toxicant in a volatile solvent were evaporated in the test vessels before water or water and sediment were added. The exposure regime was semi-static, with aqueous test solutions being changed every 48 hours and sediment-water mixtures every 96 hours. The sediment, consisting of silt and clay (83%) and sand (17%), was 30 mm deep and covered with 15 mm of water. The 12-day LC50 values for worms exposed to seawater only and to seawater in the presence of sediment were 100 µg l^{-1}. Stressed worms in the test with sediment emerged from the sediment and subsequently did not burrow, even after the sediment was changed. The LC50 in the sediment-water experiment expressed in terms of the concentration of endosulfan in the sediment was 340 µg kg^{-1}.

B19.5 Bioaccumulation

The bioaccumulation of endosulfan has also been summarised in Crane and Jones (1991).

A maximum BCF of 22.5 was reported for mussels exposed to 100 µg l^{-1} endosulfan for 70 days; the BCF decreased to 17 after 112 days (Roberts 1972). Exposure to concentrations of 500 and 1,000 µg l^{-1} resulted in greater tissue levels but bioaccumulation factors (BCFs) of only 11 and 8.1 after 112 days. Ernst (1977) also tested mussels but used a-endosulfan in a mixture of pesticides and worked at much lower concentrations. Ernst reported a BCF of 600 for mussels at 10 °C in water initially containing 2.05 µg l^{-1} a-endosulfan. The BCF was calculated using the steady-state water concentration of 0.14 µg l^{-1} and tissue concentration of 84 µg kg^{-1} wet weight obtained within 50 hours. The paper reports a half-life of 34 hours for a-endosulfan in mussels based on a one-compartment model. However, on considering the data presented, it appeared that more than 50% of the accumulated pesticide is lost after only 9 hours in clean water.

Haya and Burridge (1988) exposed the polychaete worm *Nereis virens* to solutions of endosulfan in aquaria containing seawater and sediments. The worms were exposed to concentrations of 60 µg l^{-1} under hypoxic (12% saturated) and normoxic (presumably close to air-saturation) conditions at 7 °C for four days, with the test solutions being renewed after two days. After four days, the animals were transferred to clean water for the depuration phase. Uptake of endosulfan appeared to be linear under both hypoxic and normoxic conditions, although the bioaccumulation rate was nearly three times faster in the oxygen-deficient conditions. The maximum concentrations in the worms under hypoxic and normoxic conditions were about 4.4 and 1.7 mg/g lipid, respectively, and were recorded at the end of the exposure period and in neither case was equilibrium reached. The half-life for elimination of the endosulfan was approximately 60 hours.

During their investigation of the toxicity of endosulfan to two species of shrimp and three species of fish, Schimmel *et al* (1977) investigated the uptake of endosulfan by the test animals. In all cases where measurable (10 µg/kg wet tissue) residues were found after exposure for 96 hours to a technical mixture of a- and b-endosulfan, the predominant form in the tissue was endosulfan sulphate. The pink shrimp, although extremely sensitive to the acute toxic effects of endosulfan, does not appear to accumulate the chemical. Even when exposed to the highest test concentration of 0.089 µg l^{-1}, no residue was detected in the shrimp tissues. Bioaccumulation factors of 81 to

245 were calculated for the grass shrimp based on measured concentrations of 0.16 to 1.75 µg l^{-1}. The highest concentration in this test gave 65% mortality and residues of endosulfan of 78, 42 and 360 µg/kg (a, b and sulphate respectively). BCFs reported for pinfish *Lagodon rhomboides*, spot and striped mullet *Mugil cephalus* after exposure for 96 hours reached 1,299, 895 and 1,344, respectively.

In the same paper, the authors also reported that, during the course of a 28-day experiment, juvenile striped mullet exposed to an endosulfan concentration of 0.035 µg l^{-1} reached a BCF of 1,000 after 96 hours and 2,755 after 28 days with tissue concentrations still increasing at the end of the test. The concentration of endosulfan sulphate in the fish was, at 80 µg/kg, nearly five times greater than that of b-endosulfan (17 µg/kg), whereas a-endosulfan was below the detection limit (10 µg/kg). The endosulfan was totally eliminated after only 48 hours in clean water. At the nominal concentration of 0.008 µg l^{-1} in the water (which could not be measured accurately) no residues were detectable in the fish.

B19.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxic effects to algae and invertebrates (particularly crustaceans) at concentrations above the EQS of 0.003 Fg l^{-1} in the water column;

! sediment-dwelling organisms, especially crustaceans, may be at risk because the ultimate fate of endosulfan, its metabolites and degradation products is not known;

! identification as an endocrine disrupting substance.

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B20. Synthetic pyrethroids

B20.1 Entry into the marine environment

Synthetic pyrethroids are a group of chemicals which act as neuropoisons, acting on the axons in the peripheral and central nervous systems. They are believed to interfere with sodium channels and the permeability of nerve cells so affecting the transmission of nerve impulses. Various pyrethroids are commonly used as insecticides in a variety of applications.

Some examples of pyrethroids commercially available include allethrin, resmethrin, d-phenothrin and tetramethrin (for insects of public health importance); cypermethrin. deltamethrin, fenvalerate, cyhalothrin, cyfluthrin, lambda-cyhalothrin and permethrin (mainly for agricultural insect pests). Cypermethrin is used in cage fish farming for sea lice treatments and in sheep dip. Thus entry into the aquatic environment may be through diffuse or point sources.

B20.2 Recorded levels in the marine environment

Synthetic pyrethroids are not routinely monitored for in the UK marine environment (see Appendix D).

B20.3 Fate and behaviour in the marine environment

The pyrethroids tend to be of low solubility and adsorb readily to suspended solids and sediments. Once adsorbed, they are thought to be less bioavailable. However, at present no methods are available to analyse or assess the bioavailable fraction of the pyrethroids present.

Pyrethroids are generally rapidly removed from the water column (via degradation and sorption) with half-lives of a few days. The half-lives of pyrethroids adsorbed to suspended solids and sediments tends to be considerably longer, i.e. several months.

B20.4 Effects on the marine environment

B20.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of synthetic pyrethroids to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Zabel *et al* 1988, WHO 1989). The most sensitive groups of organisms have been identified.

Both aquatic invertebrates (especially insects and crustaceans) and fish have been found to be highly sensitive to these chemicals. In addition, based on their mode of action, effects on aquatic mammals from certain pyrethroids could be expected. However, data on such effects do not appear to be available.

As pyrethroids adsorb readily on sediments, there is a need for sediment standards. There are some concerns over bioavailability and the effects on benthic and sediment dwelling organisms. This is an area where investigations are on-going and the results so far are uncertain.

Of the pyrethroids available for use in the UK, only two (permethrin and cyfluthrin) currently have statutory EQSs for the protection of aquatic life, although standards for a few other pyrethroids (e.g. cypermethrin) are under development.

Zabel *et al* (1988) reviewed data on the toxicity of permethrin and cyfluthrin to marine organisms and a summary of these conclusions is presented below. In addition, cypermethrin is a pyrethroid which is being increasingly used (such as in formulations for use against ecotoparasites on sheep and for sea lice treatments in cage fish farming). Further information on this is also presented below.

B20.4.1.1 Permethrin

Invertebrates were found to be more sensitive to permethrin than fish. The lowest reported LC50 value was 0.02 Fg l^{-1} for newly-hatched estuarine mysids (as the test result concentrations were not analysed there was some uncertainty about these). The LC50s for *Crangon septemspinosa* and *Pennies duorarum* of 0.13 Fg l^{-1} and 0.22 Fg l^{-1}, respectively, were based on measured concentrations in the water.

B20.4.1.2 Cyfluthrin

Available data on the toxicity to aquatic organisms was limited to two species of fresh water invertebrates and three species of freshwater fish. Invertebrates were the more sensitive organisms. Acute LC/EC50 values of >=5 ng l^{-1} were found for freshwater organisms. No data were available on the toxicity of cyfluthrin to saltwater organisms.

B20.4.1.3 Cypermethrin

Available data on the toxicity of cypermethrin to saltwater organisms indicate that acute LC50s for crustaceans and fish range, in general, from 0.05 µg l^{-1} upwards (WHO 1989), although an LC50 as low as 0.005 µg l^{-1} was reported for the mysid shrimp *Mysidopsis bahia* (Hill 1985). In addition, the LC50 for the lobster *Homarus americanus* could be as low as 0.003 µg l^{-1}, based on a geometric mean of available toxicity data (McLeese *et al* 1980).

SEPA Policy No. 30 provides EQSs for cypermethrin on its use in cage fish farming (see Section B26). The SEPA Fish Farming Manual describes the application of these EQSs.

B20.5 Bioaccumulation

The log Kows of these chemicals suggest that bioaccumulation should be high. However, while there appears to be uptake of some of these chemicals as a result of rapid metabolism, bioaccumulation does not appear to be a problem (WHO 1989).

B20.6 Potential effects on the interest features of European marine sites

Potential effects include:

! acute toxic effects on invertebrates, in particular crustaceans, and fish at concentrations above EQS values of 0.001 Fg l^{-1} for cyfluthrin and 0.01 Fg l^{-1} for permethrin in the water column. An EQS for cypermethrin in under development (see Section B26);

- accumulation in sediments where concerns exist about the effects of sediment dwelling organisms;
- identification of permethrin as an endocrine disrupting substance.

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B21. Organophosphate pesticides

Organophosphates are a group of chemicals which act by inhibiting the enzyme acetylcholinesterase (AChE) in the nervous system. Organophosphorus pesticides are effective insecticides and are widely used in the UK. However, they can have a harmful effect on non-target organisms by inhibiting AChE activity. Toxic effects of AChE inhibition vary with the degree of exposure and the type and concentration of organophosphate pesticide. Sub-lethal effects are poorly understood, but have shown changes in behaviour, reproduction, ability to cope with food and environmental stress, leading to paralysis, convulsions and ultimately death.

The solubility, sorption, potential to bioaccumulate and extent of toxicity to aquatic life tend to vary according to the organophosphate. In addition, based on their mode of action, effects on aquatic mammals could be expected. However, data on such effects do not appear to be available.

Azinphos-methyl, malathion, fenitrothion and dimethoate have been identified as of potential concern in the marine environment. Profiles of these organophosphates are presented in Sections B22, B23, B24 and B25 respectively.

Azamethiphos is an organophosphate pesticide used for the treatment of sea lice in cage fish farming. The control of this substance in this application is detailed in SEPA's Fish Farming Manual which includes operational EQSs for azamethiphos (SEPA Policy No. 17). The reader is referred to the Fish Farm Manual for further information on this substance.

B22. Azinphos-methyl

B22.1 Entry into the marine environment

Azinphos-methyl is a broad spectrum, non-systemic, organophosphorus insecticide and acaricide with contact and stomach action. It is an inhibitor of acetylcholinesterase (AChE). It is used for the control of chewing and sucking insects in agriculture and forestry.

Entry into the aquatic environment arise from accidental spillages during transport, storage, use or bad practice. Diffuse pollution sources include spray-drift during application, agricultural run-off from treated land and the waste disposal of azinphos-methyl products.

B22.2 Recorded levels in the marine environment

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. One water column concentration was found to exceed the EQS value (see Appendix D) in the NRA survey. However, no details on the actual concentration or the reason for exceedence are available. Monitoring data were not available for sediments or biota.

The available data suggest that concentrations of in UK coastal and estuarine waters are generally unlikely to exceed relevant quality standards derived for the protection of saltwater life.

B22.3 Fate and behaviour in the marine environment

The fate and behaviour of azinphos-methyl was reviewed by Jones *et al* (1996). Azinphos-methyl is only sparingly soluble in water (14 mg l^{-1} at 15 °C) and the octanol/water partition coefficient is moderate (log Kow = 2.99 to 3.77). Based on the soil organic carbon sorption coefficient (log Koc = 3.56), sorption on suspended solids and aquatic sediments is likely.

Meyer (1965) applied azinphos-methyl WP directly to a farm pond containing algal, plant and fish life and calculated a half-life of approximately 2 days.

Flint *et al* (1970, cited in US EPA 1986) determined the half-life of Guthion (a formulation containing azinphos-methyl) at 30 °C in illuminated pond water and in phosphate buffer protected from light in the laboratory. The half-life in pond water was 1.2 days (pH 6.9), whereas that in the buffer solution (pH 7) was 10 days. The more rapid degradation in pond water was attributed to the effect of sunlight and micro-organisms.

B22.4 Effects on the marine environment

B22.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of azinphos-methyl to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Jones *et al* 1996). The most sensitive groups of organisms have been identified.

The toxicity of azinphos-methyl to aquatic organisms was reviewed by Jones *et al* (1996). Few data were available for marine organisms.

Invertebrates

Jones *et al* (1996) concluded that crustaceans were the most sensitive group of saltwater species. For the European species pink shrimp *Pandalus montagui* and brown shrimp *Crangon crangon* 48-hour LC50 values between 0.3 and 1 µg l^{-1} have been reported, whereas the cockle *Cerastoderma edule* was the least sensitive species tested, with a 48-hour LC50 greater than 10 mg l^{-1} (Portmann and Wilson 1971).

Fish

A number of acute LC50 values were reported for fish species. For the threespined stickleback *Gasterosteus aculeatus*, a 96-hour LC50 of 12.1 µg l^{-1} was obtained in slightly saline water (5 ppt) and of 4.8 µg l^{-1} in water with a salinity of 25 ppt (Katz 1961). Similar LC50s of 8 µg l^{-1} (96-hour; Lahav and Sarig 1969, cited in US EPA 1986) and 3.2 µg l^{-1} (48-hour; Mayer 1987) have been reported for the striped mullet *Mugil cephalus*. The 24-hour LC50 for the white mullet *Mugil curema* was found to be 5.5 µg l^{-1} (Butler 1963, cited in US EPA 1986).

Inhibition of acetylcholinesterase (AChE) activity and mortality caused by exposure to azinphos-methyl was investigated by Coppage (1972) in a static test in 4 ppt salinity using the sheepshead minnow *Cyprinodon variegatus* as test species. After 48 hours exposure greater than 80%, AChE inhibition and 40 to 60% mortality were observed at 3.5 µg l^{-1}. After 120 hours exposure to 2 µg l^{-1} 78%, AChE inhibition was observed but there were no mortalities.

In a partial life-cycle toxicity test on the sheepshead minnow *Cyprinodon variegatus* (Cripe *et al* 1984), significant reductions in egg numbers from spawning adults were observed at 0.42 µg l^{-1}.
No data could be located for sediment-dwelling organisms.

B22.5 Bioaccumulation

Jones *et al* (1996) found no reliable data to quantify the bioaccumulation potential of azinphos-methyl but, based on the octanol/water partition coefficient (Log Kow 2.99-3.77), the authors concluded that it is only likely to be moderate.

B22.6 Potential effects on interest features of European marine sites

Potential effects include:

! acute toxicity to invertebrates, in particular crustacea, and fish at concentrations above the EQS of 0.01 Fg l^{-1} (annual average) and 0.04 Fg l^{-1} (maximum allowable concentration);

! accumulation in sediments and potential effects on sediment dwelling organisms, although no data were available;

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B23. Malathion

B23.1 Entry into the marine environment

Malathion is a contact- and stomach-acting organophosphorus pesticide which inhibits acetylcholinesterase (AChE) activity, thus disrupting the nervous system and making it toxic to all innervated animals. In higher vertebrates, it is readily hydrolysed to inactive derivatives. Malathion's broad-spectrum action has led to widespread use against insect and other invertebrate pests. In Europe, most malathion is used in agriculture, principally against mite and insect pests of oilseed rape, root crops, vegetables and fruits. Other uses include domestic, horticultural and glasshouse pest control (mostly against aphids), and application against ectoparasites of humans and animals.

Malathion may enter the aquatic environment, either directly in industrial effluents, or indirectly in run-off from land or by deposition from the atmosphere (following spray drift or in precipitation).

B23.2 Recorded levels in the marine environment

80 river and estuary sites were sampled twice for malathion over the winter of 1988-89 (SAC Scientific 1989 cited in Hedgecott (1991)). At 11 sites, malathion was detected once, with a mean concentration of 1.5 ng l^{-1} (range 1.0 to 3.0 ng l^{-1}). At a 12th, malathion concentrations of 5.1 and 7.8 ng l^{-1} were recorded. At all other sites, malathion was below the detection limit of 1 ng l^{-1} (there is no further information as to whether malathion was detected at any of the estuary sites).

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. No water column concentration was found to exceed the EQS value (see Appendix D). Monitoring data were not available for sediments or biota.

The data suggest that concentrations of malathion in UK coastal and estuarine water do not exceed relevant quality standards derived for the protection of saltwater life.

B23.3 Fate and behaviour in the marine environment

The available data indicate that biodegradation is an important removal process for malathion in the aquatic environment, with various species of bacteria and fungi able to utilise it as a source of either carbon or phosphorus. Paris *et al* (1975a, 1975b) estimated half-lives for degradation by freshwater bacteria of 28 and 41 hours (initial concentrations approximately 1.5 and 1.1 mg l^{-1}). Efficient biodegradation has also been observed in saline waters (Bourquin 1977). The Marine Biological Association (MBA) (1979) report biodegradation rates for estuarine and saltwater micro-organisms corresponding to half-lives of 0.5 to 9 days and 3 to 12 days or more, respectively.

Malathion has a low vapour pressure and does not readily volatilise. Sorption to suspended solids and sediments will account for some removal from water. The major abiotic removal process in water is hydrolysis. The MBA (MBA 1979) provides estimates of half-lives in sea water, ranging from 7 to 40 days at 10 °C, and from 2 to 9 days in sterile sea water at 25 °C.

B23.4 Effects on the marine environment

B23.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of malathion to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Hedgecott 1991). The most sensitive groups of organisms have been identified.

Invertebrates

The most sensitive saltwater organisms tested are certain crustaceans, with lowest acute LC50s or EC50s of 0.4 to 3.1 µg l^{-1} for Dungeness crabs *Cancer magister* and mysid shrimps *Mysidopsis bahia* (Caldwell 1977, Goodman *et al* 1988), and retarded development of Dungeness crab eggs and larvae at 0.3 µg l^{-1} (reported by MBA 1979). Hedgecott (1991) concluded that early life stages of crustaceans may be more sensitive than adult stages.

Fish

Fish species appear to be less sensitive with a maximum acceptable concentration of 6 µg l^{-1} reported for a full life cycle test with sheepshead minnows *Cyprinodon variegatus* (reported by Suter and Rosen 1988). An acute LC50 of 300 µg l^{-1} has been reported by the MBA (1979) for adult sheepshead minnows.

B23.5 Bioaccumulation

Hedgecott (1991) found no bioaccumulation data for saltwater species, but concluded it would not expected to differ greatly from that found for freshwater organisms (i.e. low).

B23.6 Potential effects on interest features of European marine sites

Potential effects include:

! acute toxicity to invertebrate (particularly crustacea) and fish to concentrations above the EQS of 0.02 Fg l^{-1} (annual average) and 0.5 Fg l^{-1} (maximum allowable concentration) in the water column.

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B24. Fenitrothion

B24.1 Entry into the aquatic environment

Fenitrothion is a contact-acting organophosphorus pesticide which inhibits acetylcholinesterase (AChE) activity, thus disrupting the nervous system. In view of its broad-spectrum action, it is widely used against insect pests. Most fenitrothion applied in Europe is used in agriculture, but is also used in conjunction with pyrethroids to protect stored grain against insect damage, and in a number of domestic ant and fly killers.

Most input of fenitrothion into estuarine and marine waters is likely to be associated with river outflows.

B24.2 Recorded levels in the marine environment

Hedgecott (1996) reported limited information on the concentration of fenitrothion in marine waters. In a survey of 80 UK rivers and estuaries conducted in the winter of 1988-89, fenitrothion was below the detection limit of 10 ng l^{-1} in all samples (SAC Scientific 1989).

The few data reported for aquatic (freshwater) sediments indicate low levels of adsorbed fenitrothion.

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. No water column concentration was found to exceed the EQS value (see Appendix D). Monitoring data were not available for sediments or biota.

The available data suggest that concentrations of fenitrothion in UK coastal and estuarine water do not exceed relevant quality standards derived for the protection of saltwater life.

B24.3 Fate and behaviour in the marine environment

Hedgecott (1996) reviewed the fate and behaviour of fenitrothion. It is not particularly soluble, and combined with a log octanol-water partition coefficient (Kow) of 3.38, suggests a moderate tendency to associate with solids and organic matter. The low vapour pressure indicates a low tendency to volatilise.

Fenitrothion is readily degraded by micro-organisms found in sludge, soil and water via dealkylation, hydrolysis, oxidation and reduction. The main abiotic removal process acting on dissolved fenitrothion is photolysis, with carboxy fenitrothion as the main product. Weinberger *et al* (1982b) noted that fenitrothion dissolved in either fresh or estuarine water was reduced by 80% (from 2.5 to 0.5 mg l^{-1}) within six hours when exposed to natural sunlight in static laboratory systems. Degradation was more efficient in the estuarine water. In flowing systems, degradation was slower, possibly as a result of increased turbidity.

Caunter and Weinberger (1988) determined a half-life of about 31 hours for fenitrothion in the light in the laboratory, with photodegradation apparently being the major removal process. In the presence of algae, under similar conditions, the half-life was only about 16 hours. Sorption to the algae, and possibly also enhanced photodegradation following sorption, were responsible for this higher rate of loss.

Sorption to aquatic sediments (and soils) is directly related to their organic content and so varies between sites. Weinberger *et al* (1982a) considered sediments to be a major sink for fenitrothion in lake microcosms in both the laboratory and the field.

B24.4 Effects on the marine environment

B24.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of fenitrothion to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Hedgecott 1996). The most sensitive groups of organisms have been identified.

Invertebrates

Persoone *et al* (1985) concluded that saltwater and freshwater crustaceans had similar sensitivities to fenitrothion, although this conclusion was based on limited data. Data suggesting similar sensitivities of fish were somewhat more extensive. There are too few recent data to assess the validity of these conclusions. However, Hedgecott (1996) concluded that data from laboratory studies indicated that certain species of arthropods were more sensitive to fenitrothion than any other tested freshwater organisms.

For the tiger shrimp *Pennies japonicus* Kobayashi *et al* (1985) obtained 50% survival times of approximately 24 hours at 1 µg l^{-1} and 10 hours at 2 µg l^{-1}. Mayer (1987) reported an EC50 of 1.5 µg l^{-1} for mobility of brown shrimps *Pennies aztecus*. For molluscs, Mayer (1987) reported a 96 hour EC50 of 450 µg l^{-1} for shell deposition in juvenile oysters *Crassostrea virginica*.

Fish

Takimoto *et al* (1987) estimated 96 hour LC50s of 2.1 mg l^{-1} and 2.6 mg l^{-1} for adult killifish *Oryzias latipes* and mullet *Mugil cephalus* respectively when acclimated to and exposed in water of 23 ppt salinity. Equivalent LC50s in freshwater were similar, at 3.5 and 2.6 mg l^{-1} respectively.

B24.5 Bioaccumulation

Hedgecott *et al* (196) observed low to moderate bioaccumulation in marine organisms.

The data on bioaccumulation of fenitrothion by marine organisms suggest similar levels as those in freshwater organisms, with BCFs of 179 and 303 for fish and 139 for the tiger shrimp (Takimoto *et al* 1987, Kobayashi *et al* 1985). Although the shrimp BCF is higher than the figures for similar freshwater invertebrates, the difference is not large. McLeese *et al* (1979) noted that uptake rates by soft-shelled clams *Mya arenaria* and mussels *Mytilus edulis* were quite low and excretion rates quite high. The authors suggested that water concentrations below 0.01 mg l^{-1} were unlikely to result in significant contamination of tissues of these organisms.

B24.6 Potential effects on interest features of European marine sites

Potential effects include:

- acute toxicity to invertebrates and fish at concentrations above the EQS of 0.01 Fg l^{-1} (annual average) and 0.25 Fg l^{-1} (maximum allowable concentration) in the water column.

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B25. Dimethoate

B25.1 Entry into the marine environment

Dimethoate is extensively used as contact and systemic organophosphate insecticides on a wide range of crops.

Point sources for the contamination of surface waters is from the accidental spillage at manufacture sites, formulation and storage, and during transport and handling. Farms are another potential point source by either discharging directly into water courses or indirectly through the sewer network, or in surface run-off. Diffuse sources include run-off and leaching from agricultural land after pesticide application, spray drift during application and discharge of wastes from the domestic sector (either direct or via the sewer system) (Seager 1987).

However, the input of dimethoate to the marine environment is likely to be associated primarily with river outflow.

B25.2 Recorded levels in the marine environment

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D.

B25.3 Fate and behaviour in the marine environment

Dimethoate is soluble in water, and will not be expected to sorb onto sediment or bioconcentrate in aquatic organisms. Degradation of dimethoate is dependent on environmental conditions, such as temperature and pH. Heavy metal ions have been found to act as catalysts in the hydrolysis of dimethoate (Murgatroyd and Patel 1996).

Aqueous solutions of dimethoate are thought to be relatively stable. A half-life of 56 days (20 °C; pH 7.3-8.0) has been reported for the biological and chemical degradation of dimethoate in a natural river system (Eichelberger and Lichtenberg 1971). Degradation through hydrolysis may be significant, especially in alkaline waters; half-lives for hydrolysis of 3.7 and 118 days at pH 9 and 7 have been reported (Howard 1991). However, direct photolysis and evaporation of dimethoate from water are not expected to be important processes. A half-life of 8 weeks for biodegradation has been quoted (Howard 1991). However, this may be partially due to hydrolysis and oxidation.

B25.4 Effects on the marine environment

B25.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of dimethoate to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Murgatroyd and Patel 1996). The most sensitive groups of organisms have been identified.

Algae

There is some evidence that marine autotrophs are particularly sensitive to dimethoate exposure. Ramachandran *et al* (1984) noted significant reductions in respiration and photosynthesis in five out of six species of `seaweeds' exposed to nominal concentrations of 50 µg l^{-1} dimethoate. Similar effects were found with the diatomic alga *Concinodiscus‑concinnus*, with a nominal EC50 of 40 µg l^{-1} for growth and disruption of cell morphology at 50 µg l^{-1} (Ramachandran *et al.* 1980). However, these values are much lower than those reported for algae by Ibrahim (1983 and 1984), with EC50s for growth ranging from 4.5 to 13 mg l^{-1}.

Invertebrates

The data for marine animals vary widely, particularly for crustaceans. Portmann and Wilson (1971) reported a 48 hour LC50 between 0.3 and 1 µg l^{-1} for the common shrimp *Crangon crangon*, but LC50s for two other crustaceans were both above the highest test concentrations of 33 µg l^{-1} and 3.3 mg l^{-1} respectively. In other tests, 1 mg l^{-1} dimethoate caused 20% and 0% mortality in brown shrimps *Pennies aztecus* (Butler 1964) and prawns *Pennies monodon* (Vogt 1987) respectively. Crustaceans are probably the most sensitive organisms, but more studies are needed to confirm this assertion and to provide a more reliable set of data.

Fish

The same concentration of 1 mg l^{-1} had no effect on longnose killifish *Fundulus similis* (Butler 1964), whereas for the fish *Therapon jarbua*, a 96 hour LC50 of 0.7 mg l^{-1} was reported (Lingaraja and Venugopalan 1978).

B25.5 Bioaccumulation

Experimental evidence for bioaccumulation of dimethoate in aquatic organisms is limited to a very few tests, with no data for saltwater species. For the freshwater ciliate protozoan *Tetrahymena pyriformis* Bhatnagar *et al.* (1988) obtained a bioconcentration factor (BCF) of 3,547 based on dry weight following exposure for 12 hours to 1 mg l^{-1} dimethoate. An equivalent wet weight bioconcentration factor is likely to be between one and two orders of magnitude lower. Kumar *et al.* (1988) found that the freshwater blue-greens *Anabaena* sp. and *Aulosira fertilissima* attained maximum bioconcentration factors based on dry weight of only 71 and 120 respectively when exposed to 1 to 10 mg l^{-1} dimethoate over five days, indicating much lower accumulation than in *Tetrahymena*. The nature of chemical accumulation in unicellular organisms means that bioaccumulation tends to be much greater than in higher organisms, suggesting that bioaccumulation factors in higher organisms are likely to be lower than those indicated here.

Dimethoate has a high water solubility (25 g l^{-1} at 21 °C), and a relatively low octanol-water partition coefficient (log Kow 2.71), both of which suggest that the substance will have a low tendency to accumulate in biotic tissues.

B25.6 Potential effects on interest features of European marine sites

Potential effects include:

! acute toxicity to algae, invertebrates (particularly crustacea) and fish at concentrations above the EQS of 1 Fg l^{-1} (annual average) in the water column.

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B26. Chemicals used in fish farms

Chemicals used in marine fish farms can be broadly divided into two categories:

- hygiene products for disinfection or for environmental control, e.g. antifouling agents for fish cages, and

- medicinal products, divided into chemotherapeutic agents for therapy or prophylaxis of disease which act on the invading organisms, and pharmacological drugs which act on the target animal.

Inevitably when such therapeutants are applied to farmed stocks, a significant proportion will not reach the target species but will enter the environment. Route of entry and potential concentrations will depend on the volumes used and method of application. For example chemicals could enter the marine environment through faeces, uneaten food, or from bath treatments. Greater volumes can be expected for chemicals used in bath treatments, compared to chemicals applied through food.

Sea lice treatments are necessarily toxic medicines which are applied, either as bath treatments or as in-feed treatments. The fate and effects of these chemicals in the environment depend upon their physical and chemicals properties. They may persist in the water column and affect plankton and/or affect the seabed and its benthic fauna.

A Nature Conservancy Council report in 1989 (NCC 1989) identified impacts in the environment from mariculture. This included a consideration of chemical pollution from aquaculture; feed additives, pharmaceuticals and other treatments, e.g. antibiotics, immersion and antifoulant treatments to equipment. The reader is referred to this review for background information. SEPA has recently published a document entitled *Regulation and monitoring of marine cage fish farming in Scotland - A procedures manual* (SEPA Fish Farming Manual) which details the procedures SEPA will follow in the control of fish farm chemicals and includes EQSs in the water column and the sediments. **This document is freely available and should be used as a companion to this manual when considering the impact of fish farm chemicals on European marine sites.**

Table B26.1 lists the main chemicals used in marine cage fish farming and indicates where standards exist and where further information can be found.

Hydrogen peroxide is administered as a bath treatment for the removal of sea lice by enclosing the cage in a tarpaulin. It is the recommended treatment for the removal of sea lice by SEPA. The Environment Agency is investigating its effects on aquatic organisms.

Dichlorvos is also administered as a bath treatment and EQSs have been proposed (see Section B28) for the water column in the form of annual averages and maximum allowable concentrations.

Table B26.1 Main chemicals used in cage fish farming

Use/chemical	Water quality standards	Sediment quality standards	Reference
Sea lice treatment			
Hydrogen peroxide	No	No	
Dichlorvos	Yes	No	Jones and Stewart (1991) (see Section B28)
Azamethiphos	Yes	No	Lewis *et al* (1998) SEPA Policy No. 17
Cypermethrin	Yes	No	SEPA Policy No. 30
Teflubenzuron	Yes	Yes	SEPA Policy No. 29
Ivermectin	Yes	No	Codling *et al* (1998) SEPA Policy No. 2 (see Section B27)
Antimicrobials/ disinfectants			
Oxolinic acid	Yes	No	Murgatroyd *et al* (1994)
Oxytetracycline	Yes	No	Gendebien *et al* 1994
Malachite green	Yes	No	Burchmore and Wilkinson (1993)
Formaldehyde	Yes	No	Jerman and Wilkinson (1993)

Azamethiphos is an organophosphate (see Section B21 for general information on organophosphate pesticides) that has recently been granted market authorisation by SEPA for use as a bath treatment for the removal of sea lice. EQSs have been proposed by Lewis *et al* (1998) for the protection of saltwater life in the form of annual averages and maximum allowable concentrations (these are non-statutory). SEPA Policy No. 17 contains short term (3 to 72 hours) EQSs in the form of maximum allowable concentrations. The SEPA Fish Farming Manual explains the application of these EQSs.

Cypermethrin is a synthetic pyrethroid (see Section B20 for general information on synthetic pyrethroid pesticides) that has recently been granted market authorisation by SEPA as a bath treatment for the removal of sea lice. The Environment Agency is currently investigating the effects of cypermethrin on aquatic organisms with a view to deriving EQSs. SEPA Policy No. 30 contains EQSs in the form of short-term maximum allowable concentrations and an annual average. The SEPA Fish Farming Manual explains the application of these EQSs.

Teflubenzuron is the active ingredient of Calcide which is a new in-feed sea lice treatment which has recently been granted limited market authorisation by SEPA. SEPA Policy No. 29 contains EQSs for this chemical in the water column in the form of a short-term (3 hour) maximum allowable concentration and in the sediment in the form of a maximum allowable concentration in surface sediment outside an allowable impact zone and as an average for surface sediment within the zone of impact. The SEPA Fish Farming Manual explains the application of these EQSs.

Ivermectin is an in-feed sea lice treatment and EQSs have been proposed in the water column (see Section B27) in the form of annual averages and maximum allowable concentrations (these are non-statutory). SEPA Policy No. 2 deals with the application of ivermectin in fish farming and the SEPA Fish Farm Manual explains the application of the existing standards.

Antimicrobials are used as treatments for diseases. These chemicals can be persistent in seabed sediments and reduce metabolic processes of micro-organisms. Problems caused by a bacterial infection, furunculosis, in the 1980s required the use of substantial quantities of antibiotics which had the potential of causing environmental harm. Reviews, and (where possible) EQSs (although these are not statutory) have been proposed for the protection of saltwater organisms for a number of chemicals used as antimicrobials or disinfectants, namely oxolinic acid, oxytetracycline, malachite green and formaldehyde (Murgatroyd *et al* 1994; Gendebien *et al* 1994; Burchmore and Wilkinson 1993; Jerman and Wilkinson 1993). The reader is referred to these studies for further information on the effects of saltwater organisms. However, SEPA has suggested that the industry is no longer dependent on chemical treatments following the introduction of vaccination.

Antifoulant paints (see Sections B30 and B32) which contain toxic chemicals for preventing growth of marine plants and animals are used on fish cage structures and nets. These chemicals will gradually be released to the marine environment. The move to deploy bigger net enclosures is viewed with concern as this involves the use of increased chemical antifoulant coating as the nets are larger and it becomes uneconomical to change them regularly. The washing of antifoulant coated nets also causes concern as the spent washings have been found to contain unacceptably high concentrations of copper (see Section B7) and zinc (see Section B6).

Micro-nutrients (e.g. zinc (see Section B6)) are added to fish feeds. There are indications of elevated levels in sediments below cages which require further investigation. Anaesthetics and disinfectants are also used, but, according to SEPA, these are not currently perceived to pose a significant environmental risk.

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B27. Ivermectin

B27.1 Entry into the marine environment

Ivermectin is used in the UK in veterinary products for the control of parasitic infestations of insects, nematodes and mites in livestock. However, its use to control sea lice infestations has recently been investigated

Ivermectin is a xenobiotic compound and would therefore not be found naturally in the environment.

B27.2 Recorded levels in the marine environment

Codling *et al* (1998) approached the appropriate regulatory authorities (Environment Agency in England and Wales, and the Scottish Environment Protection Agency (SEPA) in Scotland) for data on the concentrations of ivermectin in the environment.

Concentrations of ivermectin in sediments have been measured by the Scottish Salmon Growers Association (SSGA) around fish cages in Loch Nevis and Loch Ainort. In most cases, levels were undetectable but some low concentrations were found in Loch Nevis. Research at the Institute of Aquaculture, Stirling, has shown that ivermectin does not cause liquifaction of fish faeces and there is no leaching of ivermectin from fish faeces. These were suspected as being the reasons why so little ivermectin had been found in the sediments (Codling *et al* 1998). However, research by SEPA is still on-going.

B27.3 Fate and behaviour in the marine environment

Ivermectin is one of a structurally similar group of compounds known as avermectins. The principal features of these chemicals in relation to their fate and behaviour are their low solubility in water (ivermectin 5 mg a.i. l-) and their log Koc values greater than 3.6, suggesting that they are likely to have an affinity for organic matter in soil and sediments and suspended solids in the aquatic environment. Ivermectin is likely to photodegrade rapidly in aqueous solution (half-life <13 hours) and is likely to biodegrade in aerobic soil (ivermectin: half-life = 7 to 240 days). However, a study on the rate of degradation in marine sediments has found degradation to be slow (half-life in excess of 100 days) (Codling *et al* 1998) .

B27.4 Effects on the marine environment

B27.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of ivermectin to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Codling *et al* 1998). The most sensitive groups of organisms have been identified.

Few relevant toxicity studies for saltwater organisms are available in the open literature. However, the Scottish Salmon Growers Association (SSGA) has recently commissioned a number of studies on the toxicity and bioaccumulation of ivermectin (via waterbourne exposure) to marine invertebrates in order to provide sufficient information to the Scottish Environment

Protection Agency (SEPA) to consider the use of ivermectin to be licensed for the control of sea lice. These data indicate that certain species of crustaceans may be particularly sensitive to ivermectin, with a 96 hour LC50 of 0.07 µg l^{-1} cited for the mysid shrimp *Neomysis integer* (SSGA 1996, cited in Codling *et al* 1998).

B27.4.2 Sediment dwelling organisms

Due to the high adsorptive capacity of ivermectin and with releases to water liable to result in adsorption to sediment, information on the toxicity of ivermectin to sediment-dwelling or sediment associated organisms is of importance.

Studies on sediment-dwelling or sediment associated organisms have been reported by Codling *et al* (1998) .

A 10 day LC50 of 18 µg ivermectin kg^{-1} (wet sediment) for the lugworm *Arenicola marina* (suggesting high sensitivity). Sub-lethal effects on feeding activity were apparent at all concentrations tested (0.005 - 0.105 mg kg^{-1}). A re-burial test with surviving worms indicated that a concentration above 0.008 mg kg^{-1} (wet sediment) affected the ability to burrow into clean sediment. The data for other organisms exposed in sediment, i.e. 10 day LC50s of 180 and 23,600 µg kg^{-1} dry sediment (18,400 µg kg^{-1} wet sediment) for the sediment re-working amphipod *Corophium volutator* and the sediment scavenging echinoderm *Asterias rubens* respectively, indicate lower sensitivity.

B27.5 Bioaccumulation

Data on bioaccumulation is limited.

The mussel *Mytilus edulis* was exposed to an average concentration of 6.9 µg l^{-1} ivermectin over 6 days with maximum levels of 5.2 mg kg^{-1} detected, resulting in a bioconcentration factor of 752. On transfer to clean water, tissue concentrations dropped to 0.06 mg kg^{-1} over 150 days and a slow depuration half-life of 22 days was determined. No adverse effects were reported for the mussels during the 6 day exposure period or the 150 day depuration phase.

However, Codling *et al* (1998) proposed that despite a high log Kows and high calculated BCF for fish, the large size of the ivermectin molecule may prevent bioaccumulation in fish. However, further experimental data are needed before this can be confirmed.

B27.6 Potential effects on interest features of European marine sites

Potential effects include:

! acute toxicity to invertebrates (particularly crustacea) at concentrations above the EQS of 0.001 Fg l^{-1} (annual average) and 0.01 Fg l^{-1} (maximum allowable concentration) in the water column;

! accumulation in the sediments and potential toxicity to sediment dwelling organisms.

References

CODLING, I.D., MASCARENHAS, R. and SUTTON, A. 1998. Proposed Environmental Quality Standards for Avermectins (abamectin, ivermectin and doramectin) in Water. WRc Report No. DoE 4197/1

B28. Dichlorvos

B28.1 Entry into the marine environment

Dichlorvos is a contact and stomach-acting insecticide and is used as a household and public health insecticide. Dichlorvos, as the active ingredient of Nuvan 500 EC (also known as Nuvan 50 EC and Aquaguard, 50% wt/vol or 500 g ai l^{-1}), was used extensively in salmon farming to control the salmon louse *Lepeophtheirus salmonis* (although it appears its use in this industry is diminishing).

The principal, direct routes of entry for dichlorvos into waters include industrial effluents and accidental discharges (e.g. from pesticide manufacturing plants, formulation plants and marketing outlets), use in salmon fisheries, disposal of unused insecticide and the cleaning of application and mixing equipment. Dichlorvos may also indirectly enter the aquatic environment via spray drift during application and in land run-off.

B28.2 Recorded levels in the marine environment

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. Only one water column concentration was found to approach the EQS value (see Appendix D). Monitoring data were not available for sediments or biota.

The available data suggest that concentrations of dichlorvos in UK coastal and estuarine water are unlikely to generally exceed relevant quality standards derived for the protection of saltwater life.

B28.3 Fate and behaviour in the marine environment

Dichlorvos is rapidly degraded in water both chemically and biologically. The main degradation process is hydrolysis. Persistence in water is low (days) and depends on the pH and temperature (Jones and Stewart 1996).

The vapour pressure of dichlorvos is relatively low so it is therefore unlikely that volatilisation is a significant removal process from the aquatic environment. Adsorption is not expected to be a significant removal pathway due to the low octanol-water (log Kow = 1.4) and soil organic carbon-water (log Koc = 1.34) partition coefficients.

B28.4 Effects on the marine environment

B28.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of dichlorvos to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Jones and Stewart 1996). The most sensitive groups of organisms have been identified.

The principal source of dichlorvos in the marine environment is the direct application to salmon farms located in estuaries and coastal waters.

Algae

Only two studies investigating the toxicity of dichlorvos to marine algae have been reported and the results indicate a relatively high tolerance compared to other phyla.

Invertebrates

Jones and Stewart (1996) reviewed data on the toxicity of dichlorvos to marine organisms. The authors concluded that crustaceans were the most sensitive class. The lowest acute 96 hour LC50 values for adult crustacean species include 4 µg l^{-1} for the sand shrimp *Crangon septemspinosa*, 15 µg l^{-1} for the grass shrimp *Palaemonetes vulgaris* (Eisler 1969), 4.4 µg l^{-1} for the shrimp *Crangon crangon* and 9 µg l^{-1} for the amphipod *Hyale nilssoni* (Thain *et al* 1990, McHenery *et al* 1990a).

Early life stages of the common lobster *Homarus gammarus* show similar sensitivity to the effects of dichlorvos as the adult sand shrimp. The 12, 24, 48 and 96 hour LC50s for stage 5 lobster larvae were 53, 28, 11 and 5.7 µg l^{-1}, respectively (Ciba-Geigy SP 3560.25 cites in Jones and Stewart 1996) and the corresponding calculated 12 and 96 hour NOEC values were 6.25 and 1.56 µg l^{-1}, respectively (McHenery *et al* 1990b).

Fish

Marine fish species appear to have similar sensitivities to the toxic effects of dichlorvos as freshwater fish species. Reported acute LC50 values for adult fish range from 200 µg l^{-1} for striped mullet (Eisler 1970) to 5 mg l^{-1} for goby (Hirose and Kitsukawa 1976). Early life stages of herring appear to be only marginally more sensitive with a 96 hour LC50 of 122 µg l^{-1} (Ciba-Geigy SP 3560.25 cited in Jones and Stewart 1996).

B28.5 Bioaccumulation

Jones and Stewart (1996) concluded that bioaccumulation in marine organisms was likely to be low.

B28.6 Potential effects on interest features of European marine sites

Potential effects include:

- toxicity to invertebrates (particularly crustacea) and fish to concentrations above the EQS of 0.04 µg l^{-1} (annual average) and 0.6 µg l^{-1} (maximum allowable concentration) in the water column.

References

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B29. Mothproofing chemicals

B29.1 Entry into the marine environment

The term ‘mothproofing’ describes the treatment of wool or wool-based fabrics to prevent damage by the larvae of a number of insect pests from the order of *Coleptera* (beetles) and *Lepidoptera* (butterflies and moths) capable of digesting keratin.

At the end of the 1970s, the pattern of mothproofing agent use altered considerably. The discovery that dieldrin was highly toxic to mammals and aquatic life and also persistent led to a decline in its use and replacement by formulations based on PCSDs (polychloro chloromethyl sulphonamido diphenyl ether); flucofuron and sulcofuron. However, with the advent of formulations based on synthetic pyrethroids, the use of these products has also declined.

Environmental Quality Standards (EQSs) for the protection of saltwater life have been proposed (and were put into legislation in 1989) for the following chemicals used as mothproofing agents; PCSDs; cyfluthrin; sulcofuron; flucofuron and permethrin.

Sources of mothproofing chemicals include both production and formulation plants and factories where they are used in the treatment of textiles and carpets. Hence, they may enter the aquatic environment, either in direct discharges or in sewage effluents. Since the pyrethroids may have a number of other applications, they may enter the aquatic environment from a number of other sources.

PCSDs , flucofuron and sulcofuron exert their toxic effect on the target organism by inhibiting the synthesis of the enzyme required to break down keratin. Pyrethroids, such as cyfluthrin and permethrin, are neurotoxins (the reader is referred to section B20 on synthetic pyrethroids for an outline of the effects of these chemicals). The summary presented here is therefore mainly limited to information on the remaining three chemicals.

Zabel *et al* (1988) reviewed the aquatic toxicity and bioaccumulation of these chemicals which is summarised below.

B29.2 Levels recorded in the marine environment

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. The information presented suggests that in 1994 some samples of PCSDs in excess of 0.1 Fg l^{-1} were reported (which would exceed the EQS of 0.05 Fg l^{-1}). However, the data are not highlighted as an exceedence, and since no further information is available, it is not possible to make a further assessment of the data.

Monitoring data were not available for sediments or biota.

Based on available data, it is not possible to assess whether concentrations of mothproofing agents in UK coastal and estuarine waters are likely to exceed relevant quality standards derived for the protection of saltwater life.

B29.3 Fate and behaviour in the marine environment

From the data available at the time, Zabel *et al* (1988) were unable to assess the likely fate and behaviour of these chemicals in the aquatic environment.

B29.4 Effects on the marine environment

B29.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of mothproofing chemicals to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Zabel 1988). The most sensitive groups of organisms have been identified.

Environmental data for PCSDs were limited and Zabel *et al* (1988) stated that further work was necessary to understand their partitioning in the environment. However, the authors concluded that PCSDs readily accumulate in the tissues of fish and were lethal at low concentrations to fish and invertebrates (acute toxic effect were reported at concentrations as low as 1Fg l^{-1}).

Data were also scarce for flucofuron and sulcofuron. However, Zabel *et al* (1988) concluded that they were less toxic and less likely to accumulate than PCSDs, although, based on the available data they can still be considered to be highly toxic to fish and invertebrates.

B29.5 Bioaccumulation

PCSDs readily accumulate in the tissues of fish. Flucofuron and sulcofuron are less likely to bioaccumulate than PCSDs.

B29.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxicity of PCSDs to invertebrates and fish at concentrations above the EQS of 0.05 Fg l^{-1} in the water column;

! toxicity of flucofuron to invertebrates and fish at concentrations above the EQS of 1 Fg l^{-1} in the water column;

! toxicity of sulcofuron to invertebrates and fish at concentrations above the EQS of 25 Fg l^{-1} in the water column;

! toxicity of cyfluthrin to saltwater life at concentrations above the EQS of 0.001 Fg l^{-1} in the water column;

! toxicity of permethrin to saltwater life at concentrations above the EQS of 0.01 Fg l^{-1} in the water column;

! potential for accumulation in sediments, although little is known of the fate and behaviour of these chemicals is known;

! potential for bioaccumulation of PCSDs in fish, birds and Annex II sea mammals.

References

ZABEL. T., SEAGER, J. and OAKLEY, S. 1988. Proposed Environmental Quality Standards for List II Substances in Water - Mothproofing Agents. WRc Technical Report TR261.

B30. Antifoulant paints

Fouling is the successive build up of bacteria, macroalgae, mussels, barnacles and other invertebrates on underwater surfaces. In order to prevent or reduce such fouling, paints containing biocides are applied to ship and boat hulls and other underwater structures to prevent or reduce fouling. These paints are known as antifoulants. Antifoulant paints contain biocides which are released slowly over a period of time minimising fouling. As they are by their very nature toxic to aquatic organisms, antifouling biocides could have an impact on non-target organisms.

In the past, organotins and copper were used. However, while copper is still used, the legal use of tributyltin is now limited to vessels greater than 25 m in length.

Some common algae (e.g. *Enteromorpha* and *Amphora* sp) are tolerant to copper. Consequently, manufacturers have introduced additional biocides for use on vessels less than 25 m and on certain larger vessels. These biocides are generally used in combination with copper and are termed booster biocides.

Readily available information on copper is provided in the profile in Section B7, on organotins in Section B31 and on booster biocides in Section B32.

B31. Organotins

B31.1 Entry into the marine environment

The principal organotins of concern are compounds of tributyltin (TBT). However, triphenyltins have also been used in antifoulant paints.

Tributyltin oxide (TBTO) is the commercially available active ingredient. TBTO is poorly soluble in water, varying between <1 and >100 mg l^{-1}, depending on the pH, temperature and anions present in the water. In seawater and under normal conditions, TBT exists as three species (hydroxide, chloride and carbonate) which remain in equilibrium. The log Kow is 3.54 for seawater indicating that it partitions to the organic solvent and adsorbs strongly to particulate matter (WHO 1990).

TBT compounds have been registered as molluscicides, antifoulants (on boats, ships, quays, buoys, crab pots, fish nets and cages), wood preservatives (see Section B33), slimicides on masonry, disinfectants, and as biocides for cooling systems, power station cooling towers, pulp and paper mills, breweries, leather processing and textile mills (WHO 1990).

There are four main ways in which TBTs can enter the marine environment:

! during the application of the antifouling paint to boats or cage fish farm nets;

! leaching from paint on the hulls of vessels or from cage fish farm nets;

! when paint is removed;

! when paint remnants are discarded.

Controls on the use of TBT in antifouling paints were introduced in 1986 when the sale of TBT-based paints was banned. In 1987, the use of TBT-based paints on boats under 25 m and mariculture equipment was also prohibited. Further controls are proposed (see Section 2). These measures have reduced the potential routes of entry into the marine environment and successfully reduced environmental concentrations (Waite *et al* 1991). However, because TBT is strongly adsorbed to organic matter, the sediments retain concentrations of TBT which can be mobilised when the sediment is disturbed.

B31.2 Recorded levels in the marine environment

TBT is found in the water column, sediments and the biota. Higher levels have been reported close to pleasure boating activity, especially in or near marinas, boat yards and dry docks (WHO 1990). In Scotland, high levels have been reported in sea lochs where cage fish farming occurs. WHO (1990) and Waite *et al* (1991) reported concentrations in the water column, sediment and biota but these were for measurements taken in the late 1980s and WHO (1990) indicated that ‘older’ measurements may not be comparable with ‘newer’ measurements because of advances in analytical techniques.

Michel and Averty (1999) report concentrations of TBT in the water column at marinas and commercial and military harbours on the French coast of the English channel in 1997 ranging from 0.0017 to 0.0877 Fg l^{-1} and 0.0023 to 0.280 Fg l^{-1} respectively. The majority of these measurements are above the EQS in the UK (0.002 Fg l^{-1}).

Recent monitoring of TBT in the marine environment has been undertaken by using biological effects monitoring. Gibbs *et al* (1987) conclusively linked the condition of imposex (see section B31.4.1) in gastropod molluscs to the presence of organotins in the environment. This phenomenon was first observed in dogwhelks. The measurement of the degree of imposex in this species has developed into an effective monitoring technique for organotins which is cheaper and more sensitive than measuring chemical determinands (MPMMG 1998). This technique was included in the National Monitoring Programme and results were presented from Northern Ireland for 1994 in MPMMG (1998). Dogwhelks from sites within Belfast Lough showed clear signs of the imposex phenomenon, indicating the continuing presence of organotins. For the North Sea coast of the UK, similar results were derived from the TBT Imposex Survey of the North Sea (Harding *et al* 1997 cited in MPMMG 1998). This survey indicated that imposex remained widespread throughout the North Sea and English Channel from Shetland to Land's End. Harding *et al* (1998) report results for Western Coastal areas (including the UK west coast and coast of Northern Ireland and the Irish Republic) sampled in 1997 and concluded that the effects of TBT pollution could be observed over most of the area. Only at sites very close to sources of pollution (commercial and fishing harbours) could severe imposex effects be observed and at sites where TBT was once used (marinas and cage fish farm locations) measures of imposex could not be distinguished from background.

CEFAS (1998) report concentrations of monobutyltin (MBT), dibutyltin (DBT) and TBT in the livers of porpoises and grey seals found stranded around the coast of England and Wales between 1992 and 1996. Concentrations of total butyltins (the sum of MBT, DBT and TBT) ranged from 22 to 640 Fg kg^{-1} wet weight in porpoise and 3 to 22 Fg kg^{-1} wet weight in grey seals. DBT was the dominant form of organotin in the liver.

B31.3 Fate and behaviour in the marine environment

The main removal process for TBT in the water column is through adsorption onto particles. WHO (1990) suggested that between 10 and 95% of TBTO was estimated to undergo particle adsorption.

Progressive disappearance of adsorbed TBT is due to degradation. Biodegradation by micro-organisms and metabolism by higher organisms are probably the dominant processes. Biodegradation depends on environmental conditions, such as temperature, oxygenation, pH, level of mineral elements, the presence of easily biodegradable organic substances for co-metabolism and the nature of the microflora (WHO 1990). It also depends on the TBT concentration being below the lethal or inhibitory threshold of the micro-organisms. TBT is broken down into DBT and MBT. Half-lives for TBT in the environment vary widely (WHO 1990).

B31.4 Effects on the marine environment

B31.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of organotins to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Zabel *et al* 1988, WHO 1990). The most sensitive groups of organisms have been identified.

TBT is very toxic to algae, molluscs, crustacea and fish. TBT has been identified as an endocrine disrupting substance (Environment Agency 1998) with observable effects in gastropod molluscs and suggested effects in marine mammals (CEFAS 1998).

The development of the motile spores of a green macroalga was impaired by exposure to TBT (5-day EC50 of 0.001 Fg l^{-1}) and this stage was considered to be the most sensitive. The growth of a marine angiosperm was reduced at TBT concentrations of 1 mg kg^{-1} of sediment but no effect were observed at 0.1 mg kg^{-1}.

Marine molluscs have been observed to undergo a number of changes in response to exposure to sub-lethal concentrations of TBT, including shell deposition of growing oyster, gonadal development and gender of adult oysters, settlement, growth and mortality of larval oysters and other bivalves and to cause imposex in female gastropods (e.g. Smith 1981, Waldock 1986, Zabel *et al* 1988, WHO 1990). Credible adverse effects have been observed in saltwaters organisms in laboratory tests at concentrations as low as 0.01Fg l^{-1} (Zabel *et al* 1988). The NOEL for spat of the most sensitive oyster species *Crassostrea gigas* has been reported to be in the region of 0.002 Fg l^{-1} (WHO 1990).

Imposex is a condition where the female gastropod develops a penis and a vas deferens which in severe cases block the genital pore causing reproductive failure and premature death. WHO (1990) report a NOEL for the development of imposex in female dogwhelks of below 0.0015 Fg l-1 of TBT. Imposex effects have been observed in whelks *Buccinum undatum* and *Neptunea antiqua* collected from the west coast of Scotland in 1997. These effects were observed 10 years after the ban on the use of TBT on small craft and cage fish farm nets and the effects were attributed to TBT accumulated in the sediment. No sediment concentrations of TBT were measured and the degree of imposex was not considered to be affecting the fishery potential of these species (Poloczanska and Ansell 1999).

Copepods are the most sensitive group of crustaceans, with 96-hour LC50s ranging from 0.6 to 2.2 Fg l^{-1} (WHO 1990). TBT reduces reproductive performance, neonate survival and juvenile growth in crustaceans.

The toxicity of TBT to marine fish is highly variable, with 96-hour LC50s ranging from 1.5 to 36 Fg l^{-1} with larval stages more sensitive than adults.

The EQS for TBT is 0.002 Fg l^{-1} in the water column.

Rees *et al* (1999) and Waldock *et al* (1999) studied the epifaunal and infaunal benthic communities respectively in the River Crouch, SE England in relation to decreasing environmental concentrations of TBT in water and sediment between 1986 and 1992. In both cases, changes in faunal composition could not be conclusively linked to decreasing TBT concentrations but faunal diversity increased at sites in the upper estuary where TBT levels were greater in 1987 and had been significantly reduced by 1992.

More recent studies have been conducted to determine the extent of organotin contamination in the tissues of marine mammals. TBT is bioaccumulative and the ability of cetaceans to metabolise TBT is considered to be low (CEFAS 1998). Various studies have highlighted butyltin accumulation in a range of cetacean species from Japan and the north Pacific Ocean. Recent data from CEFAS on the contamination of porpoises and seals from around England and Wales have demonstrated that low-level organotin contamination of marine mammals occurs around the UK (CEFAS 1998). However, CEFAS was unable to assess the significance of their findings and stressed that further information was needed on the threats facing these animals from possible toxic and bioaccumulation effects.

B31.5 Bioaccumulation

TBT bioaccumulates in organisms because of its solubility in fat. WHO (1990) reported BCFs of up to 7,000 in laboratory investigations with molluscs and fish and higher values have been reported from field studies. Uptake from food is more important than uptake directly from the water.

B31.6 Potential effects on the interest features of European marine sites

Potential effects include:

- toxicity to algae, invertebrates (especially molluscs) and fish of TBT in the water column at concentrations above the EQS of 0.002 Fg l^{-1};

- toxicity to algae, invertebrates (especially molluscs) and fish of triphenyltin and its derivatives in the water column at concentrations above the EQS of 0.008 Fg l^{-1};

- the presence of TBT is monitored by the degree of imposex in female gastropod molluscs rather than by direct measurements of concentrations of organotins in the water column or the sediments. Where imposex is detected within a European marine site, a precautionary approach should be adopted in the control of TBT and activities associated with its use (e.g. pleasure boating, cage fish farming);

- accumulation of TBT in sediments which could induce imposex in gastropod molluscs after several years;

- bioaccumulation of TBT in the food chain posing a potential hazard to birds and Annex II sea mammals;

- endocrine disruption impacts of TBT in invertebrates, fish and potentially Annex II sea mammals.

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B32. Booster biocides in antifoulant paints

B32.1 Entry into the marine environment

Boxall *et al* (1998) identified nine booster biocides approved for use in amateur and professional antifouling products, namely:

- zinc pyrithion;
- TCMTB (2-thiocyanomethyl-benzothiazole);
- kathon 5287;
- TCMS pyridine (2,3,5,6-tetrachloro-4-sulfuronyl pyridine);
- irgarol 1051;
- diuron;
- dichlofluanid;
- chlorthanonil, and
- zineb

Based on a consideration of their use on pleasure craft in UK coastal water, Boxall *et al* (1998) estimated that copper (1) oxide is used in the highest quantities, followed by diuron (see Section B14), copper thiocyanate, irgarol 1051, zinc pyrithion and dichlofluanid.

There are four main ways in which antifouling biocides can enter the environment:

- during the application of the antifouling paint to boats or cage fish farm nets;
- leaching from paint on the hulls of vessels or from cage fish farm nets;
- when paint is removed;
- when paint remnants are discarded.

However, the actual input of each biocide to the aquatic environment will depend on the method and location of paint application, the leaching behaviour of the biocide once a painted boat is in the water and the method in which residual antifouling paint is removed from the hull of the boat.

Boxall *et al* (1998) estimated maximum and minimum quantities of antifouling bioicides distributed or used in the UK in 1 year:

	Maximum Amount (kg yr^{-1})	**Minimum Amount (kg yr^{-1})**
copper (1) oxides	311769	75173
copper thiocyanate	4216	282
diuron	24738	3288
irgarol 1051	10186	59
zinc pyrithion	8246	1369
dichlofluanid	388	153

B32.2 Recorded levels in the marine environment

Boxall *et al* (1998) reported environmental concentrations of 0.004 - 0.130 μg l^{-1} for irgarol 1051, 0.013 - 1.0 μg l^{-1} for diuron and a median concentration of approximately 7 μg l^{-1} for Cu^{2+} in estuaries used by commercial and leisure craft.

Using a model of a marina, Boxall *et al* (1998) estimated that concentrations of each of highest use biocides in marina water would range from 0.023 - 254 μg l^{-1} (although the authors recognised that the model used had some limitations and there may be some over estimation in the concentrations given).

B32.3 Fate and behaviour in the marine environment

The fate and behaviour of diuron and copper are outlined in Sections B14 and B7 respectively. There is limited information for the remaining booster biocides. Irgarol 1051 has a log Kow of 2.8, indicating that it is unlikely to sorb strongly to sediments or suspended solids. The photolysis half-life of 273 days suggested that exposure to light was not a major fate process. Irgarol is also not readily biodegraded and could therefore be considered persistent in the marine environment (Boxall *et al* 1998).

B32.4 Effects on the marine environment

B32.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of booster biocides in antifoulant paints to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Boxall *et al* 1998). The most sensitive groups of organisms have been identified.

For an outline of the toxicity of diuron and copper to aquatic organisms, the reader is referred to Sections B14 and B7 respectively.

Toxicity data for the majority of these chemicals are limited. Data cited in Boxall *et al* (1998) reported LC50 concentrations for irgarol, diuron and dichlofluanid. For fish, these ranged from 300 - 25,000 μg l^{-1} and 1 - 16,000 μg l^{-1} for algae.

B32.5 Bioaccumulation

The reader is referred to Sections B14 and B7 respectively for an outline of the bioaccumulation potential of diuron and copper

No bioaccumulation data were reported by Boxall *et al* (1998) for irgarol or dichlofluanid but log Kow values of 2.8 and 3.7 respectively indicated that irgarol 1051 was unlikely to bioaccumulate and that dichlofluanid had the potential to bioaccumulate. Further information is required to establish the bioaccumulation potential of these substances.

B32.6 Potential effects on the interest features of European marine sites

Potential effects include:

- toxicity of diuron and dissolved copper to aquatic organisms at concentrations in the water column above the EQSs for these substances (see Sections B14 and B7);

- toxicity of irgarol and dichlofluanid to aquatic organisms in the water column, especially around sites used by leisure craft (marinas, harbours and moorings). There are no standards for these substances and monitoring of environmental concentrations is likely to be limited. A precautionary approach should be adopted in relation to these substances in European marine sites encompassing sites used extensively by leisure craft.

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B33. Timber treatment Chemicals (including creosote)

B33.1 Entry into the marine environment

Wood deterioration can be caused in a number of ways;

- fungal attack; insect attack;
- weathering;
- mechanical wear and fire.

There are numerous active ingredients (in excess of 50) registered for use in the UK (PSD/HSE 1998) which can be broadly grouped into three categories:

- organic solvents;
- water borne; and
- creosote.

Organic solvent based preservatives most commonly comprise either one or a mixture of some of the following preservatives;

- pentachlorophenol;
- pentachlorophenol laurate;
- 2-phenyl phenol;
- lindane (see Section B18);
- metal naphthenates and bis (tributyltin)oxide (TBTO) (see Section B31), dissolved in an organic solvent usually of the white spirit or kerosene type.

In addition to the active ingredients, additives such as resins, colouring agents and water repellents may also be added (HMIP 1992).

Water borne preservatives usually comprise a mixture of inorganic salts dissolved in water. The water borne preservative group is dominated by the copper-chromium-arsenic (CCA) preservatives which frequently consist of a mixture of copper sulphate, sodium dichromate and arsenic pentoxide. Copper (see Section B7) and arsenic (see Section B9) are the principal pesticidal agents while the dichromate (see Section B5) fixes the copper and arsenic in the wood. The preservative is mixed with water at the treatment site. The advantage of the CCA wood preservative is that they bind very tightly to the timber, giving the treated timber a long life even when immersed in water. Other compounds used in water borne preservative include sodium arsenate; disodium octaborate and sodium salts of chlorinated phenols, boron based compounds and quaternary ammonium compounds (Williams 1994).

The third type of preservative is creosote, a blend of distillate oils, mainly from coal tar with boiling points ranging from 200 - 400°C. It contains a high proportion of polyaromatic hydrocarbons (PAHs) (see Section B46), together with a few percent of tar acids (phenolic derivative). While the use of creosote has fallen since the early 1970s, it still accounts for a significant proportion of the UK market (Williams 1994).

The use of timber treatment chemicals falls into three main categories:

- industrial pre-treatment of timber (pressure and vacuum plants and non pressure processes such as immersion plants);

- remedial treatment (so called professional use);

- domestic (DIY) use by retail customers.

Inputs of timber treatment chemicals into the aquatic environment can emanate from point and diffuse sources.

Point sources include wastewater arising during the manufacture of active ingredients and formulations; where treatment plants use formulation with volatile ingredients, release to air may occur, and these may enter the aquatic environment through atmospheric deposition. There is the potential for spillages or releases, resulting from either bad on-site housekeeping or through accidents.

Of the three main use categories, industrial pre-treatment of timber represents the most likely point source of timber treatment chemicals due to the large quantities of chemicals handled at the pre-treatment sites.

Diffuse sources may also be significant for some preservatives, such as creosote used in remedial and domestic situations.

Williams (1994) reviewed timber treatment chemicals in order to identify chemicals with a high to medium risk to the aquatic environment for the purpose of EQS development. From the list of over 50 active ingredients registered for use in the UK, 20 were identified for the risk assessment (Table B33.1)

Table B33.1 Selected chemicals used in the timber treatment industry (from Williams 1994)

Substances with existing or proposed (UK/EU) EQSs	Legislative status	Substances with no existing or proposed (UK/EU) EQSs
arsenic (Section B9)	List II	borates
boron (Section B11)	List II	CCA salts (copper sulphate, sodium or
copper (Section B7)	List II	chromium potassium dichromate and
lindane (Section B18)	List I	arsenic pentoxide or similar mixtures)
pentachlorophenol	List I	copper naphthenate
permethrin (Section B20)	List II	creosote (PAHs, tar bases, tar acids)
tributyltin oxide (Section B 31)	List II	dichlorofluanid
zinc (Section B6)	List II	3-iodo-2propynyl butyl carbamate
chromium (Section B5)	List II	2-phenyl phenol (and salts)
cypermethrin * (Section B20)	List II	quaternary ammonium compounds
		2-(thiocyanomethylthio) benzothiazole
		zinc soaps (versatate, octoate, acypetacs, naphthenate)
		cypermethrin

* EQS development in progress

Williams (1994) concluded that the substances of greatest concern in terms of their usage, aquatic toxicity, persistence and bioaccumulation were CCAs and tributyltin naphthenate (TBTN) whilst creosote, zinc versatate, zinc octoate, acypetacs zinc and copper naphthenate were of medium concern.

CCAs and copper naphthenate are likely to exert their toxic effect due to the dissociation of copper and, therefore, the existing standards for copper (EQS) were considered sufficient for the protection of the aquatic environment (see Section B7). Similarly, the existing EQSs for TBTO (see Section B31) and zinc (see Section B6) were considered sufficient for the protection of aquatic life from TBTN and zinc compounds.

Creosote was the only remaining substance of concern with no existing EQS. The remainder of this profile concentrates on creosote using information from Williams (1994).

Creosote typically comprises 85% PAHs, 10% phenols (or tar acids) and 5% tar bases. Coal tar creosote usually consists of liquid and solid aromatic hydrocarbons, such as guaicol, phenol, cresols, pyrol and pyridine. The major PAH constituents are acenaphthene, anthracene, benzanthracene, fluoranthene, fluorene, phenanthrene and pyrene, although as many as 36 have been identified.

B33.2 Recorded levels in the environment

Creosote is not monitored under any national monitoring programme and would probably only be measured close to known sources. Concentrations of individual PAHs are occasionally measured in sediments and biota (see Appendix D). Contributions from creosote may add to these close to known sources.

Williams (1994) reported that creosote oil had been recorded in biota (molluscs and crustaceans) and that lipid concentrations of 1,046 (mussels), 459 - 3,254 (periwinkles), 202 - 354 (whelks) and 459 ppm (clams) had been measured.

B33.3 Fate and behaviour in the marine environment

Creosote is of low solubility and stable in water. Only about 9% may dissolve and be transported away from point sources (Williams 1994). Some of the constituent PAHs have been shown to accumulate in sediments. The major fate processes are believed to be biodegradation and photolysis, depending on light availability. Complete breakdown may take between 3-12 months.

B33.4 Effects on the marine environment

B33.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of creosote to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Williams 1994). The most sensitive organisms have been identified. Creosote appears to be of moderate to high toxicity to marine fish and of high toxicity to marine invertebrates with 96-hour LC50s of 0.56 - 4.42 mg l^{-1} and 0.018 - 0.24 mg l^{-1} respectively.
An EQS for creosote has not been developed because of the heterogenous nature of the mixture and associated analytical difficulties.

B33.5 Bioaccumulation

Williams (1994) report a BCF of 0.6 for the dissolved fraction in a water body, indicating that it is not likely to be bioaccumulated in aquatic organisms.

B33.6 Potential effects on the interest features of European marine sites

Potential effects include:

- toxicity of creosote in the water column to marine invertebrates and fish;
- physical effects of a spillage of large quantities of creosote may be similar to the effect observed for oil and petrochemicals (see Section B51).

References

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B34. Biocides used in Cooling Water Disinfection

B34.1 Entry into the marine environment

Biofouling by algae, fungi and bacteria can occur in cooling water systems as the systems offer a warm, moist environment, ideal for the promotion of biological growth. The growth of these organisms, if left unchecked, can rapidly lead to the formation and accumulation of slimes and biofilms which can cause obstructions in the cooling water systems. This can increase pumping costs and inhibit the effectiveness of heat transfer processes. Fouling can also lead to the proliferation of sulphate reducing bacteria, which can ultimately lead to production of hydrogen sulphide which can cause metallic corrosion problems.

Biocides are routinely employed in order to control the growth and development of such organisms. Within cooling water systems, the life of a biocide will depend on environmental factors as well as the amount added and the physical and chemical fate of the individual chemical. However, where cooling water systems discharge directly to estuaries or marine waters, there is the potential for residual quantities of biocides and their degradation/transformation products to be present in the effluents.

There are many biocides available to control biofouling in cooling water systems. These can be divided into two main groups: the oxidising biocides and the non-oxidising biocides. The classification is based on the mode of biocide action against biological material.

Oxidising biocides include chlorine and bromine-based compounds and are non selective with respect to the organisms they kill. Non-oxidising biocides are more selective, in that they may be more effective against one type of micro-organisms than another. A large variety of active ingredients are used as non-oxidising biocides, including quaternary ammonium compounds, isothiazolones, halogenated bisphenols, thiocarbamates as well as others. In view of the wide range of potentially different fate and behaviour and toxicity, consideration of the environmental fate and saltwater toxicity of biocides has been limited here to the effects of chlorine and bromine based biocides and their principal transformation products (chloroform and bromoform).

B34.2 Recorded levels in the marine environment

Chloride concentrations in cooling water discharges are unlikely to be significant relative to the background levels present in the receiving waters where mean annual average concentrations have been reported in the range < 10 - >100 mg/l (Gardiner and Smith 1990).

Monitoring data for chloroform from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. One water column concentration was found to exceed the EQS value (see Appendix D). Monitoring data were not available for sediments or biota.

The available data suggest that concentrations of chloroform may be elevated in some UK coastal and estuarine waters but in general, are unlikely to exceed relevant quality standards derived for the protection of saltwater life.

B34.3 Fate and behaviour in the marine environment

Chlorine and bromine

The chemistry of chlorine in water has been reviewed extensively elsewhere (White 1986). Consequently, only a summary of the main points is included here.

When chlorine gas is dissolved in water, it hydrolyses rapidly according to the following equation to yield hypochlorous acid:

$Cl_2 + H_2O \circ HOCl + H^+ + Cl^-$ (1)

Hypochlorous acid is also formed when sodium hypochlorite is used as the source of chlorine:
$NaOCl + H_2O \circ HOCl + Na^+ + OH^-$ (2)

Hypochlorous acid is a weak acid, and will undergo partial dissociation as follows:
$HOCl \circ H^+ + OCl^-$ (3)

In waters of pH between 6 and 9, both hypochlorous acid and hypochlorite ion will be present; the proportion of each species depending on pH and temperature. Hypochlorous acid is significantly more effective as a biocide than the hypochlorite ion.

The reaction of hypochlorous acid with ammonia results in the formation of chloramines as follows:

$NH_3 + HOCl \circ NH_2Cl + H_2O$ (4)
$NH_2Cl + HOCl \circ NHCl_2 + H_2O$ (5)
$NHCl_2 + HOCl \circ NCl_3 + H_2O$ (6)

These reactions are all dependent on pH, temperature, contact time and the relative concentrations of chlorine and ammonia. Essentially, any free chlorine will be converted to monochloramine at pH 7 to 8 when the ratio of chlorine to ammonia is equimolar (5:1 by weight) or less. At higher chlorine to ammonia ratios, or lower pH values, dichloramine and trichloramine will be formed. The interaction of the various competing reactions is complex and will not be considered here. A detailed discussion of chlorine-ammonia chemistry can be found in White (1986).

Chlorine will also oxidise bromide to form hypobromous acid:

$HOCl + Br^- \circ HOBr + Cl^{--}$ (7)

Hypobromous acid is an effective biocide. It is worth noting that, for a given pH value, the proportion of hypobromous acid relative to hypobromite is significantly greater than the corresponding values for the hypochlorous acid - hypochlorite system. Thus, for example, at pH 8 and 20°C, hypobromous acid represents 83% of the bromine species present, compared with hypochlorous acid at 28%. When ammonia is also present, the competing reactions of chlorine with bromide and ammonia are likely to result in the rapid formation of both monochloramine and hypobromous acid. A number of other reactions can then occur:

$NH_2Cl + Br^- + 2H_2O \rightarrow HOBr + NH_4OH + Cl^-$ (8)
$HOBr + NH_4OH \rightarrow NH_2Br + 2H_2O$ (9)
$NH_2Br + HOBr \rightarrow NHBr_2 + H_2O$ (10)

Chlorine can also react with nitrogen-containing organic compounds, such as amino acids to form organic chloramines. Little is known about the biocidal properties of these compounds.

In natural waters, chlorine can undergo a range of reactions in addition to those discussed above. It will react with inorganic constituents of water such as iron (II), manganese (II), nitrite and sulphide.

The reaction of chlorine with organic constituents in aqueous solution can be grouped into several types:

(a) Oxidation, where chlorine is reduced to chloride ion, e.g.

$RCHO + HOCl \rightarrow RCOOH + H^+ + Cl^-$ (11)

(b) Addition, to unsaturated double bonds, e.g.

$RC = CR' + HOCl \rightarrow RCOHCClR'$ (12)

(c) Substitution to form N-chlorinated compounds, e.g.

$RNH_2 + HOCl \rightarrow RNHCl + H_2O$ (13)

or C-chlorinated compounds, e.g.

$RCOCH_3 + 3HOCl \rightarrow RCOOH + CHCl_3 + 2H_2O$ (14)

Chlorine substitution reactions can lead to the formation of halogenated compounds, such as chloroform (e.g. reaction 14), and, where HOBr is present, mixed halogenated and brominated organic compounds. Although such reactions are significant in terms of the resultant halogenated by-products, it has been estimated that only a few percent of the applied chlorine ends up as halogenated organic products. Chlorine is a powerful oxidant, and a significant proportion of the applied chlorine is likely to be consumed in reactions such as 11, leading to the formation of non-halogenated organic products, with chlorine being reduced to chloride.

A number of other source water characteristics is likely to have an impact on the concentrations of organic by-products present in cooling water discharges:

- Natural organic matter in water is the major precursor of halogenated organic by-products, and hence the organic content of the source water (often measured as total organic carbon, TOC) may affect the concentration of by-products formed. In general, the higher the organic content of the source water, the higher the potential for by-product formation. Whether this potential is realised will depend primarily on the applied chlorine dose, as well as the extent of competing reactions that lead to the consumption of chlorine. Freshwaters typically contain higher amounts of TOC than marine or estuarine, and hence have the potential to produce higher levels of halogenated organic compounds during chlorination. Any pre-treatment (e.g. settling) of the cooling water is likely to reduce by-product formation through the removal of organic precursors.

! The ammonia concentration is likely to affect the extent of by-product formation, through reaction with chlorine to form chloramines. Although seawater generally contains low concentrations of ammonia than freshwater, under certain conditions (dependent on chlorine dose:ammonia nitrogen concentration) it can compete with bromide for the available chlorine to form monochloramine. In addition, hypobromous acid can react with ammonia to form bromamines. Although the sequence of reactions is complex, it is likely that the reaction of either hypochlorous or hypobromous acid with ammonia to form halamines will reduce organic by-product formation during the chlorination of seawater.

! The pH of the incoming cooling water could also affect the nature of the by-products formed. Trihalomethanes (THMs) formation has been shown to rise with increasing pH, probably due to base-catalysed hydrolysis of intermediates in the haloform reaction. TCA formation on the other hand has been shown to decrease significantly at pH values above 7, possibly due to the reduced oxidising power of hypochlorite ion compared with hypochlorous acid (Miller and Uden 1983). In general, while variations in pH are likely to affect the concentrations of individual by-products, the overall quantity formed (i.e. AOX content) is likely to remain relatively constant. At sites where the pH is adjusted to reduce problems with scaling, a reduction in THM formation could occur, possibly at the expense of an increase in haloacetic acid production.

! The presence of certain pollutants in source waters could lead to an increase in the levels of certain halogenated organics. The presence of phenol, for example, can lead to the formation of chlorophenols (see Section B42). THMs and halogenated phenols have been identified in a number of chlorinated cooling waters. Chloroform is the major THM formed at sites using freshwater sources, whereas bromoform predominates at estuarine and marine sites.

In estuarine and marine sites, where chlorination or bromination has been used in the cooling water, brominated products will predominate due to the influence of bromide in saline waters.

Chloroform and bromoform

Chloroform (trichloromethane) and bromoform (tribromomethane) are highly volatile and only moderately soluble in water (IARC 1979, Merck Index 1989). Chloroform is a commonly encountered chemical, having many industrial uses, hence, a lot of information is available on the environmental fate of this compound. Based on the data available in the literature, chloroform and bromoform do not adsorb onto sediments and soils to any great extent. Consequently, this process is not considered to be an important means of removing chloroform or bromoform from the aquatic environment (CCME 1992). Volatilisation (followed by oxidation) is the major fate process for removing chloroform (and most likely bromoform) from the aquatic environment. Biodegradation is slow but has a significant effect on the removal of chloroform or bromoform from soils and sediments. Hydrolysis, adsorption, photo-oxidation, photolysis, hydraulic processes, and bioaccumulation do not appear to reduce chloroform concentrations substantially in the environment.

B34.4 Effects in the marine environment

B34.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of chlorine, bromine, chloroform and bromoform to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Lewis *et al*. 1994, 1997). The most sensitive groups of organisms have been identified.

Chlorine and bromine

A review of data on the toxicity of chlorine and bromine to saltwater organisms indicates that far more information is available on the toxicity of chlorine and chloramines to saltwater organisms than for bromine and bromamines with invertebrates (especially crustaceans) exhibiting greatest sensitivity (Lewis *et al* 1994 and Lewis *et al* 1997). However, Lewis *et al* (1997) has presented a comparison the toxicity of bromine and chlorine. Investigating the difference in sensitivity for two saltwater organisms, the silverside *Menidia beryllina* and the mysid *Mysidopsis bahia* only a slight increase in toxicity (by a factor of 2) was noted, the chlorine-induced oxidants appearing slightly more toxic than bromine-induced oxidants.

Liden *et al* (1980) used continuous flow bioassays to compare the effects of bromochlorinated and chlorinated condenser cooling effluent on several estuarine food-chain organisms. Two fish species, Atlantic menhaden *Brevoortia tyrannus* and spot *Leiostomus xanthurus*, two bivalve species, American oyster *Crassostrea virginica* and brackish water clam *Rangia cuneata* have been investigated. Similar total survival of menhaden and spot as well as oysters and clams exposed to BrCl and Cl_2 treated effluents indicated that the toxicities of the residual oxidants were similar for both halogens.

Roberts and Gleeson (1978) determined the acute toxicity of bromochlorinated estuarine seawater (ca 20 ‰) for several estuarine organisms. When the BrCl toxicity data were compared with Cl_2 toxicity data for the same species and LC50s are expressed as equivalents per litre, BrCl was found to be two to four times less toxic than Cl_2. The ranking of species in terms of sensitivity was found to be the same for both disinfectants.

Bradley (1977) reported a calculated 24 hour static LC50 for *Acartia tonsa* of 362 ± 26 µg l^{-1} bromide chloride (applied in the form of sodium hypochlorite and sodium hypobromite). Toxicity was found to be similar to chlorine (applied as sodium hypochlorite) with a 24 hour static LC50 for *Acartia tonsa* of 403 ± 46 µg l^{-1}.

Chloroform and bromoform

Studies on the toxicity of chloroform and bromoform to saltwater organisms are outlined below. These indicate that chloroform is of moderate to high toxicity to aquatic organisms. Fewer data are available on the toxicity of bromoform than for chloroform. However, as for chloroform, the data indicate that bromoform is of moderate to high toxicity. The saltwater mollusc *Crassostrea* *virginica* appears to be particularly sensitive to bromoform, with lethal and sub-lethal effects being reported at concentrations of 0.05 mg l^{-1} and less.

Experiments to determine the effect of chloroform on marine algal species *Glenodinium halli, Isochrysis galbana, Skeletonema costatum* and *Thalassiosira pseudonana* have been carried out by Erikson and Freeman (1978). After 7 days exposure at 20 °C, none of the species showed any inhibition of cell division at a nominal chloroform concentration of 32 mg l^{-1}. Stimulation of cell division was observed in the species at varying concentrations - *G. halli* at 32 mg l^{-1}, *I. galbana* at 0.5 mg l^{-1}, *S. costatum* at 8 mg l^{-1}, and *T. pseudonana* at 32 mg l^{-1} nominal dose. However, due to the test conditions, it is likely that, because of evaporation, the actual concentration of chloroform at the end of the 7 day test period would be much lower than the initial 32 mg l^{-1}.

Okubo and Okubo (1962) carried out bioassays with the brine shrimp *Artemia salina* and the amphibious crab *Sesarma haematocheir*. The LC100 of the brine shrimp was found to lie between 464 and 800 mg l^{-1}, and concentrations of 480 mg l^{-1} resulted in 100 % mortality of the crab species. Bentley *et al* (1975) reported an LC50 of 81.5 mg l^{-1} for the pink shrimp *Pennies duorarum*.

Tests have been performed with two species of molluscs, the eastern oyster *Crassostrea virginica* and the common mussel *Mytilus edulis*. Fertilised eggs of *C. virginica* were exposed to chloroform and the survival of the larvae after 48 hour exposure was determined (Stewart *et al* 1979). Even though the test beakers were covered with aluminium foil to minimise evaporative losses, a loss of 85 % was found from one exposure concentration (100 µg l^{-1}). A 48 hour LC50 of 1 mg l^{-1} was found. However, if the same losses due to volatilisation can be assumed, then an 48 hour LC50 of 0.15 mg l^{-1} is probably more realistic. Okubo and Okubo (1962) reported that embryonic development of *M. edulis* was unaffected by 800 mg l^{-1}.

Okubo and Okubo (1962) also studied the effects of chloroform on the fertilised eggs of the sea urchin *Hemicentrotus pulcherrimus*. Embryonic development was unaffected by concentrations of up to 800 mg l^{-1} which indicates that this life stage is very tolerant to exposure to chloroform.

Data for marine fish are limited to one test. Madeley (1973) carried out experiments with the dab *Limanda limanda* and reported LC0 and LC50 values of 23 and 28 mg l^{-1} respectively. The figures are similar to those recorded for freshwater fish. No reports of chronic studies have been found.

Sung *et al* (1978) state that the current practice of chlorination of seawater for power station cooling systems will produce acute toxic effects on marine organisms exposed for periods of 1-25 minutes. It has been known for some time that reproductive tissues, especially sperm, and the immature stages of the organisms are sensitive to very low concentrations of organohalogens, such as bromoform (Davis and Middaugh 1978, cited in Ali and Riley 1986).

Erikson and Freeman (1978) reported that a concentration of >32 mg l^{-1} bromoform was needed to cause a 50 % reduction in the cell division (EC50) to four species of marine phytoplankton, the marine diatom *Skeletonema costatum*; *Thalassiosira pseudonana*, a rapid-growing unicellular diatom; *Glenodinium halli*, a dinoflagellate; and *Isochrysis galbana* a microflagellate.

Gibson *et al* (1979a) studied the toxicity and effects of bromoform on five marine species (3 bivalve molluscs, 1 penaeid shrimp and 1 fish). Considerable difficulty was experienced in

maintaining experimental concentrations, due to the volatility of bromoform. *Protothaca staminea* (littleneck clam), at concentrations of 300-400 mg l^{-1} were seen to close up their shells and retract their siphons, and thus able to avoid exposure to bromoform. At concentrations of 800 mg l^{-1}, the clams died. The other two bivalve molluscs, *Crassostrea virginica* and *Mercenaria mercenaria*, ceased filter-feeding and closed their shells at <10 mg l^{-1} bromoform. Although there were no mortalities during exposure to 27 mg l^{-1}, some test organisms died immediately after exposure. The LC50 was estimated to lie between 40 and 150 mg l^{-1} for both species (Gibson *et al* 1979a).
The species of crustacean tested by Gibson *et al* (1979a) was *Pennies aztecus* (a shrimp). This species was found to be more sensitive to bromoform than the mollusc species, with a 96-hour LC50 of 26 mg l^{-1}. Bromoform was pumped in via an air supply at one end of the tank, and within 60 seconds of exposure, the animals had moved as far away from the source as possible. Sub-lethal effects occurred before death including the animals lying on their sides at the bottom of the tank undulating their abdominal appendages.

Stewart *et al* (1979) found that the by-products formed during chlorination of a power plant cooling water may have adverse effects on the growth of marine invertebrates during their larval stages. They found that concentrations as low as 0.05 mg l^{-1} were significantly toxic to the larval stages of the marine oyster *Crassostrea virginica* (approximately 20 % mortality), with a 48 hour LC50 of 1 mg l^{-1}. Scott *et al* (1982 cited in Ali and Riley 1986) reported that adult oysters of the species *Crassostrea virginica* which had been exposed to seawater containing 25 µg l^{-1} of bromoform had an increased rate of respiration while the rate of feeding and the size of gonads had been reduced. There are no data to confirm if this test was acute or chronic exposure. Rapid uptake of the compound occurred, but on removal to clean water, depuration was complete within 96 hours. Although the feeding rate then returned to normal, the damage to the gonads was irreversible.

The menhaden *Brevoortia tyrannus* was found to be the most sensitive species tested by Gibson *et al* (1979a), with a LC50 of 12 mg l^{-1}. As individuals approached death, they experienced a loss of equilibrium and lay on the bottom of the tank. Opercular movement gradually decreased until it eventually stopped. Ward and Parrish (1980) conducted a 28 day (chronic) early-life stage test with the sheepshead minnow *Cyprinodon variegata* to determine the toxic effect of bromoform to embryo and juvenile growth and mortality. The results show that juvenile mortality was a more sensitive indicator of toxicity than the hatching success of embryos, whereas growth appeared to be comparatively non-sensitive. The lowest concentration resulting in juvenile mortality was found to be < 24 mg l^{-1}.

B34.5 Bioaccumulation

Chlorine and bromine

There are no available data on the bioaccumulation of bromine or bromamines in saltwater organisms. However, CCREM (1987) concluded that, for freshwater organisms, since chlorine and chloramines do not appear to have any potential for bioaccumulation or bioconcentration, it is reasonable to assume that this is probably the same for bromine and bromamines. Additional data are needed to confirm this. In addition, the reaction of residual oxidants with organic substances may yield brominated organic compounds which may well bioaccumulate.

Chloroform and bromoform

Bioaccumulation data for chloroform are contradictory and it appears that slight to moderate bioaccumulation may occur in some aquatic organisms. Based on the available bioaccumulation studies and estimated BCFs, bromoform appears to have a low potential for bioaccumulation.

Chloroform is highly volatile and has a relatively low octanol/water partition coefficient (log Kow = 1.97) Consequently, the bioaccumulation potential is expected to be relatively low and this is illustrated by the low BCFs. An estimated BCF of 18 was derived by Veith *et al* (1979) for fish and invertebrates. However, Mailhot (1987) calculated a bioconcentration factor (BCF) of 690 for the green alga *Selenastrum capricornutum*. For bluegill sunfish, channel catfish, largemouth bass and rainbow trout, BCFs ranged from 1.6 to 10 after a 1 day exposure (Anderson and Lusty 1980).

Concentrations of up to 180 µg/kg wet weight have been reported (Pearson and McConnell 1975, cited in Oakley 1988). For *Cerastoderma edule* (cockle) from Liverpool Bay, concentrations as high as 150 µg/kg (wet weight) have been obtained, compared with a maximum measured water concentration of 1 µg l^{-1} in the bay. This would indicate a BCF of around 150.

Bioaccumulation potential of the trihalomethanes appears to be low, compared to many chlorinated organic compounds. Gibson *et al* (1979b) conducted 28 day uptake and depuration tests on five commercially and recreationally important species. These included three species of Penaeid shrimp and one species of fish. The authors found that both uptake and depuration were rapid, with an equilibrium reached after 24 hours. Bioconcentration factors were relatively low (between <1 and 10 times the water concentration). For example, experiments using the marine oyster *Crassostrea virginica* have shown that exposure to 90 µg l^{-1} bromoform for 24 hours resulted in a bioconcentration factor of 7.6. Uptake and depuration of bromoform were both rapid, both being essentially complete in 24-48 hours. However, it was concluded that the rate of uptake and depuration was dependent on the individual, the species and the concentration of bromoform in the water.

B34.6 Potential effects on the interest features of European marine sites

Potential effects include:

! toxicity of chloroform to invertebrates (in particular molluscs) at concentrations above the EQS of 12 Fg l^{-1};

! where chloroform is likely to form in the water column, confirmation that bioaccumulation in invertebrates, fish, birds and Annex II sea mammals should be sought.

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B35. Benzene

B35.1 Entry into the marine environment

Benzene (C_6H_6) is a liquid at room temperature and pressure, is soluble in water (720-2,200 mg l^{-1} variously reported, with probable typical values in freshwater of 720 mg l^{-1} and in seawater of 1,224-1,550 mg l^{-1}), has a low to moderate log Kow value (2.13) and is highly volatile.

Production of benzene is associated primarily (>90%) with the petrochemical industry, with a smaller proportion produced as a by-product of coke production and small quantities derived from natural gas. Benzene is produced widely in the EC at high tonnage, including in the UK. Annual UK production was variously estimated around 690-1,025 Ktonnes during 1988-1990, with estimated annual capacity around 1,210 Ktonnes (Nielsen *et al* 1991) to 1,405 Ktonnes, at six sites (ChemInform 1992). The UK is a net exporter, with estimated usage in 1988-1990 of 694-879 Ktonnes (Nielsen *et al* 1991).

Most benzene is used as a constituent of BTX (benzene-toluene-xylene) in vehicle, aviation and other fuels, where benzene is used to increase the octane rating. This use has increased globally with the widespread introduction of unleaded petrol and the increasing use of vehicular transport in developing nations. However, in the EC and elsewhere, the benzene content of fuels is now coming under closer scrutiny and control. Benzene is limited to 2% by volume in leaded and unleaded fuel in the UK (i.e. below the 5% permitted by EU legislation). The other major area of use is as an intermediate in chemicals manufacture, particularly in the production of styrene, cyclohexane, ethylbenzene, nitrobenzenes and cumene. Benzene has also had widespread use as a solvent, although this is now declining and is probably insignificant in the UK; it is no longer regarded as a commercial solvent by the UK Hydrocarbon Solvent Association (Hedgecott and Lewis 1997).

During production and use, benzene is released primarily to the atmosphere, although it is quite mobile between environmental compartments. The principal anthropogenic releases of benzene include:

- accidental and deliberate release of crude oils and petrochemical products (including during refining of crude oils and distribution and use of products);

- production of benzene and derivative chemicals; exhaust emissions from fossil fuel combustion; and

- emissions from coal tar distillation plants and coal processing plants.

Entry into water may be direct or via atmospheric deposition, run-off and leaching. Low but significant levels may also arise from releases from natural sources, such as vegetation and fossil fuels.

B35.2 Recorded levels in the environment

Benzene has been reported in oceans, estuaries, precipitation, rivers, groundwaters, potable sources and drinking water, as well as aquatic sediments and biota (Jones *et al* 1990, Nielsen *et al* 1991). High usage and release, high mobility in the atmosphere, and natural sources all contribute to widespread occurrence in waters. Many of the data are for estuarine and coastal waters, with benzene apparently detected in relation to both industrial discharges and releases during oil extraction and transport. However, Hedgecott and Lewis (1997) concluded that none of the reported average concentrations in surface waters exceeded the proposed annual average EQSs of 30 µg l^{-1} benzene in fresh and salt waters.

In the North-East region of the Environment Agency, 23% of 823 river and estuary samples over the period 1993-95 contained benzene, with a mean concentration of under 2 µg l^{-1} and highest concentrations of 312 and 54 µg l^{-1} (the only values that were higher than the proposed EQSs). Only one of 26 seawater samples contained detectable benzene (Hedgecott and Lewis 1997).

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. However, benzene was not monitored in either survey.

The available data suggest that, while benzene has been detected in UK coastal and estuarine waters, in general, concentrations do not exceed relevant quality standards derived for the protection of saltwater life.

B35.3 Fate and behaviour in the marine environment

Hedgecott and Lewis (1997) reviewed data on the fate and behaviour of benzene. Benzene appears to be susceptible to microbial degradation by a variety of species. Mixed aerobic cultures have been reported to degrade benzene, with half-lives as low as 15-20 hours up to a few days or more depending on the source of the inoculum and the history of pre-exposure. Degradation in pure aerobic cultures of a variety of bacterial species has also been reported, with *Pseudomonas* spp. apparently being the major environmental degraders. Anaerobic degradation can potentially occur but is apparently subject to a long lag period (of the order of 20 weeks) and is nitrogen-limited. Without additional nitrogen, degradation has been reported to take six months to three years.

Only a low to moderate tendency to sorb to organic solids is suggested by the log Kow value of 2.13 and log Koc value of 1.91. In surface waters, only small amounts of benzene will sorb to aquatic sediments (Hedgecott and Lewis 1997).

Benzene is very volatile and is probably the major single removal process in most surface waters, particularly under conditions unfavourable to biodegradation. Theoretical volatilisation half-lives of 37 and 290 minutes have been calculated for a 1 m deep water column with completely mixed water and still water respectively. The importance of mixing in increasing the rate of volatilisation has also been demonstrated in experimental mesocosms, with half-lives of 13 days in winter (well mixed) but 23 days in spring (less well mixed) (Hedgecott and Lewis 1997).

B35.4 Effects on the marine environment

B35.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of benzene to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Hedgecott and Lewis 1997). The most sensitive groups of organisms have been identified.

Hedgecott and Lewis (1997) reviewed data on the aquatic toxicity of benzene. In a previous review (Jones *et al* 1990), the authors found that saltwater data were primarily derived from tests using static exposure conditions and nominal exposure concentrations, and there were some concerns that these would under-estimate benzene's toxicity. Most of the information was derived from acute studies, and the lowest reliable data were acute LC50s of 4.9 mg l^{-1} for sockeye salmon *O. nerka* and 5.5 mg l^{-1} for Dolly Varden char *Salvelinus malma*. These results were based on analysed benzene exposures and were, therefore, considered to be reliable. However, Jones *et al* (1990) recommended that further research with echinoderms (which were found to be potentially sensitive) should be undertaken.

Additional data for bacteria (one species), invertebrates (five species) and fish (two species) were summarised by Hedgecott and Lewis (1997). All from acute studies, apart from one chronic study with an edible crab *Scylla serrata* . This appeared to be the most sensitive organism under acute exposure, with 72 hour LC50s of 3.3 and 4.6 mg l^{-1}, depending on reproductive status. In the chronic study, biochemical changes were seen when exposed for 3-30 days to 0.56 mg l^{-1} or higher. However, their reliability was uncertain (Hedgecott and Lewis 1997). The lowest toxicity data based on analysis of benzene are a 96 hour LC50 of 9.03 mg l^{-1} for the sole *Solea solea*. No data for sediment dwelling organisms could be located.

B35.5 Bioaccumulation

Data summarised in Jones *et al* (1990) for freshwater and saltwater studies were limited, but indicated that bioaccumulation of benzene was not significant, with maximum BCF values of 225 in fresh waters and 135 for salt waters. Few additional bioaccumulation data were available for Hedgecott and Lewis (1997), but they do not indicate higher bioaccumulation potential than that indicated previously.

B35.6 Potential effects on the interest features of European marine sites

Potential effects includes:

- Toxicity of benzene to invertebrates and fish at concentrations above the EQS of 30 Fg l^{-1} (annual average) in the water column.

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B36. Biphenyl

B36.1 Entry into the marine environment

Until the mid-1970s, biphenyl was used extensively in the manufacture of polychlorinated biphenyls (PCBs). The subsequent banning of PCBs meant that biphenyl's primary use was as a dye carrier in the textile industry. Barry and Wilkinson (1994) reviewed the data on biphenyl, but were unable to locate data on amounts used in the UK. However, in 1976 in the US, approximately 50% of the biphenyl manufactured was used as a dye carrier (Weaver 1979). The US EPA (1976) estimated that the market for biphenyl as a dye carrier would remain static or even increase by 1985. Other uses of biphenyl include:

- as a heat transfer agent, a market that was expected to remain static throughout the 1980s;
- as an impregnate in citrus fruit wrappers where it acts as a mild fungicide, a shrinking market given the increased efficiency of fruit transport; in the manufacture of plasticisers; and
- in optical brighteners (Weaver 1979).

Biphenyl is also a by-product of several important industrial processes, notably in: the manufacture of high octane motor and aviation fuels; catalytic cracking to form lighter gasoline components; and as a high boiling point component of coal tar, a component that is often used in the manufacture of creosote.

Little information is available on the volume of biphenyl produced annually. EC production was reported as >10,000 tonnes/year in 1985 (SRI 1985) and appeared to be confined to two manufacturers in Germany. No production was reported in the UK.

Biphenyl is a component of creosote, a substance that has widespread applications as a weather proofing agent for wood. Much of the biphenyl present in the creosote may, potentially, be leached to the aquatic environment or volatilised to the atmosphere. The other main threat to the aquatic environment is likely to be from by biphenyl being leached from landfills. For example, biphenyl may be present as a by-product in the wastewater produced during the manufacture of naphthalene feedstocks and hydrocarbon fuels.

Biphenyl's range of uses suggests that release to the aquatic environment from both point and diffuse sources will be of primary concern. However, few data exist to quantify biphenyl's presence therein.

B36.2 Recorded levels in the marine environment

Barry and Wilkinson (1994) found few data on the presence of biphenyl in the environment, partly because biphenyl is often present in complex organic matrices that are difficult to resolve and quantify.

The authors found no reported concentrations of biphenyl in the UK environment, although its presence in the River Thames was reported in a European Council document (CEC 1979).

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. However, biphenyl was not monitored in either survey.

At present, there is insufficient information to compare expected environmental concentrations with toxicity data or environmental standards.

B36.3 Fate and behaviour in the marine environment

The US EPA (1976) suggests that any biphenyl released to the aquatic environment will be rapidly removed (mainly by volatilisation). Mackay (1975) investigated the evaporation of low-solubility contaminants from water bodies to the atmosphere. The half-life of biphenyl in water 1 m deep was estimated to be 7.5 hours. It was reported that, for depths greater than 1 m, the half-life would be expected to increase. However, based on its low solubility ($0.37x10^{-1}$ g cm^{-3}) and log Kow of 3.9, it is probable that some adsorption to suspended solids or sediments will occur.

B36.4 Effects on the marine environment

B36.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of biphenyl to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Barry and Wilkinson 1994). The most sensitive groups of organisms have been identified.

Barry and Wilkinson (1994) reviewed data on the toxicity of biphenyl to saltwater organisms. Limited data were available, although the authors concluded that sensitivity was likely to be similar to that observed for freshwater organisms, with crustaceans and fish exhibiting greatest sensitivity.

Abernethy (1986) reported that the 24 hour LC_{50} for *Artemia* sp. was 4 mg l^{-1}using nominal concentrations in a closed system. Donkin (1989) investigated the effect of biphenyl on the rate of feeding of the mussel *Mytilus edulis* obtained from an intertidal zone. The effect was expressed in terms of the biphenyl concentration in water and tissue required to reduce the feeding rate by 50%, the WEC50 and TEC50. The reported WEC50 and TEC50 were 0.30 mg l^{-1} and 15.6 mg kg^{-1} respectively.

Dill *et al.* (1982) reported a 96 hour LC50 for biphenyl on sheepshead minnow *Cyprinodon variegatus* of 4.6 mg l^{-1} using nominal concentrations in open containers. No data could be located for sediment dwelling organisms.

B36.5 Bioaccumulation

Barry and Wilkinson (1994) found no data on the bioaccumulation of biphenyl in the marine environment.

However, they did report a study by Neff (1976) who investigated the accumulation and release of petroleum derived aromatic hydrocarbons by marine animals. An oyster *Crassostrea virginica* was shown to contain a concentration of 0.3 ppm of biphenyl in its tissue after being exposed to a fuel oil (1% oil in water) for 8 hours under flow through conditions. After removal of the oyster to uncontaminated seawater, the concentration of biphenyl in the tissue had fallen to 0.1 ppm after 5 days and to background amounts after 28 days. The experiment was repeated with a clam *Rangia cuneta*. After 8 hours exposure to the fuel oil contaminated seawater, the clam was observed to contain a concentration of 0.1 ppm of biphenyl in its tissue. This was removed in less than 3 hours in uncontaminated seawater suggesting that bioaccumulation is unlikely to be a problem.

The US EPA (1976) suggested that biphenyl was a hydrophobic substance and had a moderate tendency to accumulate in sediment and biota.

B36.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxicity of biphenyl to invertebrates and fish at concentrations above the EQS of 25 Fg l^{-1} (annual average) in the water column.

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B37. 4-chloro-3-methyl phenol

B37.1 Entry into the marine environment

The principal use of 4-chloro-3-methyl is as a general biocide to prevent micro-organisms degrading organic material. More than 50% of the production volume of 4-chloro-3-methyl phenol is used in metal working fluids. These fluids, used to lubricate and cool during metal grinding or in plant machinery, are rich in proteins which provide a source of nutrition for bacterial growth. The other major use is as a pharmaceutical preservative. For example, hand and body creams containing organic compounds in an aqueous phase may contain 4-chloro-3-methyl to prevent micro-organisms degrading the ingredients (Dixon *et al* 1997).

4-chloro-3-methyl phenol is authorised for use (according to Article 4 of Directive 91/414/EEC on the placing of plant protection products on the market, CEC (1991)) as fungicide in plant protection products in Ireland. However, its use as an agricultural fungicide has not been reported in the UK .

Other minor uses reported are as a disinfectant, in external germicides, as a preservative for cosmetics, medications, glues, gums, paints, inks, textile and leather goods. In medicine and veterinary medicine, use of 4-chloro-3-methyl phenol has been reported as a topical antiseptic (HSDB 1996).

Environmental release of 3-methyl-4-chloro phenol may occur from product formulation waste waters and by the use and disposal of products containing 4-chloro-3-methyl phenol, such as metal working fluids and pharmaceutical products.

B37.2 Recorded levels in the marine environment

Dixon *et al* (1997) provided data from the Environment Agency on concentrations of 4-chloro-3-methyl phenol in UK marine waters from the North-West.

The average for 1995 in marine and estuarine waters was 0.3 µg l^{-1} (a high of 0.6 µg l^{-1}) (it should be noted that these annual average concentrations may be artificially low due to the treatment of <LOD results as zero, particularly when the LOD is high).

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. However, 4-chloro-3-methyl phenol was not monitored in either survey.

Available monitoring data are very limited and can be considered insufficient for a comparison to be made with expected environmental concentrations and toxicity data or environmental standards.

B37.3 Fate and behaviour in the marine environment

In water, 4-chloro-3-methyl phenol will not hydrolyse to any significant degree. However, as the pH of the water becomes more alkaline, the phenolic group will dissociate increasingly. Photolysis is an important fate process for this compound in water, half-lives of 3.3 hours under a mercury vapour lamp to 46 hours under sunlight have been reported. Although biodegradation is not as important a fate mechanism in water as it is in soil, it is still significant with reported half-lives ranging from days to weeks. Sorption to suspended or bed sediments is likely to be limited (log Koc and Kow of 1.7 and 3.1 respectively) and high water solubility of the compound (4,000 mg l^{-1} at 25°C) (Dixon *et al* 1997).

B37.4 Effects on the marine environment

B37.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of 4-chloro-3-methyl to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Dixon *et al* 1997). The most sensitive groups of organisms have been identified.

Dixon *et al* (1997) were unable to find any reliable data on the toxicity of 4-chloro-3-methyl phenol to saltwater organisms. Until further data become available, it must be assumed they have broadly similar sensitivities as freshwater organisms.

In freshwaters, acute and chronic EC/LC50s of >=1 mg l^{-1} have been reported for algae, crustacea and fish. No data could be located for sediment-dwelling organisms.

B37.5 Bioaccumulation

Dixon *et* al (1997) concluded that bioaccumulation was unlikely to occur.

B37.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxicity to algae, invertebrates and fish at concentrations above the EQS of 40 Fg l^{-1} (annual average) and 200 Fg l^{-1} (maximum allowable concentration) in the water column.

References

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B38. Carbon Tetrachloride

B38.1 Entry into the marine environment

Carbon tetrachloride is a volatile, clear, colourless, heavy liquid. This substance is an ozone-depleting substance and, as a result, its production and use (except for essential uses) within the European Community was due to be phased out by 1st January 1995**.** Carbon tetrachloride production in the United Kingdom has recently ceased and the major use for carbon tetrachloride (production of CFC-11 and CFC-12) is now in decline. The majority of the reported levels of carbon tetrachloride in the environment were measured before these controls were introduced and therefore may not accurately reflect the present situation.

A Coopers Lybrand and Deloitte report for the Department of Trade and Industry (DTI) states that the United Kingdom consumption of carbon tetrachloride was 40,000-50,000 tonnes per annum in 1990 (DTI, 1990). Willis *et al* (1994) estimated that to be far less in 1994 due to the reduction in the production of CFC-11 and CFC-12, which was a major use of carbon tetrachloride.

Most carbon tetrachloride produced is used in the manufacture of chlorofluorocarbons (CFCs). Other recorded uses of carbon tetrachloride include in fire extinguishers, as a grain fumigant, flammability suppressant, solvent, metal degreaser and various roles in the production of paint, plastics, semi-conductors and petrol additives (CEC, 1986). Carbon tetrachloride is used as a chemical intermediate in the manufacture of pharmaceutical and pesticide products. It is widely used as a reagent in laboratories (RSC, 1981).

B38.2 Recorded levels in the marine environment

Carbon tetrachloride is ubiquitous in the global atmospheric and aquatic environments and numerous measurements of carbon tetrachloride levels have been made and reported.

Willis *et al* (1998) found that carbon tetrachloride levels in the atmosphere had been measured extensively (as the atmosphere is acknowledged to be the major sink for carbon tetrachloride). The authors estimated the global background level of carbon tetrachloride to be around 0.7-1.0 Fg m^{-3}.

For UK freshwaters, the authors reported concentrations in the range 0.3-24 Fg l^{-1} (the higher levels generally having been measured near to source dominated areas). Typical levels away from sources of carbon tetrachloride were <lFg l^{-1}.

For UK marine waters, Willis *et al* (1994) reported levels to be between <0.1 - 44 Fg l^{-1}. Again, higher levels were found in source dominated areas. Levels measured in the open ocean were generally much lower, at around 0.5 ng l^{-1}.

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. Only one water column concentration was found to approach the EQS value (see Appendix D). Monitoring data were not available for sediments or biota.

The available data suggest that concentrations of carbon tetrachloride in UK coastal and estuarine waters do not, generally exceed relevant quality standards derived for the protection of saltwater life.

B38.3 Fate and behaviour in the marine environment

Willis *et* al (1994) reviewed the environmental fate and behaviour of carbon tetrachloride. The authors concluded that the major removal process from water bodies was volatilisation to the atmosphere. Laboratory tests have suggested a volatilisation lifetime from water between 29 minutes and a few hours, depending on the degree of agitation (Dilling et al, 1975; Versar Inc., 1979). Zoeteman *et al* (1980) calculated half-life values for carbon tetrachloride in rivers and lakes, and groundwaters of 0.3-3 days and 30-300 days respectively.

Adsorption of carbon tetrachloride onto soil and sediment may occur to a small extent (Organic carbon-water partition coefficient (Koc) of 439 (log 2.6) (Eastwood *et al* 1991)) have been reported for carbon tetrachloride, but carbon tetrachloride is likely to be mobile in such media. Carbon tetrachloride is highly resistant to photolysis and photo-oxidation reactions in the troposphere. The major removal process for carbon tetrachloride in the troposphere is transfer to the stratosphere. Once in the stratosphere, carbon tetrachloride is photodegraded by short wavelength radiation and contributes to ozone depleting processes. The overall atmospheric lifetime for carbon tetrachloride is around 50 years, the lifetime being dominated by the troposphere to stratosphere turnover time.

Carbon tetrachloride does not appear to biodegrade under aerobic conditions. Many bacteria have been shown to dehalogenate carbon tetrachloride under anaerobic conditions.

B38.4 Effects on the marine environment

B38.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of carbon tetrachloride to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Willis *et al* 1994). The most sensitive groups of organisms have been identified.

Willis *et al* (1994) reviewed data on the aquatic toxicity of carbon tetrachloride. No toxicity data appear to be available for marine species of algae. However, for freshwater algae, the lowest toxic concentration of carbon tetrachloride was 105 mg 1^{-1} which caused a reduction in cell multiplication in the freshwater algae *Microcystis aeruginosa*.

For invertebrates, Willis *et al* (1994) only found data for the freshwater crustacean *Daphnia magna* with the lowest acute LC50 reported being 35 mg l^{-1}.

For marine fish, the lowest acute LC50 found was 50 mg l^{-1} for dab *Limanda limanda*. In comparison, for freshwater species, an LC50 of 1.97 mg l^{-1} was reported for the embryo-larval stages of rainbow trout *Oncorhynchus mykiss*. However, the results of this test have been criticised as they are an order of magnitude lower than reported in other studies.

No data could be located for sediment-dwelling organisms.

B38.5 Bioaccumulation

The log octanol-water partition coefficient of carbon tetrachloride is 2.64. This indicates a moderate potential for bioaccumulation under conditions of constant exposure. However, studies cited in Willis *et al* (1994) have shown that the compound's short tissue lifetime reduces this tendency. Barrows *et al* (1980) reported a tissue half-life of less than 1 day for the bluegill sunfish, and a bioconcentration factor of 30. A similar tissue half-life of <l day has been reported for trout muscle (Niimi, 1987) and a steady state bioconcentration factor for rainbow trout of 17.7 has been measured (Neely *et al*, 1974). No significant bioaccumulation in marine food chains was found in an extensive study by Pearson and McConnell (1975).

A slightly higher bioconcentration factor of 300 (on a wet weight basis) has been measured for carbon tetrachloride in the green alga *Chlorella fusco* exposed to 50 Fg l^{-1} of carbon tetrachloride for at least 24 hours (Geyer *et al* 1984).

B38.6 Potential effects on the interest features of European marine sites

Potential effects include:

! toxicity to algae, invertebrates and fish at concentrations above the EQS of 12 Fg l^{-1} (annual average) in the water column.

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B39. Chlorinated Ethylenes

B39.1 Entry into the marine environment

Chlorinated ethylenes are produced in large quantities and widely used in industry in the production of food packaging, synthetic fibres and industrial solvents.

The major route by which chlorinated ethylenes enter the environment is by volatilisation during production and use. Their presence in water may result from a direct discharge or atmospheric deposition. They may also be formed during the chlorination of water. In addition, diffuse inputs chlorinated ethylenes used in food packaging from land fill sites could occur.

B39.2 Recorded levels in the environment

Some information on concentrations in UK marine water is available. Pearson and McConnell (1975) reported concentrations in Liverpool Bay of up to 2.6 Fg l^{-1} (and average of 0.38 Fg l^{-1}). A mean concentration in the range 1-100 ng l^{-1} (highest concentration of 43 Fg l^{-1}) has also been reported for river and estuarine samples of 80 sites in the UK (SAC Scientific 1987).

Marine sediment samples form Liverpool Bay taken in 1972 contained tetrachloroethylene at concentrations of 0.02 - 4.8 Fg/kg (Pearson and McConnel, 1975).

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. Water column concentrations for trichloroethylene and tetrachloroethylene were all found to be below the EQS values (see Appendix D). Monitoring data were not available for sediments or biota.

The available data suggest that concentrations of chloroethylenes in UK coastal and estuarine waters appear unlikely to exceed relevant quality standards derived for the protection of saltwater life.

B39.3 Fate and behaviour in the environment

Chlorinated ethylenes are unsaturated, low-molecular weight C_2 compounds in which one or more hydrogen atoms have been replaced with chlorine. With the exception of monochloroethylene, all chlorinated ethylenes are low-boiling liquids that have high vapour pressures and are moderately soluble in water. Vapour pressures and water solubility decrease with increasing chlorine substitution (CCME 1992).

Volatilisation is considered to be the main removal process from water. For example, the major sink tetrachloroethylene appears to be to the atmosphere, where it undergoes oxidation by reaction with hydroxyl radicals (half-life < 0.4 year). The half-life is sufficiently long, however, to allow a small proportion of the tetrachloroethylene released into the atmosphere to reach the stratosphere (Brooke *et al* 1993).

In addition, evaporative half-lives below 1 hour for chloroethylenes at an aqueous concentration of approximately 1 mg l^{-1} have been reported (Dilling *et al* 1975).

Direct photolysis oxidation and hydrolysis are not considered to be important removal processes. Few data have been found on the degradation of chloroethylenes in the aquatic environment, and what are available suggest that, while some degradation may occur, in general, chlorinated ethylenes are fairly resistant to biodegradation (CCME 1992). In addition, limited sorption capacity has been reported for chlorinated ethylenes (CCME 1992).

For example, Brooke *et al* (1993) reviewed the environmental fate and behaviour of tetrachloroethylene. The authors concluded that the major removal process from aquatic systems appeared to be volatilisation to the atmosphere, with half-lives ranging from a few minutes to a few days, depending on the conditions. Degradation of tetrachloroethylene appears to occur under anaerobic conditions when a suitable carbon source is present. There is less conclusive evidence for degradation of tetrachloroethylene under aerobic conditions.

B39.4 Effects on the marine environment

B39.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of chlorinated ethylenes to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (CCME 1992, Brooke *et al* 1993). The most sensitive groups of organisms have been identified.

CCME (1992) reported that there appeared to be a degree of correlation between the degree of chlorination of ethylenes and toxicity, with tetrachloroethylene more toxic than dichloroethylene. The toxicity of trichloroethylene is intermediate between the toxicities of the dichloroethylenes and tetrachloroethylene.

Data for tetrachloroethylene suggest moderate toxicity to marine plants, invertebrates and fish. For the marine alga *Skeletonema costatum* , 96 hour EC50s value of 509 mg l^{-1} for chlorophyll-A content and 504 mg l^{-1} for cell numbers have been reported (US EPA 1978). Greater sensitivity has been exhibited by *Phaeodactylum tricorntum*, with a 50% reduction in carbon uptake from CO_2 in photosynthesis occurring at a concentration of 10.5 mg l^{-1}.

Pearson and McConnel (1975) reported a 48 hour LC50 of 3.5 mg l^{-1} for barnacle larvae *Eliminius modestus*. For the mysid shrimp *Mysidopsis bahia*, a 96 hour LC50 of 10.2 mg l^{-1} and a chronic value (tested over a whole life stage) of 0.45 mg l^{-1} (US EPA 1980).

For fish, 95 hour LC50 of 5 and >29-<52 mg l^{-1} have been reported for dab and sheepshead minnow respectively.

No data could be located for sediment-dwelling organisms.

B39.5 Bioaccumulation

Brooke *et al* (1993) reviewed data on the bioaccumulation of tetrachloroethylene in aquatic organisms and found low to moderate (generally <100) bioconcentration factors in a variety of aquatic species.

Since most of the chloroethylenes have small octanol/water coefficients, bioaccumulation can be expected to be low.

B39.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxicity of tri- and tetrachloroethylene to algae, invertebrates and fish at concentrations above the EQS of 10 Fg l^{-1} (annual average) in the water column.

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B40. Chloronitrotoluenes

B40.1 Entry in the marine environment

Chloronitrotoluenes are used in the manufacture of dyestuffs, herbicides and fine chemicals, such as chlorotoluidines or dichlorobenzaldehyde. They are not manufactured in large quantities in the EC (Jerman and Young 1992)

Chloronitrotoluenes (CNTs) are mainly used as intermediates and diffuse release into the environment is unlikely. Point source contamination, apart from accidental spillage of chemicals, will be confined to effluent discharges from factories involved in CNT production and use. Consequently, releases into the marine environment are likely to be limited.

B40.2 Recorded levels in the marine environment

No information on concentrations of CNTs in the marine environment could be located.

B40.3 Fate and behaviour in the marine environment

Jerman and Young (1992) found limited information on the fate and behaviour of CNTs. It was concluded that some limited biodegradation may occur. However, volatilisation could be significant and therefore CNTs were not expected to be persistent in the water column. There was also the potential for CNTs to be moderately adsorbed to sediment and suspended solids.

B40.4 Effects on the marine environment

B40.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of CNTs to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Jerman and Young 1992). The most sensitive groups of organisms have been identified.

Jerman and Young (1992) found toxicity data for saltwater life limited to one study, a microtox assay. Therefore, their assessment was based on the toxicity to freshwater life. Again, freshwater data were limited, but CNTs appear to be of moderate to low toxicity to aquatic life, with algae, invertebrates and fish exhibiting similar sensitivities.

B40.5 Bioaccumulation

Estimations of bioaccumulation suggested that moderate bioaccumulation could occur, but further data were required to make a proper asessment of bioaccumulation potential.

B40.6 Potential effects on interest features of European marine sites

Potential effects include:

- potential toxicity to algae, invertebrates and fish at concentrations above the EQS of 10 μg l^{-1} (annual average) and 100 μg l^{-1} (maximum allowable concentration) in the water column;

- given the uncertainty over bioaccumulation, confirmation that bioaccumulation is not occurring should be sought where CNTs are found in the water column;

- some potential for accumulation in sediments and therefore a potential hazard to sediment-dwelling organisms.

References

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B41. Chlorinated paraffins

B41.1 Entry into the marine environment

Chlorinated paraffins (CPs), identified collectively under the CAS number 63449-39-8, are chlorinated linear hydrocarbons with between 10 and 30 carbon atoms. They contain varying numbers of chlorine atoms, with a maximum of one chlorine per carbon. There are an array of commercially available CPs with each CP corresponding to a mixture of isomers and congeners whose carbon skeletons belong to one of three main groups (in terms of chain length) C10-13, C14-17, C18-26. Commercial CPs are usually identified by a trade name followed by a number reflecting the chlorine percentage. Commercial products have a chlorine content of 40 - 70% (Hardie 1964, cited in Howard *et al* 1975).

CPs are physically homogeneous, viscous yellowish liquids or low melting solids. They are described as having a colour ranging from light amber to yellow (the actual shade will depend on the storage conditions and the manufacturing process with the colour darkening with prolonged heating due to the evolution of hydrogen chloride gas) and a slightly unpleasant odour due to the presence of small quantities of lower molecular weight products. CPs with a chlorine content higher than 40% are non-flammable, while those with a lower chlorine percentage will burn with difficulty (Mukherjee 1990).

CPs have similar properties to polychlorinated biphenyls (PCBs), although not as thermally stable, and have replaced PCB compounds in many applications (Howard *et al* 1975). Chlorinated paraffins have a variety of uses, depending on the carbon chain length. Short chain chlorinated paraffins (C10-13) are used as lubricants, additives and sealants, medium chain length (C14-17) as secondary PVC plasticisers and long chain length (C20-30) in paints, lubricants and additives (Campbell and McConnell 1980).

At present, the main uses of chlorinated paraffins are as fire retardants and secondary plasticisers. Secondary plasticisers are used as a substitute for primary plasticisers, such as phthalates, usually through cost considerations. However, the addition of chlorinated paraffins to PVC, for example, also provides flame retardancy whilst maintaining the low temperature properties, e.g. strength of the plastic. Chlorinated paraffins are also used as an additive in cutting oils to improve the surface roughness of the cutting surface.

In the UK, the manufacture of CPs is presently carried out by ICI Chemicals and Polymers Group. ICI has stated that the bulk of their Cereclor production in Europe, some 80 KT annually, is in the UK (approximately 50KT). Of this, about 70% is exported (BRE 1992).

The major source of environmental contamination is more likely to be via the use or disposal of products containing CPs. CPs have a very low volatility and are therefore not expected to be present at any significant level in the atmosphere, although minor inputs into the atmosphere from secondary plasticisers (where the CPs are not chemically bound up into plastics and are thus able to volatilise to some extent) and flame retardant applications may occur.

Chlorinated paraffin containing products such as plastics, building materials and oils are likely to be disposed of in dumps or landfills and, to a lesser extent, by incineration. Due to the relatively low thermal stability of CPs, the latter process should result in the destruction of CP material. Removal of CPs in landfills due to leaching is likely to be slow due to their low water solubility and their high log Kows which infers that CPs becoming dispersed in the environment will tend to be adsorbed onto solids and sediments, thus reducing their availability for uptake by biota. Madeley and Birtley (1980) predicted that the main input of CPs to the aquatic environment was likely to remain adsorbed to the sediment.

It can be concluded that there is unlikely to be a significant input of CPs into the aquatic environment from the atmosphere or via leaching from landfills. Instead, entry is more likely to originate from direct emissions into the aquatic environment via industrial and sewage treatment plant effluents in areas where CPs are used.

B41.2 Recorded levels in the marine environment

Investigations into the environmental concentrations of CPs are currently limited to old studies carried out by Campbell and McConnell (1980).

Campbell and McConnell (1980) investigated the concentration of CPs in the environment and reported concentrations for marine and freshwaters and sediment, using a thin-layer chromatographic technique. This technique enabled the authors to differentiate between CPs of C10-20 and C20-30 chain length but not between 45 and 52% chlorination, nor between C10-13 or C14-17 chain length.

In UK marine waters, CP concentrations were found in the range non-detected to 4 µg l^{-1} for C10-20 CPs and not detected to 2 µg l^{-1} for C20-C30 CPs. CP concentrations in marine sediments from coinciding sites were in the range not detected to 0.5 mg l^{-1} for C10-20 CPs and not detected to 0.6 mg l^{-1} for C20-30 CPs. CP levels in non-marine waters, freshwaters and sediments in industry free areas ranged from 0-1 µg l^{-1} of either CP type. While 65% of samples contained no CPs (almost twice that found for seawaters), when CPs were detected, levels were close to that found in marine waters. Sediment levels in freshwater were also found to be comparable with marine sediments.

Campbell and McConnell (1980) also reported CP concentrations in UK waters and sediments receiving industrial/domestic effluents. CP levels in water were found to be 1-6 µg l^{-1} and 1-10 mg l^{-1} in sediments (CPs of C10-20 chain length predominated).

Campbell and McConnell (1980) investigated CP concentrations in plaice *Pleuronectes platessa* pouting *Trisopterua luscus* mussel *Mytilis edulis* pike *Esox lucius* and the liver and blubber of grey seal *Halichorus grypus*. C20-30 CPs were barely detectable in tissues (a maximum of 0.2 mg/kg) and CPs of C20-30 were seen only at 0.4 mg/kg in organisms from waters not receiving effluent from CP plant effluents. However, mussels from water receiving a CP manufacturing plant effluent had, in general, concentrations of up to 1 mg/kg C10-20 CPs with concentrations of 6 - 12 mg/kg close to the effluent discharge.

When comparing sediment CP levels with aquatic organism tissue levels, Campbell and McConnell (1980) found little or no accumulation. Tissue levels were found to be similar to those in the sediment near where organisms lived. In addition, the authors found no indication of biomagnification in any food chain, aquatic or on land, including the human food chain.

B41.3 Fate and behaviour in the marine environment

Since CPs are heterogeneous (i.e. a particular sample may contain from ten to one hundred different molecular species), the chemical properties of CPs are the average of the chemical properties of the different molecules. The properties vary with the nature of the paraffinic raw materials, the temperature of chlorination and the chlorine content.

Chlorinated paraffins are virtually insoluble in water and lower alcohols but partially soluble in higher alcohols, such as octanol. They are stable mixtures but can undergo slow hydrolysis or dehydrochlorination in aqueous solution. When subjected to high temperature, the substances release HCl. Commercial CPs are often stabilised against decomposition by the addition of small quantities of substances that can act as acid acceptors. The high log Kow values for chlorinated paraffins (Lyman 1982, cited in Mukherjee 1990), calculated log Kows in the range of 5.06 or a CP of formula C10 H18 Cl4 to 12.68 for a CP of formula C26 H44 Cl10) suggest that they will adsorb onto sediments rather than remain in water.

Under ambient and neutral conditions, CPs hydrolyse very slowly (Howard *et al* 1975). The short chain CPs (C10-13) appear to be rapidly degraded by acclimatised micro-organisms. Sewage treatment organisms also brought about significant breakdown of these short chain CPs. For longer chain paraffins chlorinated up to 45%, the biodegradation, although slower and reduced, indicated substantial breakdown by acclimatised organisms. Similarly, a wax-grade CP (C20-30, 42% Cl w/w) was also degraded when organisms were previously acclimatised.

It can be concluded that chlorinated paraffins are chemically stable under ambient temperatures and will not undergo hydrolysis, photolysis or oxidation at any significant rate. Micro-organisms have been found to biodegrade chlorinated paraffins and acclimatisation increases the ability of micro-organisms to degrade long chain CPs. However, the longer the carbon chain in the molecule and the greater the percentage of chlorination, the more recalcitrant the compound.

In view of the highly complex composition of CPs, it is difficult to distinguish between desirable (i.e. straight chain derivatives) ingredients and structurally related compounds (a factor that may be important when investigating the ecotoxicity of these compounds). However, while few investigations into the presence of such impurities have been conducted, available information indicates that their presence is only likely at low concentrations. Stabilisers are frequently added to CPs to inhibit decomposition, especially when the product is intended for elevated temperature use. Stabilisers used cover a wide range of compounds and include: hydrocarbons; alcohols; ethers; epoxy compounds; organometallic compounds; organic nitrogen compounds, and inorganic compounds (Svanberg 1983).

B41.4 Effects on the marine environment

B41.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of chlorinated paraffins to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (BRE 1992). The most sensitive groups of organisms have been identified.

Data on the toxicity of chlorinated paraffins to marine organisms indicate that toxicity increases as the chain size decreases. High sensitivity is exhibited by marine invertebrates and fish exposed to short chain molecules.

Invertebrates

Tarkpea *et al* (1981 cited in Svanberg 1983) reported that the harpacticoid *Nitocra spinipes* appeared more sensitive to short chain than long chain CPs. Reported 96 hour LC50s for short chain CPs range from 0.06 - 9 mg l^{-1}, while for long chain CPs, the 96 hour LC50s are >1,000 mg l^{-1}.

Madeley and Birtley (1980) found no significant mortality in mussels fed for 47 days with dry yeast contaminated with 524 µg/g (dry weight) of Cereclor 42.

Fish

Svanberg *et al* (1978) reported sublethal effects in bleak *Alburnus alburnus* when exposed over a 14 day period to 1.0 and 0.1 Fg l^{-1} of Huls chloparaffin 70C (C10-13, 70%Cl w/w) (added to the test water from acetone solution). Fish showed signs of disorientation and tetanic spasm which may have led to the death of three individuals.

Linden *et al* (1979) also investigated the acute toxicity (96 hour) of CPs to bleak. The tests were carried out under static conditions in brackish water (7 ppt). No renewal, aeration or control analysis of the test solutions was carried out. Nine different trade name CPs were tested, with carbon lengths ranging from C10 - C26 and chlorine percentage ranging from 42 to 71. All 96 hour LC50 were greater than 5,000 mg l^{-1}.

Haux *et al* (1982) reported the effects of the CP preparations Witachlor 149 (C12, 49% chlorine w/w) and Hulz 70C (C12, 70% chlorine w/w) on the haematology, osmoregulation, ionic regulation, intermediary metabolism, hepatic mixed-function oxidase system and steroid metabolising enzymes in male and female flounder *Platichthys flesus* L. in brackish and marine water. CPs were administered orally via a stomach tube. The fish were fed twice (day 1 and day 4) to obtain a total exposure of 1,000 mg kg^{-1} body weight of each CP. Sampling was at 13 and 27 days after the first administration of CP. Witachlor 149 and Hulz 70C caused some sublethal effects, mainly on the haematology, glucose metabolism and xenobiotic and steroid metabolising enzymes of female fish. However, the authors were unable to interpret the physiological and ecological significance of these findings.

B41.5 Bioaccumulation

Svanberg *et al* (1978) investigated the bioaccumulation of Chlorparaffin Huls 70C in bleak. The fish were exposed to concentrations of 0.1 or 1.0 mg CPl^{-1} under semi-static conditions at 10°C in brackish waters (7 ppt) (test solutions were renewed every two or three days). During the experiment, individual fish exhibited signs of neurotoxic effects at the dose of 1 mg CPl^{-1} after 14 days and some mortality occurred at both concentrations. The whole body chlorine content indicated that the CP was taken up but the uptake did not appear to differ significantly between the two concentrations. After 29 days, the mean whole body chlorine content (wet weight) of fish exposed to 0.1 mg CPl^{-1} was 26.2 µg Cl g^{-1} and 28.6 µg Cl g^{-1} for fish exposed to 1.0 mg Cl l.$^{-1}$.

Svanberg (1983) reported some unpublished observations of Tarkpea and Renberg (1982). Mussels *Mytilus edulis* accumulated 14C-labelled C16-chloro-alkane when exposed via water, resulting in a bioconcentration factor of about 6,000.

Campbell and McConnell (1980) concluded from investigations into levels of CPs found in the environment that there was no evidence to suggest that aquatic organisms accumulated CPs to levels above those found in nearby sediments. The authors also concluded that there was no evidence of CP biomagnification through the food chain. However, it appears that CPs of low molecular weight maybe accumulated while those of high molecular weight are not. Madeley and Birtley (1980) proposed that CPs of high molecular weight would be limited in their potential for bioaccumulation in the aquatic environment due to their low water solubility and because their strong tendency to adsorb onto suspended particles would decrease their availability to food-chain organisms. Zitko and Arsenault (1974) concluded that the uptake of CPs decreased or was completely inhibited when the molecular weight of the CP exceeded 600 (this would correspond to a carbon chain length of 24 and a chlorination level just below 50%).

B41.6 Potential effects on interest features of European marine sites

Potential effects include:

- toxicity of chlorinated paraffins (especially short chain, low molecular weight species) to invertebrates and fish in the water column (there is no EQS for chlorinated paraffins);

- accumulation in sediments and a largely unknown potential for low molecular weight chlorinated paraffins to bioaccumulate.

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B42. Chlorophenols (CP) and Dichlorophenols (DCP)

B41.2 Entry into the marine environment

The principal use of the monochlorinated phenols is as intermediates in the synthesis of the higher chlorinated congeners and certain dyes and pesticides. The chief use of 2,4-DCP is as an intermediate in the production of 2,4-D and other herbicides. 2,4-DCP is also used as an ingredient in antiseptics (Grimwood and Mascarenhas 1997).

The main route of entry of 2-, 3- and 4-CP and 2,4-DCP to the aquatic environment is likely to be as a result of discharges from plants manufacturing the compounds or from plants using the compounds as intermediates in the production of higher chlorinated phenols and other products, such as phenoxy herbicides.

Indirect sources include discharges from paper mills, where they are formed as by-products of the bleaching process, as a result of the disinfection of sewage, industrial wastes and drinking water with chlorine, and from the microbial breakdown of agricultural herbicides such as 2,4-D and subsequent run-off/leaching of the products.

Grimwood and Mascarenhas (1997) found that reliable data on the production levels of chlorophenols other than pentachlorophenol were not available in open literature. In 1975, the combined global production of all chlorophenols approached 200 million kilograms. More than half consisted of chlorophenols other than PCP, with 2,4-DCP, 2,4,5-TCP and 2,3,4,6-TCP predominating (WHO 1989). Krijgsheld and van der Gen (1986, cited in WHO 1989) reported European production levels of 4.5 and 9.1 million kilograms for total monochlorophenols and 2,4-DCP respectively (year not stated), while in 1972, total chlorophenol production in the UK was reported to be 1.14 million

B42.2 Recorded levels in the marine environment

Data for 2-CP from the South-West Region of the Environment Agency over the monitoring period 1992 to 1995 indicated that the great majority of concentrations at sites associated with routine monitoring in fresh and saltwaters were less than 0.2 µg l^{-1}.

Residues of all chlorophenol isomers have been detected in aquatic systems (WHO 1989). Generally, residues are present at measurable concentrations in discharges from such sources as manufacturing plants, wood-treatment facilities, municipal waste discharges and in receiving waters adjacent to these sources. Concentrations in other surface waters are more sporadic and usually low, although some isomers have been detected in some of the world's cleanest waters (WHO 1989).

These values are supported by the limited data reported in various other studies. For example, 2-CP, 3-CP and 4-CP have been detected at Fg l^{-1} levels in effluents from European sewage treatment plants and cooling water from power stations as a result of disinfection by chlorination (cited in WHO 1989), while in coastal areas and in rivers flowing through industrialised regions of the Netherlands, Piet and deGrunt (1975, cited in WHO 1989) reported that concentrations of monochlorophenols ranged from not-detected up to 20 Fg l^{-1} and dichlorophenols from not-detected up to 1.5 Fg l^{-1}.

Chlorophenol concentrations in sediments are generally higher than in overlying water. This may be as a result of adsorption onto suspended solids in the water column and subsequent sedimentation. However, very few data are available for mono- and dichlorophenols.

At a site 2 km distant from a sulphate pulp mill, sediments in the Baltic sea were reported to contain a 2,4-DCP concentration of 0.9 Fg kg^{-1} (Xie 1983, cited in WHO 1989), while in a later survey, the same authors reported a sediment concentration of 16 Fg kg^{-1} 2 km from the discharge and 0 Fg kg^{-1} 5-10 km from the discharge.

B42.3 Fate and behaviour in the marine environment

Despite the high solubility of these compounds, some adsorption to the organic carbon content of aquatic sediments may occur as indicated by the moderate octanol-water (Kow) partition coefficients. However, the high solubilities and lower organic-carbon coefficients (Koc) for some soils, suggest that the lower chlorinated phenols may be susceptible to leaching to surface and ground waters. The low Henry's Law Constants for these compounds suggest that volatilisation from surface waters is not likely to be an important removal route (Grimwood and Mascarenhas 1997).

Since chlorophenols are weak acids in aqueous solution, one of the major factors affecting environmental transport, degradation and toxicity is the degree to which the compounds are dissociated in natural waters. Under acidic conditions, chlorophenols exist primarily in the toxic molecular (undissociated) form, while under basic conditions, the dissociated form predominates. The pKa values (pH at which an acid compound is 50% dissociated) of 2-, 3- and 4-CP and 2,4-DCP indicate that at the pH range characterising most physiological and environmental conditions, these compounds will exist predominately in the more active undissociated form. Furthermore, as pH decreases, the proportion of molecules in the undissociated state will increase further, leading to yet higher activity as shown by parameters, such as adsorption to suspended solids and sediments and toxicity.

Chlorophenols are susceptible to photolysis and biodegradation. Photolysis is only expected to be an important process near the surface of water bodies (particularly in summer months). In deeper waters and sediments, aerobic and anaerobic biodegradation will be the main route of removal for chlorophenols. Photolysis of polychlorinated phenols appears to be higher than for monochlorinated congeners. Respective summer/winter half-lives for complete photomineralisation (i.e. breakdown to CO_2) of 6/14 and 53/334 days have been reported for 2,4-DCP and 4-CP in estuarine samples (Hwang and Hodson 1986). The higher rates in summer were attributed to higher irradiance in this season.

2-, 3-, 4-CP and 2,4-DCP all undergo microbial degradation under aerobic conditions via oxidative dechlorination and hydroxylation. Biodegradation is more rapid in sediments (and soils) as a result of more complex/active microbial communities and more favourable environmental conditions in these media (e.g. organic matter content, nutrient status, pH, etc.). The data also suggest that aerobic biodegradation is less rapid for *meta*- (3-) and *para*- (4-) substituted compounds and for the highly chlorinated congeners. This pattern is more apparent on an observation of the whole chlorophenol series from the mono- compounds through the di-, tri- and tetrachlorophenols up to pentachlorophenol. In addition, there is often a lag period associated with chlorophenol biodegradation in water and sediment. Such lag periods are usually attributed to the period required by resident micro-organisms to become physiologically acclimated to toxic compounds or to the period in which small populations of resident DCP degraders increases to large enough numbers, such that DCP biodegradation becomes detectable. In the water column and sediments of aquatic ecosystems, aerobic biodegradation half-lives of 2-36 days have been reported for the monochlorinated congeners at ambient temperatures. Corresponding values of 70-100% biodegradation of 2,4-DCP in 10-30 days have been reported. Some of these values may also incorporate removal by photolysis. Indeed, respective half-lives in estuarine water samples that account for both photolysis and microbial degradation of 4-CP and 2,4-DCP, have been reported to be 10/95 and 4/17 days in summer/winter, respectively.

Under anaerobic conditions in aquatic sediments, chlorophenols are biodegraded by reductive dechlorination (progressive replacement of the chlorines by hydrogen), usually by a consortium of several different microbial species. Under these conditions, *meta*- (3-) and *para*- (4-) substituted congeners appear to be more resistant to biodegradation. Moreover, in the complete mineralisation (i.e. reductive dechlorination to methane) of the higher chlorinated congeners, the breakdown of 4-CP is the rate limiting step. This is shown by values for complete biodegradation of 28-30, 15-61, 61 and 90 days for 2-CP, 3-CP, 4-CP and 2,4-DCP respectively. As with aerobic biodegradation, a lag period is usually associated with anaerobic biodegradation in aquatic sediments.

B42.4 Effects on the marine environment

B42.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of chlorophenols and dichlorophenols to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Grimwood and Mascarenhas 1997). The most sensitive groups of organisms have been identified.

Grimwood and Mascarenhas (1997) reviewed the data on the aquatic toxicity and concluded that saltwater data were considerably more limited than for freshwater organisms, but also that no one group of organisms was more sensitive than any other group. The majority of reported L(E)C50 data ranging from 0.6-19.5, 2.55-29.7 and 5-7 mg l^{-1} for algae, crustaceans and fish, respectively, indicating moderate to high acute toxicity. These data mainly represent 4-CP and 2,4-DCP, with 2- and 3-CP data for fish only. The only long-term exposure data available for saltwater organisms relate to a mesocosm study conducted under field conditions in which a 4-CP and 2,4-DCP concentration of 1.0 mg l^{-1} was found to cause severe inhibition of growth and biomass of natural phytoplankton communities (mixed species) (Kuiper and Hanstevit 1984).

The lowest reported toxicity data for 4-CP include 5-day NOECs, of 0.39 (total cell volume) and 1.08 (total cell count) mg l^{-1} for the diatom *Skeletonema costatum* (Cowgill *et al* 1989), and a 96 hour NOEC (mortality) of 3.2 mg l^{-1} for juveniles of sheepshead minnow *Cyprinodon variegatus*, while the lowest reported data for 2,4-DCP include a 96-hour LC50 and a 72-hour EC50 (growth) of 2.55 and 0.6 mg l^{-1} for the grass shrimp *Palaemonetes pugio* and diatom *Phaeodactylum tricornutum* respectively (Rao *et al* 1981, cited in WHO 1989 and Kusk and Nyholm 1992). Toxicity data for 2- and 3-CP are limited to just one or two fish values, with the lowest being 96-hour LC50s of 6.6 and 4.0 mg l^{-1} for sole *Solea solea* and flounder *Platichthys flesus* respectively (Smith *et al* 1994).

In fish, polychlorophenols appear to be Type II ‘polar’ narcotics. In other words, compounds that cause narcosis associated with a specific mode of action. This has been identified as an uncoupling of electron transport (oxidative phosphorylation) in mitochondria. However, the mechanism of toxicity in invertebrates and of the monochlorophenols appears to be less specific (Grimwood and Mascarenhas 1997).

The toxicity of chlorophenols to aquatic organisms rises with increasing degree of chlorination and substitution away from the *ortho*- (2-) position. The higher toxicity of the more highly chlorinated congeners can be ascribed to an increase in lipophilicity which leads to a greater potential for uptake into the organism. *Ortho*-substituted congeners are generally of lower toxicity than the *meta*- and *para*- substituted compounds, as the close proximity of the *ortho*-substituted chlorine to the OH group on the molecule appears to ‘shield’ the OH, which apparently interacts with the active site in aquatic organisms, causing the observed toxic effects (Grimwood and Mascarenhas 1997).

Toxicity also depends on the extent to which the chlorophenol molecules are dissociated in the exposure medium, with increased toxicity observed with a decrease in pH. This is because the more toxic non-dissociated form predominates at lower pH, while at higher pH, the less toxic dissociated form is predominant. Moreover, the pKa values of 2-, 3- and 4-CP and 2,4-DCP indicate that at the pH range characterising most environmental conditions, these compounds will exist predominately in the more active non-dissociated form.

No data could be located for sediment dwelling organisms.

B42.5 Bioaccumulation

Grimwood and Mascarenhas (1997) concluded that the vast majority of aquatic organisms did not readily accumulate monochlorophenols or 2,4-DCP to high levels, with BCFs in fish ranging from 3.8-34.0 at neutral pH, and depuration half-lives in the order of hours to days. Since toxicity is directly linked to bioaccumulation, Grimwood and Mascarenhas (1997) also concluded that all the issues concerning the effects of degree of chlorination and dissociation on the toxicity of chlorophenols, also related to the uptake and bioaccumulation of these compounds. Therefore, an observation of bioaccumulation data for the whole chlorophenol series would show that the higher chlorinated congeners (e.g. tri-, tetra- and PCP) are accumulated to higher levels, with BCFs ranging from 10^2-10^3.

B42.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxicity of 2-chlorophenol to algae, invertebrates and fish at concentrations above the EQS of 50 Fg l^{-1} (annual average) and 250 Fg l^{-1} (maximum allowable concentration) in the water column;

! toxicity of 2-4-dichlorophenol to algae, invertebrates and fish at concentrations above the EQS of 20 Fg l^{-1} (annual average) and 140 Fg l^{-1} (maximum allowable concentration) in the water column.

- potential for bioaccumulation for the higher chlorinated (tri-, tetra- and pentachlorophenol) compounds in the series.

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B43. Dichlorobenzenes

B43.2 Entry into the marine environment

Dichlorobenzene ($C_6H_4Cl_2$) occurs as three isomers (1,2-DCB, 1,3-DCB and 1,4-DCB) which vary in the relative sites of attachment on the benzene ring of the two chlorine groups. 1,2-DCB and 1,3-DCB are liquids at room temperature and pressure, whilst 1,4-DCB is solid. Solubilities in water are 147, 106 and 83 mg l^{-1} for 1,2-DCB, 1,3-DCB and 1,4-DCB, respectively, and log Kow values (preferred values) are in the range 3.28 to 3.62. Dichlorobenzenes tend to volatilise. Crane and Fawell (1989) and Hobbs *et al.* (1996) both report production and usage volume data for dichlorobenzenes in the 1980s, but more recent figures do not seem to be available in the literature. Hobbs *et al.* (1996) reported that 1,4-dichlorobenzene was no longer produced in the UK, and that imports were probably about 750 tonnes per annum, i.e. a significant (75%) decrease compared to the 1980s as a result of increasing use of replacement chemicals in toilet blocks and other space deodorants.

Industrially, 1,2-DCB and 1,4-DCB are more significant than 1,3-DCB.

Notable uses of 1,2-DCB include as a solvent and degreasing agent in various applications, a chemical intermediate, a fuel additive, a dye carrier in the textiles industry and an active ingredient and production chemical in some pesticides and wood preservative (along with 1,4-DCB as a more minor ingredient). Crane and Fawell (1989) report the principal uses in the UK as production of agrochemicals (50%) and as a dye solvent (50%), but more recent data are not available.

The primary applications of 1,4-DCB are as a space deodorant and as a moth repellent, with more minor uses including a precursor in the production of certain chemicals, as a catalyst in the production of mercapto acids, as a dye carrier, for mould and mildew control and in wood preservative (along with 1,2-DCB). Crane and Fawell (1989) report the principal uses in the UK as moth repellent and space deodoriser (90% combined) and as a chemical intermediate (10%). However, all uses, including as a deodorant and a moth repellent, have declined significantly in the UK. Hobbs *et al.* (1996) indicated that all 1,4-DCB now imported in to the UK were used to manufacture toilet and air deodorants.

The only notable use of 1,3-DCB is as an intermediate in chemical synthesis.

Potential industrial point sources will include aqueous effluent from any industry where dichlorobenzenes are made, formulated, used as process solvents or used as intermediates. A particularly significant diffuse source of 1,4-DCB would be its use as a space deodorant in lavatory systems, with direct release to sewers or other sewerage disposal routes, and the relative importance of this source will have increased with the decline in other uses of 1,4-DCB.

Dichlorobenzenes can also be produced in water by chlorination of raw drinking waters, and a number of authors have reported the consequent presence of all three isomers in supply (although overall Crane and Fawell 1989 concluded that significant production of dichlorobenzenes by chlorination was unlikely).

Production of dichlorobenzenes can result from the biodegradation of higher-chlorinated benzenes already in the environment, either in aquatic systems or with the potential for input into aquatic systems. Dichlorobenzenes have also been reported to be produced during incineration of municipal waste, sewage sludge, fossil fuels and, in particular, chlorinated polymers, such as polyvinyl chloride and chlorinated polyethylenes. In each case, input of dichlorobenzenes to the atmosphere may subsequently result in depositional input to aquatic systems.

B43.2 Recorded levels in the marine environment

The widespread occurrence of dichlorobenzenes in the atmosphere confers the potential for contamination of all associated surface waters, even in the absence of manufacturing or use-related inputs. Based on a theoretical population centre of 1 million people in 100 km^2 using typical amounts of dichlorobenzene, a concentration of 2 µg l^{-1} 1,4-DCB in surface waters was predicted by Rippen *et al.* (1984) (reported in Crane and Fawell 1989). Generally, it was the 1,4-DCB isomer which had been reported at the highest concentrations in surface waters up to 1989, at concentrations from 0.004 to 310 µg l^{-1}, but the 1,3-isomer may be more significant in aquatic sediments (Crane and Fawell 1989).

Studies of fresh and saline waters reported by the Foundation for Water Research (FWR) (1990) similarly indicated concentrations were below the µg l^{-1} level, although concentrations associated with suspended sediment had been reported as high as tens of mg kg^{-1}.

B43.3 Fate and behaviour in the marine environment

The fate and behaviour of dichlorobenzenes has been summarised by Hedgecott *et al* (1998).

Dichlorobenzenes do not demonstrate extremes of aqueous solubility or lipophilicity, but are volatile. Models describing their environmental partitioning indicate that dichlorobenzenes in surface waters will be prone to removal from the water column by volatilisation and also by sorption to particulates which settle out into sediments. Models for environmental volatilisation, and real monitoring data, suggest 50% or more may volatilise from flowing waters in 8 hours to 3 days, whilst this may increase from 3 to 100 days (but mostly less than 30 days) for lakes and seawater mesocosms.

In the atmosphere, dichlorobenzenes may be degraded by chemical- or sunlight-catalysed reactions, and may also sorb to particulates which are subsequently deposited (whilst losses of dichlorobenzenes dissolved in rain are not expected to be significant). A tendency to sorb to organic solids is also suggested by the log Kow values of 3.28 to 3.62 and log Koc values of 2.2 to 3.0.

Different standard aerobic biodegradability tests indicate that dichlorobenzenes can be classified as ‘readily biodegradable’ through to ‘resistant to biodegradation’, depending on the test type and conditions. There do not appear to be any reports of standard anaerobic biodegradability tests. Biodegradation of dichlorobenzenes in aerobic aqueous and soils systems has been widely reported. However, its environmental significance is probably limited, except where volatilisation is impeded. Studies of anaerobic systems (e.g. sediment cores) provide no evidence of biodegradation.

Sorption to suspended solids in surface waters also occurs, and has been reported by Hobbs *et al.* (1996) to result in significant contamination of settled solids by 1,4-DCB following sedimentation.

B43.4 Effects on the marine environment

B43.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of dichlorobenzenes to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Hedgecott *et al* 1998). The most sensitive groups of organisms have been identified.

The available dataset was found to be limited. However, no particular taxa appear to be significantly sensitive to dichlorobenzenes, with the toxicity of the three isomers appearing to be similar.

Crane and Fawell (1989) found the mysid shrimp *Mysidopsis bahia* to be the most sensitive of those species considered with acute LC50 values of 2.0 to 2.9 mg l^{-1} for the three isomers of DCB.

More recent data summarised by Hedgecott *et al* (1998) included a 24 hour LOEC for growth of 1 mg l^{-1} 1,2-DCB for the pacific oyster and with 96 hour 'toxic' effects at 1.28 mg l^{-1} 1,2-DCB, for plaice. However, four species of algae did not grow when exposed for 10 days to 13 mg l^{-1} 1,2-DCB, and it is reasonable to assume that the threshold effects concentration for these species might also be around, or even below, 1 mg l^{-1}.

In an echinoderm reproduction study previously considered by Crane and Fawell (1989), adverse effects were seen at 0.15 mg l^{-1}. However, the ecological implications of the observed pattern of effects were unclear and, therefore, a possible safe concentration could not be determined.

No data could be located for sediment dwelling organisms.

B43.5 Bioaccumulation

Crane and Fawell (1989) reviewed both fresh and saltwater studies and concluded that bioaccumulation of dichlorobenzenes resulted in a maximum BCF value of 1,400 in freshwater organisms (in rainbow trout exposed to 1,4-DCB), with no experimental information for saltwater species (although tentative BCFs between 36 and 280 might be deduced from one particular field study).

Hedgecott *et al* (1998) found that few conventional bioaccumulation data had become available since Crane and Fawell's review, but BCFs can also be determined from a few freshwater tests investigating lethal and non-lethal body burdens of dichlorobenzenes. These data indicate low BCFs (<100) for aquatic plants exposed to 1,2-DCB, higher values (c.600) for *Daphnia* (the only water column invertebrate investigated) exposed to 1,2-DCB and values ranging from 13 to 741 (and 1,800 based on lipid weight) for fish exposed to any of the three isomers.

Generally, these data suggest a similar range of freshwater BCFs as those previously identified by Crane and Fawell (1989). Data for saltwater species are limited to a single study with a species of crab, with a lipid-based BCF of 1,445 determined for 1,4-DCB, implying a similar extent of accumulation as seen in freshwater fish.

B43.6 Potential effects on interest features of European marine sites

Potential effects include:

- toxicity of dichlorobenzenes (sum of all isomers) to invertebrates at concentrations above the EQS of 20 Fg l^{-1} (annual average) and 200 Fg l^{-1} (maximum allowable concentration) in the water column;

- potential for bioaccumulation in saltwater organisms based on information for freshwater organisms.

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B44. Chlorinated Ethanes

B44.1 Entry into the marine environment

Chlorinated ethanes are used as industrial solvents and in the production of other organochlorine compounds. They are also used as dry-cleaning agents, as anaesthetics, in the manufacture of plastics and textiles and in the production of tetraethyllead and vinyl chloride (CCME 1992). Chloroethanes are also formed in small amounts by the aqueous chlorination of effluents.

Potential sources of contamination include direct discharge of wastewaters, accidental spillages and deposition from the atmosphere. Low level contamination of surface water by rainwater was reported by McConnel (1977) who measured the concentration of 1,1,1-TCA in two UK upland reservoirs before and after a period of prolonged rain in November 1974. The concentrations of 1,1,1-TCA in the reservoirs increased from 13 to 21 ppb at one site and from 12 to 41 ppb at the other. The levels occurring in rainwater are low (generally less than 0.1 µg l^{-1}) and it is thought that contamination of surface and groundwater is more likely to result from direct discharge of solvents to water or accidental spills to the ground, rather than by transfer of solvent vapour from the air (Pearson and McConnel 1975).

Information summarised in Rees and Bowen (1992) concluded that major global producers of 1,1,1-TCA included the United States, Western Europe and Japan. For 1983, global production of 1,1,1-TCA was estimated to be 537 ktonne/year. Production of 1,1,2-TCA is thought to be much lower, and was around 80 ktonne/year in 1983 (ECETOC 1988). The consumption of 1,1,1-TCA in Western Europe increased in the 1960s and 1970s as 1,1,1-TCA replaced other more reactive chemical compounds, but has remained fairly constant at around 150 ktonne/year since 1979 (CEFIC 1986). UK consumption was estimated to account for just over 20% of the total European consumption at around 30 ktonne/year in 1984 (CEFIC 1986).

Chlorinated ethanes are low-molecular weight saturated compounds containing two carbon atoms in which one or more hydrogen atoms have been substituted with chlorine. With the exception of hexachlorethane, all chloroethanes are low-boiling liquids, most are relatively volatile and water-soluble. In general, both volatility and water solubility decrease with increasing chlorine substitution. Volatilisation can be considered to be the primary removal process from water (CCME 1992).

Rates of disappearance of around 90% within one to two hours have been reported for both isomers of TCA from slowly stirred water. Similar rates were observed in the presence of natural absorbents, such as limestone and peat (Dilling *et al* 1975).

B44.2. Recorded levels in the marine environment

In saltwater waters, Pearson (1982) estimated typical levels to be around 0.01 µg l^{-1} in offshore areas and 0.15 µg l^{-1} for inshore areas. In Liverpool bay, in an area receiving discharges from 1,1,1-TCA production, levels were much higher at 0.2 to 3.3 µg l^{-1} (Pearson and McConnel 1975).

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. Monitoring data are available for trichloroethane, but no water column concentrations were found to exceed the EQS value (see Appendix D).

The available data suggest that concentrations of trichloroethanes in UK coastal and estuarine water are unlikely to exceed relevant quality standards derived for the protection of saltwater life. Pearson and McConnel (1975) determined the levels of 1,1,1-TCA in a wide range of organisms chosen to represent a wide range of trophic levels. Most of the samples were taken from Liverpool Bay, an area where the main UK organochlorine plants are situated. However, other samples taken from the Thames Estuary, the Firth of Forth and Tees Bay also showed some degree of contamination. The levels of 1,1,1-TCA (in µg/kg wet tissue) are:

!	Plankton	0.03-10.7;
!	Saltwater algae	10-25;
!	Molluscs	0.05-10;
!	Crustacea	0.7-34;
!	Fish flesh	0.7-5;
!	Fish liver	1-15;
!	Water birds eggs	3-30;
!	Water bird liver	1-4;
!	Seal liver	0.2-4;
!	Seal blubber	8-24.

B44.3 Fate and behaviour in the marine environment

Direct photolysis, oxidation and hydrolysis are not expected to be significant removal processes for chloroethanes in the aquatic environment. TCA has been shown to undergo both chemical and biotic degradation, but the long half-lives for the reactions involving both isomers suggest that degradation is not an important loss mechanism from surface water. Little or no degradation of chloroethanes was found during standard BOD (biochemical oxygen demand) bottle test (Pearson and McConnel 1975).

As the lower chlorinated compounds have slight affinities for lipophilic materials, sorption to organic-rich material is considered to be minimal. In laboratory tests, little or no sorption to inorganic or organic material was observed (Dilling *et al* 1975) .

B44.4 Effects on the marine environment

B44.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of chlorinated ethanes to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Rees and Bowen 1992). The most sensitive groups of organisms have been identified.

Rees and Bowen (1992) reviewed data on the aquatic toxicity of TCAs. The authors found few data on the toxicity of 1,1,1-TCA to saltwater life and none of the data were from chronic tests. More data were available for 1,1,2-TCA but most are derived from two studies; Pearson and McConnel (1975) report an LC50 of 5 mg l^{-1} and Craig (1983) cites an unknown response at 0.5 mg l^{-1} of 1,1,1-TCA for the green algae *Phaeodactylum tricornutum* suggesting that the toxicity of 1,1,1-TCA to algae is around 300 times greater in saltwater than freshwater. These results are very low compared to values obtained from similar tests with 1,1,2-TCA in which 96 hour EC50s for growth of 60, 170 and 200 mg l^{-1} were measured for *Phaeodactylum tricornutum*, *Chlorella pyrenoidosa* and *Chlorella ovalis* respectively (Adema and Vink 1981).

Annelids appear to be relatively insensitive to 1,1,2-TCA. Adema and Vink (1981) estimated a 96 hour LC50 of 190 mg l^{-1} for *Ophyrotrocha diadema*. While for three crustacean species, *Artemia salina*, *Crangon crangon* and *Temora longicornis*, 96 hour LC50s of 43 to 52 mg l^{-1} for the adult stage were found for 1,1,2-TCA. Three week tests on *Artemia* larvae estimated an EC50 of 15 mg l^{-1} and a No Observable Effect Concentration (NOEC) of 10 mg l^{-1} both for reproduction.

For 1,1,1-TCA, LC50 values of 7.5 mg l^{-1} for *Elminius modestus* and 31.2 mg l^{-1} for *Mysidopsis bahia* have been calculated (Pearson and McConnel 1975; US EPA 1980).

Fish

Acute LC50s for 1,1,1-TCA in saltwater of 33, 60 and 71 mg l^{-1} have been reported for *Limanda limanda*, *Cyprinodon variegatus* and *Lagodon rhomboides* respectively (Pearson and McConnel 1975; Heitmuller *et al* 1981; Craig 1983). Heitmuller *et al* (1981) also estimated a 96 hour NOEC of 3.5 mg l^{-1} for mortality of *Cyprinodon variegatus*. No data were found on the chronic toxicity of 1,1,1-TCA. Adema and Vink (1981) estimated a 7-day LC50 for 1,1,2-TCA of 43 mg l^{-1} for adult *Gobius minutus*. A lower 7-day LC50 of 27 mg l^{-1} was determined for larval plaice *Pleuronectes platessa*. Chronic data were available only for the egg/larval stages of *Pleuronectes platessa*. No effects were observed on the mortality, growth or development over eight weeks at 3.0 mg l^{-1} 1,1,2-TCA, and an LC50 of 5.5 mg l^{-1} was calculated for the same period.

No data could be located for sediment-dwelling organisms.

B44.5 Bioaccumulation

The potential for bioaccumulation of C1 and C2 hydrocarbons in the field was assessed by Pearson and McConnel (1975). The authors determined the levels of 1,1,1-TCA in the tissues of a wide range of organisms in samples taken from Liverpool Bay (an area where the major organochlorine industries are situated), the Thames Estuary, the Firth of Forth and Tees Bay. They found little evidence to suggest extensive bioaccumulation and transfer to food chains.

With the exception of hexachloroethane, most chloroethanes have low octanol/water partition coefficients. On this basis, only a slight potential to bioaccumulate can be expected.

B44.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxicity of 1,1,1 trichloroethane to algae, invertebrates and fish at concentrations above the EQS of 100 Fg l^{-1} (annual average) and 1,000 Fg l^{-1} (maximum allowable concentration) in the water column;

! toxicity of 1,1,2 trochloroethane to algae, invertebrates and fish at concentrations above the EQS of 300 Fg l^{-1} (annual average) and 3,000 Fg l^{-1} (maximum allowable concentration) in the water column

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B45. Hexachlorobutadiene

B45.1 Entry into the marine environment

Hexachlorobutadiene (HCBD) is a by-product of chemical industries that produce chlorinated hydrocarbons, such as tetrachloroethylene and carbon tetrachloride. It is mainly used as an industrial solvent.

HCBD is considered a List 1 compound and there have been a number of reviews outlining the fate and behaviour and aquatic toxicity of this compound (e.g. WHO 1984 and CCME 1992).

The presence of HCBD in the environment results from anthropogenic sources and occurs as a tarry by-product. Volatilisation and solublisation from this waste are the primary mechanisms for dispersal into and throughout the environment. Waste holding areas and wastewater from industry are likely to be significant source of contamination.

The main pathways of entry into the environment are emissions from waste.

B45.2 Recorded levels in the marine environment

Monitoring data from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D. However, hexachlorobutadiene was not monitored in either survey.

Insufficient data are available to assess expected hexachlorobutadiene concentrations with toxicity data or relevant standards for the protection of saltwater life.

B45.3 Fate and behaviour in the marine environment

Intercompartmental transport will chiefly occur by volatilisation, adsorption to particulate matter, and subsequent deposition or sedimentation. Hexachlorobutadiene accumulates in sediment. Photolysis, oxidation and hydrolysis are not expected to be significant removal processes from the aquatic environment. However, sorption to sediments is considered to be an important mechanism for its removal from the water column.

B45.4 Effects on the marine environment

B45.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of hexachlorobutadiene to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (WHO 1984, CCME 1992). The most sensitive groups of organisms have been identified.

Hexachlorobutadiene is moderately to highly toxic to aquatic organisms.

Fish species and crustaceans have been found to be the most sensitive, 96-h LC50 values ranging from 0.032 to 1.2 and 0.09 to approximately 1.7 mg l^{-1} for crustaceans and fish respectively. In one 28-day early-lifestage test with fathead minnows, reproduction was unaffected at concentrations of up to 0.017 mg l^{-1}, whereas increased mortality and a decreased body weight were observed at 0.013 and 0.017 mg l^{-1}.

B45.4.2 Sediment dwelling organisms

No data appear to be available on the toxicity of HCBD to sediment-dwelling organisms, but given that HCBD may accumulate in sediments, adverse effects on benthic organisms cannot be excluded.

B45.5. Bioaccumulation

The substance has a high bioaccumulating potential which has been confirmed by laboratory and field observations. Average steady-state bioconcentration factors of 5,800 and 17,000, based on wet weight, have been determined experimentally in rainbow trout.

Concentrations of hexachlorobutadiene in aquatic organisms, birds and mammals indicate bioaccumulation but not biomagnification. In polluted waters, levels of over 1,000 µg kg^{-1} wet weight have been measured in several species and 120 mg kg^{-1} (lipid base) in one species. Present levels generally remain below 100 µg kg^{-1} wet weight away from industrial outflows.

B45.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxicity of hexabutadiene to invertebrates (particularly crustacea) and fish at concentrations above the EQS of 0.1 Fg l^{-1} (annual average) in the water column;

! bioaccumulation of hexabutadiene in aquatic organisms, birds and mammals. However, there is little evidence of biomagnification through food chains.

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CCME (Canadian Council of Ministers of the Environment). 1992. Canadian Water Quality Guidelines, prepared by the Task Force on Water Quality Guidelines of the Canadian Council of Ministers of the Environment, Eco-Health Branch, Ottawa, Ontario, Canada.

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B46. PAHs (in general)

B46.1 Entry into the marine environment

Polycyclic aromatic hydrocarbons (PAHs) are a diverse group of aromatic compounds containing two or more fused arenes structures. Commonly occurring PAHs include:

- naphthalene (see Section B47)
- acenaphthalene
- acenaphthene
- fluorene
- phenanthrene
- anthracene
- pyrene
- fluoranthene
- chrysene
- benzo(a)pyrene
- benzo(b)fluoranthene
- benzo(k)fluoranthene
- indeno(1,2,3-cd)pyrene
- dibenzo(a,h)anthracene
- benzo(g,h,i)perylene
- benzo(a)anthracene.

They are formed by the incomplete/inefficient combustion of organic material, diagenesis and biosynthesis. PAHs are usually coloured crystalline solids with high melting and boiling points, low vapour pressures and low water solubilities. In general, it can be concluded that low molecular weight PAHs are more soluble and volatile and have less affinity for surfaces than do high molecular weight PAHs.

PAHs are ubiquitous in the environment, with natural background levels resulting from forest fires, volcanoes and possibly production by some plants. However, a significant fraction of PAHs resulting in the environment are due to anthropogenic sources (e.g. burning of fuel, internal combustion engines etc.). Their widespread occurrence results largely from formation and release during the incomplete combustion of coal, oil, petrol and wood, but they are also components of petroleum and its products. PAHs reach the marine environment via sewage discharges, surface run-off, industrial discharges, oil spillages and deposition from the atmosphere (CCME 1992).

B46.2 Recorded levels in the marine environment

PAHs are ubiquitous environmental contaminants. Although they can be formed naturally (e.g. forest fires), their predominant source is anthropogenic emissions, and the highest concentrations of PAH are generally found around urban centres.

Concentrations of PAHs in the aquatic environment are generally highest in sediment, intermediate in biota and lowest in the water column (CCME 1992).

Monitoring data for water and sediments from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D.

The available data suggest that significant concentrations of PAH can be found in some major estuaries. However, PAH concentrations at offshore sites were generally low or undetectable.

For sediments, while PAH concentrations are generally low or undetectable at most intermediate and offshore sites, further work should be concentrated on fine sediments and depositional areas. Significant concentrations of PAHs were found in a number of estuaries. However, the bioavailability of sediment associated PAHs and potential uptake still need to be further evaluated.

B46.3 Fate and behaviour in the marine environment

PAHs have a low water solubility and hydrophobic nature and so they will tend to be associated with inorganic and organic material in suspended solids and sediments. In general, most PAHs (with the exception of some low-molecular weight compounds, such as naphthalene) will be strongly sorbed by particulate matter and biota in the aquatic environment (CCME 1992).

B46.4 Effects on the marine environment

B46.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of PAHs to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (CCME 1992). The most sensitive groups of organisms have been identified.

The lower molecular weight PAHs can be acutely toxic to aquatic organisms, but the major concern is that some PAHs form carcinogenically-active metabolites (benzo[a]pyrene is the prime example) and PAH concentrations in sediments have been linked with liver neoplasms and other abnormalities in bottom-dwelling fish (Malins *et al.*, 1988, Vethaak and ap Rheinallt, 1992). Elevated PAH concentrations may therefore pose a threat to aquatic organisms and potentially also to human consumers of fish and shellfish (MPMMG 1998).

Environment Canada has issued interim marine sediment quality guidelines (see Section 5.5) which include data for a number of individual PAHs (Table B46.1).

Table B46.1 Interim marine sediment quality guidelines (ISQCs) and probable effect levels (PELs; dry weight) for individual PAHs (from CCME 1999)

Substance	ISQG (Fg kg^{-1})	PEL (Fg kg^{-1})
Acenaphthene	6.71	88.9
Anthracene	46.9	245
Benz(a)anthracene	74.8	693
Benzo(a)pyrene	88.8	763
Dibenz(a,h)anthracene	6.22	135
Fluorene	21.2	144

Substance	ISQG (μg kg^{-1})	PEL (μg kg^{-1})
2-Methylnaphthalene	20.2	201
Naphthalene	34.6	391
Phenanthrene	86.7	544
Pyrene	153	1 398

[1] ISQGs and PELs presented here have been calculated using a modification of the NSTP approach.

These guidelines have been derived for use in Canada and should only be used as an indication of the concentrations of individual PAHs that may affect sediment-dwelling organisms. MPMMG (1998) reported highest recorded concentrations of individual PAHs and National Monitoring Programme sites two orders of magnitude greater than the Canadian guidelines for these substances. **If such concentrations were reported from a European marine site, they should be a serious cause for concern**.

B46.5 Bioaccumulation

Aquatic organisms may accumulate PAHs from water, sediments and food. In general, PAHs dissolved in pore water are accumulated from sediment and digestion of sediment may play an important role in the uptake of PAH by some species. The relative importance of the uptake routes from food and sediment is not known.

The bioconcentration factors of PAH in different species vary greatly (WHO 1998). Species that do not metabolise PAH at all or to only a limited extent, such as algae, oligochaetes and molluscs, and the more primitive invertebrates (protozoans, porifers and cnidaria) accumulate high concentrations of PAHs, as would be expected from their high log Kow values. However, organisms that metabolise PAHs such as fish and higher invertebrates, such as arthropods, echinoderms and annelids accumulate little or no PAHs.

Biomagnification of PAHs through the food chain has been shown to occur to some degree (from annelids to fish for example) but the greater capacity of higher organisms to metabolise PAHs reduces the efficiency of the transfer.

B46.6 Potential effects on the interest features of European marine sites

Potential effects include:

- toxicity of low molecular weight PAHs to aquatic organisms in the water column;
- accumulation in sediments and potential hazard to sediment-dwelling organisms at concentrations between 6 and 150 μg kg^{-1} (dry weight), depending on the individual PAH;
- bioaccumulation of PAHs, especially in algae and lower invertebrates and some biomagnification to higher trophic levels.

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B47. Naphthalene

B47.1 Entry into the aquatic environment and fate

Naphthalene is a polyaromatic hydrocarbon (PAH) with two benzene rings.

A number of reviews on the potential environmental impact of naphthalene have been published, including reports by the United States Environmental Protection Agency (US EPA 1980) and the Commission of the European Communities (Masoero *et al.* 1985); the Building Research Establishment (BRE) (Gavin *et al.* 1996) as have EQSs for the protection of aquatic life (Bates *et al* 1997).

Naphthalene is a non-polar PAH which occurs naturally as a component of coal tar and crude oil and is manufactured for use principally as a chemical intermediate (e.g. phthalic anhydride). It may be found in a wide range of products, including petroleum products, mothballs, wood preservatives, solvents and dyes, and can be released to the aquatic environment by a variety of means (e.g. discharges or spillages from the chemical and petroleum industries, coal gasification plants, atmospheric fallout). The main source of naphthalene in the environment is believed to be vehicle exhaust (naphthalene is a combustion product of motor fuel) (Gavin *et al.* 1996).

B47.2 Recorded levels in the marine environment

In 1995, the Environment Agency routinely monitored the levels of naphthalene in English and Welsh freshwater, saltwater and groundwater systems. Annual average concentrations of 111.9, 429.7 and 329.3 ng l^{-1} respectively, were recorded.

A survey carried out by the Ministry of Agriculture Fisheries and Food (MAFF) in 1993 (and more recently reported in 1998 - see Appendix D) found low levels of PAHs, including naphthalene, in estuaries relatively unaffected by industry or urbanisation. For example, in the Tweed estuary, naphthalene was detected but at a concentration below the limits of detection (<15 ng l^{-1}). The highest concentrations were found in the industrialised Tees and Thames estuaries, with up to 17,300 ng l^{-1} (maximum concentration) occurring in the lower Tees at the Redcar. The high levels recorded in Redcar samples were explained by their proximity to an effluent outfall from a steel works, while the contamination of the Thames estuary was attributed to deposition of PAHs from combustion sources in London. The explanation given for low levels of naphthalene and other PAHs in the Outer Mersey was that PAH pollution is largely carried inland by prevailing winds. In an earlier report, Readman (1982) determined an average naphthalene concentration of 13.9 ng l^{-1} in water and 245 µg kg^{-1} (dry weight) in sediment from the Tamar estuary near Plymouth.

B47.2 Fate and behaviour in the marine environment

When released to the environment, the majority of naphthalene is expected to be released to the air (half-lives in air are generally a few hours). Naphthalene is moderately soluble in water and only moderately adsorbs to soil, sediment or suspended solids. In water volatilisation, adsorption, photolysis and aerobic biodegradation may be important fate processes, depending on local conditions. The half-lives for naphthalene in soil and water range from a few days to a few months (Bates *et al* 1997).

Examination of the reported octanol-water partition coefficients (log Kow 3.01-3.45) suggests that naphthalene is moderately hydrophobic and may thus have a tendency to adsorb to particulate matter (e.g. soil and sediment particles) and accumulate in biota (Bates *et al* 1997).

Contamination of the aquatic environment with naphthalene is most frequently associated with discharges from the chemical and petroleum industries and accidental spillages or leakages of petroleum products to land or water.

B47.4 Effects on the marine environment

B47.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of naphthalene to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Bates *et al* 1997). The most sensitive groups of organisms have been identified.

Bates *et al* (1997) have reviewed data on the toxicity of naphthalene to saltwater species. The authors found the information to be mostly limited to the results of single-species, acute laboratory tests. The majority of toxicity studies reported in the literature tested the effects of concentrations well below the solubility limit (20 mg l^{-1} in seawater) and usually, measures have been taken to minimise losses of naphthalene from the test system due to volatilisation, often with analytical confirmation of exposure concentrations.

Examination of the available toxicity data indicates that naphthalene is of high to moderate acute toxicity to saltwater life, with the majority of effect concentrations ranging from 0.4 to 5 mg l^{-1}. Limited data are available on the effects of chronic naphthalene exposure. However, significant reductions in the reproduction of estuarine copepods have been recorded after chronic exposure to concentrations as low as 0.01 mg l^{-1} and histopathological and physiological damage have been observed in fish *Fundulus heteroclitus* after sub-chronic exposure to 0.02 mg l^{-1}.

No major taxonomic group appears to be significantly more sensitive to naphthalene than any other, although acute effects have been observed for molluscs, crustaceans and fish at concentrations below 1 mg l^{-1}.

B47.4.2 Sediment-dwelling organisms

Bates *et al* (1997) found only one study which investigated the accumulation of naphthalene by saltwater annelids. *Arenicola marina* was exposed to ^{14}C-1-naphthalene via water and sediment and found that the uptake of naphthalene was more rapid when worms were exposed to water only. Accumulation factors of approximately 300 and 160 were reported for the stomach wall and oesophageal glands (the major sites of accumulation) respectively, when worms were exposed to naphthalene dissolved in water. However, almost complete depuration of the accumulated naphthalene was observed after 24 hours. When worms were exposed to labelled naphthalene in sediment, the accumulation factors reported for the stomach wall and oesophageal glands were 4.075 and 0.69 respectively, which indicated that naphthalene adsorbed to sediment was much less bioavailable than dissolved naphthalene.

The bioaccumulation of naphthalene from sediment was investigated for the baltic clam *Macoma balthica* in a laboratory flow-through system. Estuarine sediment was fortified with naphthalene-d_8 and added to filtered seawater (salinity 12.7‰) to give a nominal concentration of 15 Fg g^{-1} organic carbon (1.36% organic carbon). The study results suggest that sediment may be an important source of exposure to benthic estuarine organisms, such as clams.

Environment Canada has recently issued interim marine sediment guidelines (see Section 5.5) and these include a guideline for naphthalene of 34.6 Fg kg^{-1} (dry weight), above which effects on sediment-dwelling organisms may occur.

B47.5 Bioaccumulation

Naphthalene may accumulate significantly in aquatic biota, with the majority of BCFs between 50 and 400. However, there is evidence of metabolism and rapid depuration by invertebrates and fish. When returned to uncontaminated water, naphthalene has been shown to depurate rapidly from both fresh and saltwater invertebrates and fish (from 24 hours to a few weeks, depending on the species, life-stage and exposure concentration) (Bates *et al* 1997).

B47.6 Potential effects to interest features of European marine sites

Potential effects include:

- toxicity of naphthalene to invertebrates and fish at concentrations above the EQS of 5 Fg l^{-1} (annual average) and 80 Fg l^{-1} (maximum allowable concentration) in the water column;

- accumulation in sediments and potential hazard to sediment dwelling organisms at concentrations greater than 34.6 Fg kg^{-1} (dry weight);

- bioaccumulation of naphthalene in aquatic biota.

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B48. PCBs

There is a vast amount of information in the open literature on the fate, behaviour, toxicity and bioaccumulation of PCBs in the aquatic environment . This profile only presents an outline of the data available, and the reader is directed to more extensive reviews such as US EPA (1984), CCME (1992) and WHO (1993) for a more detailed explanation of the data and reported values.

B48.1 Entry into the marine environment

Polychlorinated biphenyls (PCBs) are mixtures of aromatic chemicals, manufactured by the chlorination of biphenyl in the presence of a suitable catalyst. The empirical formula for PCBs is $C_{12}H_{10-n}Cl_n$ where n may be any value from 1 to 10. PCBs with 5 or more chlorine atoms per molecule are referred to as ‘higher chlorobiphenyls’ and are relatively more persistent in the environment that ‘ lower chlorobiphenyls’ which have four or fewer chlorine atoms.

Individual PCBs (commonly referred to as congeners, e.g. PCB 153) vary widely in their physical and chemical properties, according to the degree and position of chlorination. Most PCBs are slightly soluble in water and the solubility decreases with chorine content. Estimates of PCB solubility range from 2.7 to 15,000 Fg l^{-1} (CCME 1992).

PCBs have been widely used in industrial applications in view of their excellent thermal stability, strong resistance to both acid and base hydrolysis, general inertness, solubility in organic solvents, excellent dielectric properties, resistance to oxidation and reduction and nonflammability (CCME 1992).

PCBs can be considered to be among the most ubiquitous and resistant pollutants in the global ecosystem.

The principal route of PCB transport to the marine environment is from waste streams to receiving waters, downstream movement by means of solution and re-adsorption onto particles and by the transport of the sediment itself, until eventually reaching estuaries and coastal waters. The marine environment appears to be the ultimate and major sink for PCBs (CCME 1992).

B48.2 Recorded levels in the marine environment

WHO (1993) stated that in the oceans, levels of 0.05 - 0.6 ng l^{-1} have been found.

Monitoring data for sediments and biota from the National Rivers Authority and the National Monitoring Programme Survey of the Quality of UK Coastal Waters are presented in Appendix D and indicate some elevated levels in certain estuaries.

B48.3 Fate and behaviour in the marine environment

In the aquatic environment, PCBs are usually found in much higher concentrations in sediments than in the overlying water. PCBs have a high affinity for suspended solids, especially those higher in organic carbon. This is supported by their low water solubility and high octanol/water partition coefficients (calculated Log Kow values range from 3.76 for biphenyl to 8.26 for decachlorobiphenyl) (CCME 1992).

PCBs, with the exception of some lower-chlorinated compounds, have low volatility and are soluble in organic solvents, particularly hydrocarbons. Temperatures in excess of 1,000^{O}C are required for their complete combustion.

Sorption to sediments is the predominate mechanism removing PCBs from the water column. Individual PCBs vary widely in their susceptibility to biodegradation. PCBs with three or fewer chlorine atoms per molecule can be biodegraded by many organisms, whereas these with 5 or more chlorines are resistant to biodegradation and biotransformation. In general, PCB congeners have a low solubility in water, and high octanol-water partition coefficients, bioaccumulation potential, and resistance to biodegradation. The physical and chemical properties of PCBs cause their removal from water by sorption to suspended particles and bottom sediments (CCME 1992).

B48.4 Effects on the marine environment

B48.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of PCBs to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (WHO 1993). The most sensitive groups of organisms have been identified.

With regard to direct toxicity, WHO (1993) reported that results had been extremely variable with no consistent relationship between percentage chlorination or environmental conditions and toxicity. Over 96 hours, under static conditions, LC50 values have ranged between 12 Fg l^{-1} to >10 mg l^{-1} for various aquatic invertebrate species. Flow-through studies showed increased toxicity. WHO (1993) reported a similar variation for PCB mixtures for fish with 96 hour LC50s varying between 0.008 and >100 mg l^{-1}. Long-term tests have shown that acute exposure, particularly in static conditions, considerably underestimates the toxicity of PCBs.

WHO (1993) also reported that for birds fed PCBs in their diet, there was evidence of egg-shell thinning, while for sea mammals, there was evidence that PCBs reduce their reproductive capacity. The main effect is on the implantation of the embryo but there can be physical changes to the female reproductive tract. Consequently, PCBs have been identified as an endocrine disrupting group of substances (see Section 4.2.3).

Accumulation of PCBs in sediments poses a potential hazard to sediment-dwelling organisms. Environment Canada has recently issued interim marine sediment quality guidelines (see Section 5.5) and these include a guideline of 21.5 Fg kg^{-1} (dry weight) of total PCBs above which effects on sediment-dwelling organisms may occur.

B48.5 Bioaccumulation

The main concern over PCBs is their high bioaccumulation capacity.

PCBs are soluble in the lipids of biological systems and therefore tend to be bioaccumulated in fatty tissues (especially the higher chlorobiphenyls). BCFs of 200,000 and greater have been reported for fathead minnows *Pimephales promelas* (Duke 1971 and Neely 1977) and pink shrimp (Klien and Weisgerber 1976) and up to 1,000,000 in other organisms. Relatively low concentrations of PCBs in the aquatic environment can result in the accumulation of relatively high PCB levels in biota.

WHO (1993) quoted experimentally determined BCFs in various aquatic species, ranging from 200 to 70,000 or more. In the open ocean, there is bioaccumulation of PCBs in higher trophic levels with an increased proportion of higher chlorinated biphenyls in high-ranking predators.

The presence of high concentrations of PCBs or their residues in marine mammals have been suggested as the cause of (or contributing towards) pathological changes and reproductive failures in Baltic seals (Helle *et al* 1976), sealions, seals and beluga whales (Addison 1989); immunity suppression (and hence the possibility of being more susceptible to disease) in harbour porpoises (Kuiken *et al* 1994) and seals (Reijnders 1986; Swart *et al*, 1994); changes in the development stability of the Baltic grey seal (Zakharov and Yablokox 1990); and premature pupping in California sea lions (Delong *et al* 1973).

B48.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxicity of PCBs to invertebrates and fish in the water column;

! accumulation in sediments and potential hazard to sediment-dwelling organisms at concentrations greater than 21.5 Fg kg^{-1} (dry weight) of total PCBs;

! bioaccumulation of PCBs in fish, birds and Annex II sea mammals with known sublethal toxicological effects;

! endocrine disruption in birds and sea mammals posing a hazard to populations of these animals.

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B49. Phthalates

B49.1 Entry into the marine environment

'Phthalates' is the generic name given to esters of 1,2-benzenedicarboxylic acid. Although some 27 phthalate esters are manufactured, only a limited number are produced in large quantities.

A review by Lewis *et al* (1998) identified a number of phthalates of particular interest in terms of their environmental fate and behaviour or because they were on the High Production Volume Chemicals List from the EC:

- dimethyl phthalate (DMP);
- diethyl phthalate (DEP);
- two isomers of dibutyl phthalate (DBPs);
- di-iso-butyl phthalate (DIBP) and di-n-butyl phthalate (DNBP);
- butylbenzyl phthalate (BBP);
- dicyclohexyl phthalate (DCHP) and three isomers of dioctyl phthalate (DOP);
- di-n-octyl phthalate (DNOP), di-iso-octyl phthalate (DIOP) and di-2-ethylhexyl phthalate (DEHP)

Phthalates are esters of 1,2-benzoldicarbonic acid (ortho-phthalic acid). The chemical structure of phthalates can be characterised by a planar aromatic ring with two slightly mobile side chains. For phthalates, in general, side chains are mainly alkyl groups with a secondary role played by allyl, benzyl, phenyl, cycloalkyl and alkoxy groups. With alkyl phthalates, a further distinction can be made between branched and unbranched side chains.

In the early 1980s, annual, world-wide production of phthalate esters was estimated to be 20 million tonnes (Schmitzer *et al,* 1988), although it may now be closer to 5 million tonnes (Lewis *et al* 1998). The total consumption of phthalate esters in the UK was estimated to be 122,000 tonnes in 1989, of which 54% was DEHP and DIOP (Brooke *et al* 1991).

Phthalates esters are manufactured world-wide on a large scale, being mainly produced for use as plasticisers in resins and polymers, especially as a softener in PVC (87% of the total production of phthalates is used for this purpose).

Phthalate esters are widely distributed in the environment because of their properties and their common usage as plasticisers. Potential sources by which phthalates may enter the aquatic environment are widely thought to be through:

- release via wastewater from production and processing activities, including losses during phthalate ester synthesis, resin and plasticiser compounding, fabrication of PVC into products, and during the production of adhesives and coatings;

- release from use and disposal of materials containing phthalate esters, including losses of plasticiser during the lifetime of products or during incineration or landfilling of refuse and other waste.

B49.2 Recorded levels in the marine environment

Phthalates can be considered to be ubiquitous in the environment and there are many studies which have investigated and reported environmental concentrations of these substances. While a few studies have been carried out in the last few years, the majority of available studies are between 10 and 20 years old. Lewis *et al* (1998) have collated a number of these studies which are summarised below.

It should be noted that contamination during collection and analysis can lead to spurious results and recorded environmental levels where due precautions have not been taken may well be in error.

Data on the concentrations of phthalate esters in environmental samples mainly focus on levels of DEHP, reflecting its predominant usage. Reported levels of DEHP in water samples from rivers in the UK, Sweden, USA and the Netherlands are all within the range 0.3 - 1.6 Fg l^{-1}(Fatoki and Vernon 1990), with levels in coastal, marine and estuarine waters between <2 ng l^{-1} and 335 ng l^{-1}. DOPs are the most hydrophobic of the phthalate esters on the HPVCs List and have been detected in river-bed sediments at concentrations between 0.1 - 1,700 mg kg^{-1}, depending on whether the samples were collected from clean or contaminated sites. For example, contaminated sediment collected from the Mersey Estuary contained up to 1,700 mg kg^{-1} of DEHP (Preston and Al-Omran 1986). It is likely that residues of DOPs accumulating in sediments will persist and that such sediments are a significant sink for those long side-chain or highly branched side-chain phthalate esters.

Sewage sludge is known to contain relatively high concentrations of phthalate esters (12-1,250 mg kg^{-1}; Shelton *et al* 1984), the predominant component being DEHP which accumulates on sludge solids because of its hydrophobicity. The disposal of sewage sludge to marine waters was an indirect route of phthalate esters entering the environment, although the discharge of sewage sludge to marine waters is a practise which has been phased out under the Urban Waste Water Treatment Directive (December 1998). The use of sewage sludge as a soil conditioner in agriculture is also a potential indirect route of phthalate esters to the environment (Rogers 1987, Crathorne *et al* 1989, Fairbanks *et al* 1985).

B49.3 Fate and behaviour in the marine environment

Since some phthalate esters have low water solubility and high octanol partition coefficient, they can become concentrated in suspended matter and sediment.

Lewis *et al* (1998) reviewed data on the fate and behaviour of phthalate esters. The authors concluded that, in general, the substances have low water solubilities and the majority are liquids at ambient temperatures, with melting points below 0°C, although DMP and DCHP have melting points of 5.5 and 63°C respectively. Boiling points are 200°C and above.

The behaviour of phthalate esters in the environment varies, depending on the individual ester. In general, the larger the alkyl side-chain or degree of branching, the more persistent the compound.

The most important aquatic degradation process for phthalate esters is biodegradation. Short side-chain phthalate esters, such as DMP, DEP and DBPs, are all likely to degrade quickly in aerobic surface waters. The longer chain PEs, such as DOPs, are likely to be more persistent, particularly as they will partition more strongly to sediments and so may be less available to microbial degradation. It is, therefore, probable that residues of DOPs in anaerobic sediments will tend to persist for long periods.

Phthalate esters show a wide range of affinities for partitioning to particulate materials in the aquatic environment. Apart from DMP and DEP, all other phthalate esters considered by Lewis *et al* (1998) show significant partitioning to suspended solids and sediments. The transport of DOPs, DBPs, and BBP in the aquatic environment is strongly influenced by their association with suspended sediments and other detritus, as is their fate during sewage or effluent treatment processes. Log Koc for the phthalate esters increase in the order DMP<DEP<BBP<DNBP<DEHP<DNOP and cover a wide range of hydrophobicities. DMP has the lowest affinity for partitioning to particulate materials and has the highest water solubility. Partitioning tendency increases with side-chain length, with DNOP having the greatest affinity for suspended, particulate material in natural waters. Consequently, the long side-chain phthalate esters that enter the aquatic environment in effluent streams are likely to show significant association with suspended particulate material and sediments or with particulates and sewage sludge during treatment processes. In particular, longer chain phthalates (e.g. DOPs) show a strong affinity for sewage sludge which may reduce the likelihood of high concentrations occurring in the effluent.

Phthalate esters have generally low volatility (vapour pressures in the range 0.02 - 1.9 m Pa) which decrease with increasing length of the alcohol side-chain of the ester. Henry's Law constants range between 10^{-8} and 10^{-5} atm m^3 mol^{-1}, indicating that phthalate esters will tend to volatilise from water, either not at all or very slowly.

DMP and DEP can be regarded as having low propensity for bioaccumulation, whilst BBP and DBPs have intermediate tendency. DEHP, DCHP, DNOP and DIOP all have a high affinity for sediments or for partitioning to biota.

B49.4 Effects on the marine environment

B49.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of phthalates to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Lewis *et al* 1998). The most sensitive groups of organisms have been identified.

The toxicity of phthalates to saltwater organisms varies, depending on the ester considered. Esters, in general, appear to be of moderate to low toxicity to aquatic organisms. However, greatest sensitivity is exhibited when exposed to short side chain phthalate esters, such as DBP and BBP.

Algae

For algae, respective EC50 (growth) and LC50 values of 54 and 125 mg l^{-1} have been reported for the diatom *Gymnodinium breve* following 96 hours exposure to DMP (Wilson *et al* 1978), while 96 hour EC50s of 26.1 and 29.8 mg l^{-1} have been reported for *Skeletonema costatum* on the basis of chlorophyll a and cell number respectively (Suggat and Foote 1981, cited in Staples

1997). For DEP, respective EC50 (growth) and LC50 values of 3 and 33 mg l^{-1} have been reported for the diatom *Gymnodinium breve* following 96 hours exposure (Wilson *et al* 1978).

For DBPs, the limited available data suggest that saltwater algae are sensitive with 96 hour EC50 (growth) and LC50 values reported for the diatom *Gymnodinium breve* ranging from 0.0034 - 0.2 and 0.002 - 0.6 mg l^{-1} respectively (Wilson *et al* 1978). However, a single 96 hour EC50 (growth rate) of 31,000 mg l^{-1} DEHP has been reported for the alga *Gymnodinium breve* indicating low acute toxicity.

Invertebrates

The available data suggest that DMP is of moderate acute toxicity to crustacean species, with a 96 hour LC50 of 68.6 mg l^{-1} reported for the mysid shrimp *Mysidopsis bahia* following exposure to a measured concentration (Adams *et al* 1995 and Suggat and Foote 1981, cited in Staples 1997). This value is supported by a 96 hour LC50 of 62 mg l^{-1} reported by Linden *et al* (1979) for the copepod *Nitocra spinipes*.

DEP also appears to be of moderate acute toxicity to saltwater crustaceans, with a 96 hour LC50 of 10.3 mg l^{-1} (measured concentration) reported by Adams *et al* (1995) for the mysid shrimp *Mysidopsis bahia*. Of somewhat lower sensitivity is the brine shrimp *Artemia salina* with a 72 hour LOEC (hatching) of 50 mg l^{-1} reported by Sugawara (1974). In this study, a corresponding NOEC of 20 mg l^{-1} was reported.

However, greater sensitivity is exhibited by saltwater invertebrates when exposed to DNBP and BBP.

24 hour LC50s of 5.6 and 8.9 mg l^{-1} for DNBP have been reported for the brine shrimp *Artemia salina* exposed to nominal concentrations in two separate studies (Hudson and Bagshaw 1978 and Hudson *et al* 1981). A lower 96 hour LC50 of 0.5 mg l^{-1} has been reported for the mysid shrimp *Mysidopsis bahia* following exposure to measured concentrations (Adams *et al* 1995).

For BBP, a 96 hour LC50 of 0.9 mg l^{-1} has been reported by Gledhill *et al* (1980) for the shrimp *Mysidopsis bahia* with a corresponding NOEC of 0.4 mg l^{-1} measured in this study. A further 96 hour NOEC of >0.9 mg l^{-1} has been reported in a similar study (Adams *et al* 1995).

In studies conducted on the copepod *Nitocra spinipes* and the mysid shrimp *Mysidopsis bahia* no effects were observed below the maximum water solubility of DEHP. L(E)C50 values for each of these species were reported to be >0.37 and >300 mg l^{-1} respectively following 96 hours exposure (Linden *et al* 1979 and Adams *et al* 1995).

Fish

For saltwater fish, reliable 96 hour LC50s of 0.51, 3 and 0.55 mg l^{-1} BBP have been reported for shiner perch C*ymatogaster aggregata*, sheepshead minnow *Cyprinodon variegates* and English sole *Parophrys vetulus* respectively (Ozretich *et al* 1983; Gledhill *et al* 1980 and Randell *et al* 1983).

The limited available data for DMP suggest that it is of moderate acute toxicity to saltwater fish, with 96 hour LC50s of 29 and 58 mg l^{-1} reported in two separate studies for the sheepshead minnow *Cyprinodon variegates* (Adams *et al* 1995 and Heitmuller *et al* 1981). However, a lower 96 hour LC50 of 107 mg l^{-1} (nominal concentration only) has been reported for the bleak *Alburnus alburnus* (Linden *et al* 1979), indicating a possible lower toxicity to this species.

It is difficult to assess the toxicity of DBPs to saltwater fish from the limited data available. In a 96 hour study, no mortality of sheepshead minnow *Cyprinodon variegatus* was observed at 0.6 mg l^{-1}, the highest concentration tested (Adams *et al* 1995). This is supported by the results of a long-term study conducted on the eggs and larvae of a cyprinid *Rivulus marmoratus*. In this study, 2-4 week NOEC and LOEC values of 1 and 2 mg l^{-1} were reported respectively, on the basis of a decrease in egg fertility and embryo viability.

A 96 hour NOEC (survival) of 550 mg l^{-1} has been reported for DEHP by Heitmuller *et al* (1981) for sheepshead minnow *Cyprinodon variegatus*. However, it is not possible to interpret this value as it is well above the solubility limit of DEHP. Similarly, no mortality was observed in the same species following exposure to the highest concentration tested (0.17 mg l^{-1}) (Adams *et al* 1995).

B49.4.2 Sediment dwelling organisms

Some information on the toxicity of phthalate esters to sediment dwelling organisms is available. However, these are for freshwater organisms.

Given the low water solubility of DEHP and its high octanol-water partition coefficient, it is likely that this compound will readily adsorb to suspended solids and sediments in the natural environment.

Streufert *et al* (1980) found that in a flow-through study utilising DEHP concentrations of 0.36 mg l^{-1} over sand and 0.24 mg l^{-1} over hydrosoil, no effects were observed on the larvae of *Chironomus plumosus* over a 35 day exposure period. Adsorption of the dissolved fraction to the sand/hydrosoil may have reduced bioavailability and hence toxicity. This observation is supported by the results of the following sediment studies. In a study utilising spiked river sediments, a NOEC of >10,000 mg kg^{-1} (survival, development and emergence) was measured for larvae of the midge *Chironomus riparius* (Brown *et al* 1996). The authors found that this value was seventeen times greater than the highest concentrations measured in contaminated sediments in the natural environment. These results are supported by the findings of Call *et al* (1997) who found that spiked sediment concentrations of 3,306 and 3,247 mg kg^{-1} (dry weight) caused no adverse effects on survival or growth of the midge *Chironomus tentans* or scud *Hyallela azteca* respectively, over a period of 10 days.

In a study conducted by Wennberg *et al* (1997), a concentration of 600 mg kg^{-1} (spiked sediments) was found to cause no adverse effects on hatching success or tadpole survival in the moor frog *Rana arvalis* over a 29 day period.

Lewis *et al* (1998) derived EQSs for the protection of saltwater life for a range of phthalate esters (Table B49.1).

Table B49.1 Proposed EQSs for the protection of saltwater life for phthalates (Fg l^{-1}) (from Lewis *et al* 1998)

Chemical	Annual average	Maximum allowable concentration	Notes
Dimethyl phthalate (DMP)	800	4000	1
Diethyl phthalate (DEP)	200	1000	1
Di-butyl phthalates (DBPs)	8	40	1,2
Butylbenzyl phthalate (BBP)	20	100	1
Di-octyl phthalate (DOPs)	20	40	1,3
Dicyclohexyl phthalate (DCHP)	-	-	4

1 Tentative standard
2 Total DBPs (DIBP; DNBP)
3 DOPs (DEHP, DIOP, DNOP)
4 Insufficient data to derive standards

B49.5 Bioaccumulation

Bioaccumulation of phthalate esters does not appear to be significant. Wofford *et al* (1981) exposed the oyster *Crassostrea virginica*, brown shrimp *Pennies aztecus* and sheepshead minnow *Cyprinodon variegatus* to concentrations of 0.1 and 0.5 mg l^{-1} (DEHP). Bioaccumulation did not vary significantly among the three species, with reported BCFs ranging from 6.9 (oyster) to 16.6 (shrimp), although exposure was for 1 day only. In longer term studies, Brown and Thompson (1982) recorded an average BCF of 2,496 for mussels (total soft tissues), following 28 days exposure to concentrations of 0.004 and 0.042 mg l^{-1}. No apparent adverse effects on the mussels were observed, and accumulated residues were rapidly eliminated following transfer to clean seawater (half-life = 3.5 days). It should be noted that, since the BCFs were based on ^{14}C levels, the values might also include metabolites of DEHP.

Wofford *et al* (1981) determined BCFs for the brown shrimp *Pennies aztecus* and sheepshead minnow *Cyprinodon variegatus* for other phthalate esters, but found them to be low (<50).

B49.6 Potential effects on the interest features of European marine sites

Potential effects include:

! toxicity of phthalates at concentrations above the relevant EQSs (see Table B49.1) in the water column;

! accumulation in sediments of long side-chain or highly branched side-chain phthalate esters (e.g. DOPs) posing a significant hazard to sediment dwelling organisms;

! phthalate esters have been identified as a group of substances causing endocrine disruption and a precautionary approach should be adopted in the control of these substances.

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B50. Polybrominated naphthalenes

B50.1 Entry into the marine environment

Brominated naphthalenes are a group of compounds based on the naphthalene ring system, but where one or more hydrogen atoms have been replaced by bromine (75 brominated naphthalenes are possible). Crookes and Howe (1993) reviewed data on brominated naphthalenes and reported that the substances had no known commercial use and were not manufactured commercially, although it has been stated that 1-bromonaphthalene is used in refractive index testing of oils (Merck Index, 1989).

While brominated napthalenes do not appear to be manufactured commercially, they are being found as by-products in various chemical mixtures and a number of such occurrences have been highlighted by Crookes and Howe (1993).

The major reported release of brominated naphthalenes occurred in Michigan in 1973. Dairy herds were accidentally fed a flame retardant mixture, Firemaster BP-6 (or FF-1). The flame retardant was a polybrominated biphenyl mixture, but it was discovered that brominated naphthalenes were present at trace amounts in the commercial product. The incident resulted in the destruction of 788 tons of feed, 30,000 livestock, 1.6 million poultry, 17 tons of dry milk products and 5 million eggs. Although the brominated naphthalenes were present at only trace amounts, it is thought that they were primarily responsible for the acute toxic effects observed (Birnbaum *et al*, 1983, Goldstein *et al*, 1979; Hass *et al*, 1978).

The polybrominated flame retardants Firemaster FF-1 and BP-6 have been analysed for the presence of brominated naphthalenes. Firemaster FF-1 was found to contain 1 mg kg^{-1} pentabromonaphthalene and 25 mg kg^{-1} hexabromonaphthalene (O'Keefe, 1979). Firemaster BP-6 (an alternative formulation of Firemaster FF-1 without calcium silicate) contained 150 mg kg^{-1} pentabromonaphthalene and 70 mg kg^{-1} hexabromonaphthalene (Hass *et al*, 1978).

Hexabromonaphthalene has been reported to be present at a level of 150 mg kg^{-1} in Firemaster FF-1 and BP-6. Tetrabromo- and pentabromonaphthalenes were also detected (Tondeur *et al*, 1984). 1-bromo-, dibromo- and bromochloronaphthalenes have been shown to be formed in the chlorination of water containing naphthalene and potassium bromide (Lin *et al*, 1984).

Monobromo-, dibromo- and bromochloronaphthalenes have been shown to be formed from naphthalene adsorbed on municipal incinerator fly ash and heated to 50-250^{0}C in a stream of hydrogen chloride and helium. The source of bromine was thought to be bromide present in the fly ash (Eiceman *et al*, 1989). Traces of brominated naphthalenes have been shown to be present in the high temperature pyrolysis products of brominated flame retardants (Thoma and Hutzjinger, 1989).

B50.2 Recorded levels in the marine environment

Crookes and Howe (1993) reported that there was limited information on the environmental occurrence of polybrominated naphthalenes.

B50.3 Fate and behaviour in the marine environment

Crookes and Howe (1993) found no information on the volatility, atmospheric reactivity, adsorption to soil or sediments, bioaccumulation or anaerobic degradability of brominated naphthalenes.

However, Walker and Wiltshire (1955) reported that two species of soil bacteria had been shown to be capable of utilising 1-bromonaphthalene as the sole carbon source.

B50.4 Effects in the marine environment

B50.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of polybrominated naphthalenes to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Crookes and Howe 1993).

Crookes and Howe (1993) could not identify any aquatic toxicity data for polybrominated naphthalenes.

B50.5 Bioaccumulation

Crookes and Howe (1993) could not identify any bioaccumulation data for polybrominated naphthalenes.

B50.6 Potential effects on interest features of European marine sites

Potential effects include:

! limited information on the occurrence, behaviour, toxicity and behaviour of these compounds in the marine environment should dictate that a precautionary approach is adopted in the control of these substances if found in European marine sites.

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B51. Oils and petrochemicals

B51.1 Entry into the marine environment

Whitehead (1983) describes crude oil as a complex mixture of many compounds comprising mainly compounds of hydrogen and carbon. The composition of crude oil is very variable and all types will contain different quantities of the many different hydrocarbons together with quantities of sulphur, oxygen, nitrogen and traces of metals. Crude oil is variously described as light, medium or heavy, sweet or sour (containing hydrogen sulphide), paraffinic (light), asphaltic (heavy) or mixed (aromatic) base oil, dependent largely on the dominant proportion of hydrocarbons.

The hydrocarbons present in crude oil can range from aliphatic (straight chain) compounds to more complex aromatic (containing a benzene ring) and polynuclear aromatic (containing two or more benzene rings) compounds. Hydrocarbons can be present in the full range of physical states from gaseous through liquids to solids. Heavy crude oils have a greater proportion of long chain aliphatic hydrocarbons than light crude oils where short chain aliphatic compounds predominate. Aromatic compounds predominate in medium (mixed base) crude oils.

Refining of crude oil produces a range of products, ranging from lubricating oils and waxes, asphalts and heavy fuel oils through aviation fuel, diesel fuel and heating oils to gasoline and liquid petroleum gases. Other processes can be used to create a wide range of petrochemicals, including familiar hydrocarbons, such as propylene, acetylene, benzene, toluene and naphthalene.

GESAMP (1993) estimated that 2.35 million tonnes of oil per year entered the marine environment from all sources. At least 15% comes from natural oil seeps. Anthropogenic sources include chronic discharges from storage facilities and refineries, discharges from tankers and other shipping along major routes and accidental events, such as oil spills and ruptures of pipelines. Sources also include river-borne discharges, diffuse discharges from industrialised municipal areas, offshore oil production (e.g. drilling, transport, refining and burning of oil and petrochemicals) and the atmosphere. Locally, an important source is the exhaust from outboard engines.

Elliott and Griffiths (1987) classify sources of hydrocarbons to the Forth estuary as petrogenic, pyrogenic and biogenic (Table B51.1) and this classification is probably applicable to oils and petrochemicals in the marine environment.

Petrogenic sources tend to be point sources of oil and petrochemicals, whereas pyrogenic and biogenic inputs are considered as diffuse sources .

Table B51.1 Sources of oils and petrochemicals or by-products to coastal waters (from Elliott and Griffiths (1987))

Sources	
Petrogenic	Oil refinery installations
	Petrochemical installations
	Production waters from oilfields
	Tanker ballast water
	Spillages
	Storm water discharges
	Municipal discharges
	Leisure craft powered by outboard engines
Pyrogenic	Resulting from incomplete burning of fossil fuels/peat/wood in domestic and industrial plant
Biogenic	Marine and terrestrial inputs
	In-situ diagenic production of hydrocarbons by chemical and microbial processes

In the UK, 14 of the 155 estuaries studied as part of the Estuaries Review (Davidson *et al* 1991) had oil refineries on them in 1989, including the Forth, Humber, Thames and Mersey. Nineteen of the 155 had import/export jetties and single point moorings and were therefore at risk from tanker related spillages. Oil spills in estuaries vary in size and their impact depends on the amount and type of oil involved. Elliott and Griffiths (1987) reported six spillages of heavy oil or diesel in the Forth estuary between 1970 and 1978, with only minor incidents up to 1987. In 1983, 6,000 tonnes of crude oil were released in to the Humber estuary at Immingham (the Sivand oil spill) (NRA, 1993). The Mersey estuary received 150 tonnes of crude oil from a fractured pipeline in 1989 and in 1996 the ‘Sea Empress’ released 72,000 tonnes of crude oil in Milford Haven.

Oils and petrochemicals also form part of municipal discharges as a result of road run-off, domestic usage and the licensed discharge of small quantities to sewer. Oils and petrochemicals are therefore found in sewage and storm water discharges, either directly into the estuary or into the freshwater tributaries.

Pyrogenic sources of petrochemicals enter estuaries either directly or indirectly from atmospheric deposition and, although this is technically a diffuse source, deposition is likely to be greater in the footprint of point sources to the atmosphere, such as coal-fired power stations. The burning of fossil fuels is a major source of polynuclear aromatic hydrocarbons (PAHs) into the environment (see Section B46).

Biogenic sources of hydrocarbons can be generated in estuaries where sediment deposits accumulate and microbial and chemical conditions are appropriate.

B51.2 Recorded levels in the marine environment

The concentration of oil in the environment and in the biota is measured in a number of different ways, including total hydrocarbons, total aliphatic hydrocarbons, total aromatic hydrocarbons, persistent oils and grease. The use of these different parameters hinders spatial comparisons.

B51.3 Fate and behaviour in the marine environment

Various reviews on the fate and weathering of petroleum spills in marine waters have been conducted (Jordan and Payne 1980; Marine Technology Society 1984; Lange 1984; Kuiper and van der Brink (1987). The persistence of oil depends on the type of oil; the season, the geomorphology of the coast and the degree of exposure (GESAMP 1993). SEEEC (1998) review the fate of oil in relation to the Sea Empress oil spill.

B51.4 Effects on the marine environment

Oil and petrochemicals exert impacts on the environment through both physical and chemical (toxic) means. Long-chain aliphatic hydrocarbons are effectively solids and exert their effects by physical means, coating surfaces and smothering organisms. Short-chain, low boiling point compounds, unsaturated compounds and aromatic hydrocarbons exert their effects by primarily chemical (toxic) means. The overall impact of a discharge of oil or petrochemical on the environment is dependent on the distribution and composition of the petroleum hydrocarbons, especially their weathering, persistence and consequently their bioavailability (GESAMP 1993).

Effects differ in open waters and in enclosed systems. In open waters, the action of waves and currents can decrease concentrations of contaminants rapidly. In enclosed systems, such as estuaries, the potential for dispersion is not so great and, on shorelines, a number of factors determine its persistence: properties of the oil, porosity of sediments, presence of animal burrows, wave action and type of vegetation (GESAMP 1993). Table B51.2 summarises the vulnerability of different coastal habitats and ranks them in order of vulnerability.

Table B51.2 Vulnerability index of shores (in order of increasing sensitivity to oil damage, adapted from Gundlach and Hayes (1978))

Exposed rocky headlands	Wave reflection keeps most of the oil offshore. No clean-up necessary.
Eroding wave-cut platforms	Wave swept. Most oil removed by natural processes within weeks.
Fine grained sand beaches	Where oil does not penetrate into the sediment, this facilitates mechanical removal if necessary. Otherwise, oil may persist for several months. However, penetration can occur, depending on water table movements in sediments.
Coarse grained beaches	Oil may sink and/or be buried rapidly, making clean-up difficult. Under moderate to high-energy conditions, oil will be removed naturally from most of the beach face.
Exposed compacted tidal flats	Most oil will not adhere to, nor penetrate into the compacted tidal flat. Clean-up is usually unnecessary.
Mixed sand and gravel beaches	Oil may penetrate the beach rapidly and become buried. Under moderate to low-energy conditions, oil may persist for years.
Gravel beaches	Same as above. Clean-up should concentrate on high tide/wash area. A solid asphalt pavement may form under heavy oil accumulations.
Sheltered rocky coasts	Areas of reduced wave action. Oil may persist for many years. Clean-up may be necessary although the sensitivity of the area should be taken into account.
Sheltered tidal flats	Areas of great biological activity and low wave energy. A number of interpretations of the ‘biological activity’ are possible. In this case, it is taken to mean a combination of high productivity, biomass and possibly bioturbation. Oil may persist for years. Clean-up is not recommended unless oil accumulations are heavy. These areas should receive priority protection by using booms or oil absorbing materials.
Saltmarshes	The most productive of aquatic environments. Cleaning of saltmarshes by burning or cutting should be undertaken only if heavily soiled. Protection of these environments by booms or absorbing material should receive first priority.

SEEEC (1998) review the effects of the Sea Empress oil spill on marine communities.

A number of projects assessing the environmental impact of the Sea Empress spill was commissioned by the Sea Empress Environmental Evaluation Committee on:

- fate of oil
- marine impacts
- shoreline impacts
- maritime vegetation and agriculture
- mammals
- birds
- reviewing the effectiveness of clean-up operations.

A list of all the reports is included within the SEEEC Report (SEEC 1998).

B51.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of oils and petrochemicals to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (e.g. GESAMP 1993, Elliott and Griffiths 1987). The most sensitive groups of organisms have been identified.

Various reviews have been conducted on the toxicity of petroleum spills on marine ecosystems and populations (Clark 1982; Geraci and St Aubin 1990), to which the reader is also referred.

Reproductive, developmental and behavioural processes are very sensitive to exposure to hydrocarbons. Generally, early life stages are more sensitive than adults and many juvenile and adult crustaceans and echinoderms are more sensitive than juvenile and adult fish. It is well established that different oils vary in their toxicities and that acute toxicity is largely due to components of the water soluble fractions and dependent upon exact conditions and duration of exposure to them (GESAMP 1993).

Chronic sublethal effects caused by petroleum hydrocarbons spilled or discharges into low energy, shallow coastal waters remain a valid concern.

The major habitats affected are intertidal and subtidal sediments and to, a lesser extent, the water column. GESAMP (1993) highlighted low-energy, marshes and seagrasses as being among the most sensitive and vulnerable shorelines to oil pollution (see also Table B51.2). Threshold effects concentration for various species and different hydrocarbons and their mixtures in water were reported as low as a few Fg l^{-1}.

Elliott and Griffiths (1987) provided a summary of the biological effects of petrochemical pollution in the Forth (Table B51.3).

Table B51.3 Biological effects of oil and petrochemical pollution in the Forth (from Elliott and Griffiths 1987)

Lethal effects	Sub-lethal effects
Faunal and floral community changes: Chronic by discharges Catastrophic by oil spillages	Contamination and changes in the rates of bioaccumulation
Acute toxic effects (near-field and far-field)	Toxic effects on fecundity, behaviour, pathobiology and productivity
	A change in MFO activity induction in fish
	Changes in mussel ecophysiology (Scope for Growth) and sub-cellular structure and functioning
	Changes in palatability of benthos and fish (tainting)

The physical effects arise from the tendency of oils to coat surfaces, including sediment surfaces, rocky shores and vegetation. Large deposits are associated with discharges or spillages of crude oil where large expanses of intertidal mud and sand flats, rocky shore and saltmarshes can be covered. When such deposits are not removed as part of a spill clean-up, they smother benthic organisms and prevent feeding by birds and fish. The response of benthic invertebrate communities is very similar to the response to organic enrichment and pollution because the primary effect is to create anoxia in the sediment by preventing exchange of water between the sediment surface and the water column.

Invertebrates

The toxic effects of crude oil and a range of petrochemicals have been demonstrated on a range of estuarine invertebrates, including polychaetes (Reish 1979), decapod crustaceans, including crabs (Williams and Duke 1979), shrimps (Couch 1979) and larval decapods (Epifanio 1979), amphipod crustaceans (Reish and Barnard 1979) and molluscs (Menzel 1979). While comparisons are difficult because of the use of different oils and various ways of preparing oil for testing, a number of laboratory tests were performed using water soluble fractions of No. 2 fuel oil and Venezuelan crude. The fuel oil was generally more toxic.

Fish

Studies on the changes in fish and macrocrustacean community structure in relation to a discharge of oil and petrochemicals in estuaries are few and have been hampered by the lack of appropriate fish community descriptors and the high levels of natural variability (GESAMP 1993).

Impacts at the fish population level are also difficult to detect but are unlikely to be great because fish will avoid localised areas polluted by oil. In enclosed systems, such as estuaries, extensive pollution by oil may reduce the holding capacity of the system for fish such that its value as a nursery or feeding ground may be reduced.

Lancaster *et al* (1998) studied the recruitment of sea bass in relation to the ‘Sea Empress’ oil spill in 1996 and concluded that although some differences were detected between estuaries, they were unlikely to be more significant than natural year-to-year variation.

Laboratory and field studies in the 1970s and 1980s demonstrated acute and chronic effects in adult fish exposed to waters and sediments contaminated with high levels of hydrocarbons (GESAMP 1993). Lethal effects on estuarine crabs, shrimp and lobsters have been demonstrated (Williams and Duke 1979, Couch 1979 and Epifanio 1979). Petroleum spills generally have a low acute toxicity potential for adult fish but fish kills may occur due to high exposure to emulsified oil in shallow waters (i.e. the Braer spill, January 1993, Shetland Isles) (GESAMP 1993). However, the creation of oil water emulsions requires a high energy system which is unlikely to occur in many European estuarine systems.

In laboratory studies with a range of fish (rainbow trout, perch, sea trout, fathead minnow and pike), the effects of exhaust from a two-stroke outboard engine were studied. Estimated environmental concentrations of 0.27 to 1.6 Fl l^{-1} of exhaust condensate in the wake of the engine were used in the laboratory experiments and effects were observed at the subcellular level (including enzyme activity) and on physiological functions (carbohydrate metabolism and on the immune system) (Balk *et al* 1994).

Seabirds

Marine wildlife (seabirds and mammals) are often the most conspicuous victims of oil spills. Diving and surface-dwelling populations of seabirds and sea otters are known to be vulnerable and sensitive to oiling.

Following a spill, seabirds may be affected in a number of ways. Although oil ingested during attempts to clean plumage may be lethal, the most common causes of death are from loss of body heat, starvation and drowning following damage to the plumage by oil. Plumage is essential to flight, heat insulation and waterproofing and even small effects on any of these functions can result in mortality. As well as external effects, birds can ingest oil when eating contaminated food. This can cause direct toxicity and lead to decreased survival, density and fecundity of bird populations (GESAMP 1993).

Sea mammals

Documentation for the field on the effects of oiling on mammals, especially cetaceans, is scarce (GESAMP 1993).

Seals and dolphins are highly mobile animals which are generally able to avoid any prolonged encounter with an oil slick. The main threats to these animals are not so much the reduction in insulation but internal damage resulting from ingesting contaminated food. Seals are vulnerable to hydrocarbons and other chemicals evaporating from the surface of oil. Exposure to these pollutants causes symptoms which include irritation to the eyes and lungs and breathing difficulties.

B51.5 Bioaccumulation

Elliott and Griffiths (1987) demonstrated bioaccumulation of hydrocarbons by flounder and plaice in the Forth estuary system and suggested that the primary route of uptake was via the food.

Biomarker studies have revealed that fish detoxify bioaccumulated hydrocarbons and the degree to which this process has been initiated. The induction, through the cytochrome P-450 pathways, of mixed function oxidases (MFO) activity has become a biomarker for hydrocarbon exposure and contamination (Payne and Fancey 1982, Elliott and Griffiths 1987). Initial studies in the Forth in 1987 indicated that MFO activity was greatest closer to the main source of hydrocarbons to the estuary (Elliott and Griffiths 1987). This response has also been detected in the Elbe estuary .

Tainting (an odour or flavour foreign to the product) has occurred in commercial species contaminated with crude and refined oils. GESAMP (1993) report studies detecting taints in fish and macro-crustaceans resulting from exposure from acute incidents, chronic discharges and in experimental studies. Tainting from acute incidents involving crude oil has been reported for mackerel, sea trout, plaice, carp, mullet, salmon, crab and lobster and involving refined oils for mackerel, herring, flounder, sea trout, salmon, haddock, saithe and lobster. Chronic discharges of refinery wastes have resulted in reported taints in grey mullet, eel, ‘flatfish,’ and rainbow trout. Taints have been induced in plaice, eels, salmon, saithe, cod, trout, shrimp and crab in experimental studies using a variety of crude and refined oils.

Experimental studies indicate that taints can be detected when fish are exposure to concentrations of oil in water in the range 0.01 to 1 mg l^{-1}. Alkylbenzenes have been indicated as capable of causing a taint in fish but this is not the only class of tainters in crude and refined oils. Fish can be tainted very rapidly on exposure - within a few hours at concentrations of oil above 1 mg l^{-1} - and have been shown to lose their taint within 1 to 4 days (experimental study on cod). However, field studies have indicated fish were still tainted days or weeks after a spill of fuel oil (GESAMP 1993).

B51.6 Potential effects on the interest features of European marine sites

Potential effects include:

- intertidal habitats are under greatest threat from the physical effects of oil pollution. The most vulnerable habitats are sheltered rocky coasts, intertidal sand and mudflats and saltmarshes;

- subtidal habitats and their associated flora and fauna may be threatened in high energy coastal situations where the likelihood of oil/water emulsions forming is greater;

- seals and dolphins are threatened by the consumption of contaminated food. An additional hazard for seals is the inhalation of volatile components of oil causing eye and lung irritation and breathing difficulties;

- damage to intertidal habitats used as seal haul-outs could be significant if the incident occurred during the breeding season;

- birds are affected by oil through the physical damage to plumage and by the consumption of contaminated food.

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B52. Surfactants

B52.1 Entry into the marine environment

Surfactants (also called surface active agents or wetting agents) are organic chemicals that reduce surface tension in water and other liquids. The most familiar use for surfactants are soaps, laundry detergents, dishwashing liquids and shampoos. Other important uses are in the many industrial applications for surfactants in lubricants, emulsion polymerisation, textile processing, mining flocculates, petroleum recovery, wastewater treatment and many other products and processes. Surfactants are also used as dispersants after oil spills.

There are hundreds of compounds that can be used as surfactants and are usually classified by their ionic behaviour in solutions: anionic, cationic, non-ionic or amphoteric (zwiterionic). Each surfactant class has its own specific properties.

There are many sources of surfactants that are discharged into natural waters. Industrial sources include textile, surfactants and detergent formulation. Surfactants are also used in laundries and households and are therefore found in discharges from sewage treatment works. They also have agricultural applications in pesticides, dilutants and dispersants (McNeely *et al* 1979).

Surfactants are compounds composed of both hydrophilic and hydrophobic or lipophobic groups. In view of their dual hydrophilic and hydrophobic nature, surfactants tend to concentrate at the interfaces of aqueous mixtures; the hydrophilic part of the surfactant orients itself towards the aqueous phase and the hydrophobic parts orients itself away from the aqueous phase into the second phase.

The hydrophobic part of a surfactant molecule is generally derived from a hydrocarbon containing 8 to 20 carbon atoms (e.g. fatty acids, paraffins, olefins, alkylbenzenes). The hydrophilic portion may either ionise in aqueous solutions (cationic, anionic) or remain un-ionise (non-ionic). Surfactants and surfactant mixtures may also be amphoteric or zwitterionic (CCME 1992).

Table B52.1 gives some examples of major commercial and industrial surfactants.

Nonylphenol and its ethoxylates (NPEs) are one of the types of surfactants causing concern. The primary source of nonylphenolic compounds in the aquatic environment is due to the incomplete degradation of NPE (nonylphenol ethoxylate) surfactants during sewage treatment, and therefore it is unlikely to be present in the aquatic environment in the absence of other NPE degradation by-products (such as nonylphenol mono- and diethoylates (NP1EO and NP2EO) and nonylphenoxy carboxylic acids (NPEC)).

Table B52.1 Some examples of major commercial and industrial surfactants (from CCME 1992)

Type/Use	Commercial and domestic examples	Major industrial examples
Anionic	Sodium linear alkylbenzene sulphonate (LABS); sodium lauryl sulphate; sodium lauryl ether sulphates	Petroleum sulphonates; linosulphonates; naphthalene sulphonates, branched alkylbenzene sulphonates; linear alkylbenzene sulphonates; alcohol sulphates
Cationic	Stearalkonium chloride; benzalkonium chloride	quaternary ammonium compounds; amine compounds
Non-ionic	Dodecyl dimethylamine oxide; coco diethanol-amide alcohol ethoxylates; linear primary alcohol polyethoxylate	alkylphenol ethoxylates; alcohol ethoxylates; EO/PO polyol block polymers; polyethylene glycol esters; fatty acid alkanolamides
Amphoteric	Cocoamphocarboxyglycinate; cocamidopropylbetaine	Betaines; imidazolines

B52.2 Recorded levels in the marine environment

Concentrations of nonylphenol in surface waters vary widely but locally high concentrations (sometimes in excess of 100 Fg l^{-1}) have been reported, especially in areas receiving industrial and sewage discharges. Higher concentrations (several mg kg^{-1}) have been detected in sediments, although much of this is unlikely to be bioavailable (Whitehouse *et al* 1998a).

B52.3 Fate and behaviour in the marine environment

In view of their hydrophilic nature, surfactants tend to be water soluble to some degree. Depending on the specific chemicals, solubility varies from very soluble (e.g. some anionic surfactants) to insoluble (e.g. some cationic surfactants) (Lewis and Wee 1983) .

Anionic surfactant are not appreciably sorbed by inorganic solids. On the other hand, cationic surfactants are strongly sorbed by solids, particularly clays. Significant sorption of anionic and non-ionic surfactants has been observed in activated sludge and organic river sediments. Depending on the nature of their hydrophobic moieties, non-ionic surfactants may be sorbed onto surfaces. Some surfactants have been found to alter the sorption to surfaces of coexisting chemical species, such as metals (CCME 1992).

In general, surfactants in modern day use are considered to be biodegradable under conditions of efficient sewage treatment, The rates of degradation depend partially on the chemical structure. Surfactants containing linear hydrophobes are generally more biodegraded than those containing branched hydrophobes. Nonylphenol and some of its ethoxylates are not readily degraded during sewage treatment (CCME 1992).

Because of the hundreds of compounds that can be used as surfactants and because the toxicity (and potential to be present in sediment) and bioaccumulation potential will vary according to the type of surfactant, an assessment is not possible here.

B52.4 Effects in the marine environment

B52.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of surfactants to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents for one surfactant (nonylphenol) as an example (Whitehouse *et al* 1998a). The most sensitive groups of organisms have been identified.

Whitehouse *et al* (1998a and 1998b) reviewed data on the saltwater toxicity of nonylphenol and octylphenol. By way of an example, their conclusions for nonylphenol are presented below.

The authors reported that, in acute studies with saltwater species, the mysid shrimp *Mysidopsis bahia* was the most sensitive species, where a 96 hour LC50 of 43 Fg l^{-1} was reported. Corresponding 96 hour LC50s values for fish were higher, ranging from 135 Fg l^{-1} for fathead minnow *Pimephales promelas* to 3,000 Fg l^{-1} for cod *Gadus morhua.* Nonylphenol was generally toxic to algae at concentrations greater than 500 Fg l^{-1} although the lowest 96 hour EC50 (for growth) was 27 Fg l^{-1} in the marine diatom, *Skeletonema costatum.*

Some toxicity data for sediment-dwelling organisms were also presented (although it relates to freshwater organisms). Whitehouse *et al* (1998) found nonylphenol dosed into sediment would not be readily bioavailable. Much higher levels of nonylphenol were required in sediment than in water to cause adverse effects to the sensitive midge larvae *Chironomus tentans* .

Whitehouse *et al* (1998a) also investigated data on the endocrine disrupting effects of nonylphenol. While no data were available for saltwater organisms, nonylphenol concentrations of 20 Fg l^{-1} and greater were found to cause effects related to oestrogenicity.

B52.5 Bioaccumulation

With regard to bioaccumulation, Whitehouse *et al* (1998a) found bioaccumulation factors for aquatic organisms to be around 300. However, much higher values were found for algae (but this may have been due to adsorption) and when radio-labelled nonylphenol was used.

B52.6 Potential effects on interest features of European marine sites

Potential effects include:

- toxicity of nonylphenol and octylphenol to algae, invertebrates and fish at concentrations above the respective EQSs of 1 Fg l^{-1} (annual average) and 2.5 Fg l^{-1} (maximum allowable concentration) for nonylphenol and 1 Fg l^{-1} (annual average) and 2.5 Fg l^{-1} (maximum allowable concentration) for octylphenol in the water column;

- accumulation of nonylphenol in sediments though bioavailability is considered to be low;

- nonylphenol has been found to have endocrine disrupting effects in freshwater organisms at concentrations of 20 Fg l^{-1}.

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B53. Toluene

B53.1 Entry into the marine environment

Toluene has a large number of applications in both industrial and consumer products.

The largest single use of unisolated toluene, as BTX mixture, is the incorporation of the reformate mixture into petrol to produce high octane fuel. In addition, approximately 35% of isolated (technically pure) toluene is backblended into petrol to increase the octane ratings (Fishbein 1985). As the lead content in petrol is reduced to 0.15 g l^{-1} and ultimately zero in EC member states, there will be an increase in the use of catalytic reformate (BTX mix) to maintain octane numbers, and it is predicted that the content of aromatic hydrocarbons in petrol will increase by approximately 20%, Clark *et al* (1984a).

Isolated toluene has a diverse range of other applications. An estimated 9.5% is used as a solvent (increasingly as a 'safe' replacement for benzene) in paints and coatings, adhesives, inks and dyes, pharmaceuticals and aerosols (Fishbein 1985).

Furthermore, toluene is used as a raw material in the chemical industry for the manufacture of phenol and toluene diisocyanate (TDI), benzoic acid, benzyl chloride, xylenes, vinyl toluene, benzaldehyde and cresols and to a lesser extent, caprolactam. Toluene is also important in the production of TNT, saccharin and detergents (toluene sulphonates).

Fishbein (1985) estimated that more than 6 million tons of toluene entered the environment annually. The atmosphere provides the main sink for toluene and relatively small amounts are lost to the aqueous environment. The total amount of toluene lost world-wide to the sea is estimated at 500,000 tons/y (Merian and Zander 1982). The greatest loss of toluene, approximately 3 to 4 million tons/y, occurs during the production and transport of petroleum products, with a further 2 million tons/y emitted in automobile exhausts. The use of toluene as a solvent accounts for losses of approximately 1 to 1.5 million tons/y.

Possible routes of entry for toluene into surface waters include; direct discharges of industrial effluents, especially from chemical production and refinery sites; spillage; leaching and run-off and atmospheric deposition.

B53.2 Recorded levels in the marine environment

Jones and Zabel (1996) reviewed data on toluene. Harland *et al* (1982) carried out a detailed study of the toluene levels in the Tees estuary, NE England. The estuary receives discharges from many industries. At one site, toluene levels ranged from 0.3 to 19.7 µg l^{-1}, whereas at Tees Dock, the levels ranged from 18.9 to 112.8 µg l^{-1}. Highest concentrations were found in samples taken from the surface freshwater layer overlying the saline water.

Gschwend *et al* (1980) suggested that toluene may originate from biogenic sources in coastal waters as increased total volatile organic concentrations near algal blooms were observed. However, concentrations were low, at less than 0.01 µg l^{-1}.

Harland *et al* (1982) took sediment samples from two sites in the Tees estuary and found toluene concentrations ranging from 2.2 to 3.7 µg kg^{-1} wet weight at one site and 1.2 to 6.4 µg kg^{-1} wet weight at the other. These values were not corrected for recovery efficiency and actual levels may be a factor of three greater than reported. Corresponding water concentrations were up to 20 and 113 µg l^{-1} respectively.

In rural Britain, Clark *et al* (1984a,b) found levels of toluene in air ranging from a mean of 1.27 ppb to a maximum of 6.4 ppb, whereas at an urban site in south west London, the levels were higher at 13.0 ppb (mean) with a maximum of 42.4 ppb. This demonstrated that increased toluene levels occurred in areas with high exhaust emissions. The proportion of toluene in emissions from vehicular exhausts range from 3.1% to 16.3% of total emitted hydrocarbons, depending on fuel and engine type (Verschueren 1983; Fishbein 1985; Sigsby *et al* 1987). Levels at a motorway site off the M1 were lower than at the urban site, probably because toluene emissions at high and constant speed tend to be lower than under urban traffic conditions.

B53.3 Fate and behaviour in the marine environment

The solubility of toluene in fresh and salt waters at 25 °C is 535 and 380 mg l^{-1} respectively. Volatilisation is an important removal process for toluene present in the aqueous environment. Particularly under conditions when biodegradation is low, volatilisation is the predominant removal process (Wakeham *et al* (1983, 1985)). Maximum winter volatilisation rate constants of 0.11/day were obtained for a controlled marine ecosystem by Wakeham *et al* (1985). This resulted in a half life of about 25 days which was reduced to only 6 days under storm conditions. Toluene is lipophilic and moderately adsorbed on soils and sediments (Jones and Zabel 1996)

B53.4 Effects on the marine environment

B53.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of toluene to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Jones and Zabel 1996). The most sensitive groups of organisms have been identified.

Jones and Zabel (1996) reviewed the aquatic toxicity data for toluene and found relatively few toxicity data for marine organisms had been reported. Most of the reported tests were carried out under static conditions with nominal exposure concentrations. Because of the high volatility of toluene and the wide variation in saltwater solubility values reported in the literature, the results of static tests with no analysis of exposure concentrations are very unreliable.

In acute tests, the crustacean *Crago franciscorum* was found to be the most sensitive species with a 96 hour LC50 of 3.7 mg l^{-1} (Benville and Korn 1977). The results appear to be based on mean analysed concentrations. However, as most deaths seem to occur during the initial few hours of exposure, the use of the mean concentration could lead to an over-estimation of the toxicity. For the crustacean, *Palaeomonetes pugio* a 24 hour LC50 of 9.5 mg l^{-1} (Tatem 1975) was obtained in a static test based on initial concentrations. In this case, the results could be an underestimation of toxicity.

Similar acute toxicities have been obtained for fish species - a 24 hour LC50 of 5.4 mg l^{-1} (Thomas and Rice 1979) and a 96 hour LC50 of 6.4 mg l^{-1} (Korn *et al* 1979) for the pink salmon, and 24 and 96 hour LC50s of 6.3 mg l^{-1} (Benville and Korn 1979) for the striped bass. The results are based on initial concentrations and the true values could be lower by more than 50%.

Bacteria and algae seem to be more resistant to the acute effects of toluene than fish and crustaceans (Jones and Zabel 1986).

The only reported chronic test was for the early life stage of the sheepshead minnow, with 7.7 mg l^{-1} causing a significant decrease in hatching. The maximum acceptable toxicant concentration was calculated as > 3.2 mg l^{-1} (Ward and Parrish 1981).

No data could be located for sediment-dwelling organisms.

B53.5 Bioaccumulation

Jones and Zabel (1996) concluded that bioaccumulation in marine organisms appeared to be low. The highest BCF of 13.2 has been reported for eel flesh based on wet weight. Also, the rate of depuration, when organisms are returned to uncontaminated water, is reported to be rapid.

B53.6 Potential effects on interest features of European marine sites

Potential effects include:

- toxicity of toluene to invertebrates and fish at concentrations above the EQS of 40 µg l^{-1} (annual average) and 400 µg l^{-1} (maximum allowable concentration) in the water column.

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B54. Xylenes

B54.1 Entry into the marine environment

Xylene ($C_6H_4(CH_3)_2$) occurs in three isomers (o-, m- and p-) which vary in the site of attachment on the benzene ring of the two methyl groups. They are liquids at room temperature and pressure, and are soluble in water (134 - 230 mg l^{-1}). They have moderate log Kow values (2.77 to 3.20) and tend to volatilise.

Production of xylenes is primarily associated with the petrochemical and coal industries, with most being produced by the catalytic reforming of naphtha, a derivative of crude oil fractionation. Most (c. 89%) xylene is produced as a mixture of isomers, along with benzene and toluene, with subsequent isolation of xylenes as required. Technical (mixed) xylene contains typical proportions of o-, m- and p- isomers of 20-24%, 42-48% and 16-20% respectively, with 10-11% ethylbenzene as an 'impurity'.

Xylene is produced widely in the EC at high tonnages (total production in the range 500 to 1,000 Ktonnes, according to the EU's IUCLID database). In the UK, production of mixed xylenes is significant, but of the isomers, only p-xylene is produced in isolation in substantial quantities. Estimated annual production capacities in the UK for the early 1990s were 150 Ktonnes mixed xylenes and 200 Ktonnes p-xylene, with major production at only two sites (ChemInform 1992).

Most xylenes (>90%) are used in mixed xylene as a solvent and a constituent (BTX - benzene-toluene-xylene) of vehicle, aviation and other fuels. This latter use has increased significantly in the EC with the widespread introduction of unleaded petrols (Crookes *et al* 1993). Globally, the increasing use of vehicular transport in developing nations is also increasing the use of BTX and, thus, xylenes. The industrial importance of individual isomers decreases in the order p-, o-, m-, with major uses including the following (Micromedex 1996):

p-	Production of polyester resins and fibres Vitamin and pharmaceutical synthesis Solvent, e.g. in insecticides
o-	Production of phthalic anhydride Solvent, e.g. in insecticides, pharmaceuticals Intermediate in synthesis of dyes Additive in motor fuels
m-	Production of isophthalic acid Solvent, e.g. in insecticides Intermediate in synthesis of organics, dyes Additive in aviation fuel

During their production and use, xylenes are released primarily to the atmosphere. The principal anthropogenic releases of xylene remain consistent, i.e.:

! accidental and deliberate release of crude oils and petrochemical products (including during refining of crude oils and distribution and use of products);

- production of xylenes and derivative chemicals; and industrial and domestic discharge of solvents and other products.).

Entry into water may be direct or via atmospheric deposition, runoff and leaching.

B54.2 Recorded levels in the marine environment

Xylenes have been regularly reported in the oceans, estuaries, precipitation, rivers, groundwaters, potable sources and drinking water, as well as aquatic sediments and biota (Hedgecott 1990, Crookes *et al.* 1993). High usage and release, high mobility in the atmosphere, and natural sources all contribute to widespread occurrence in waters. Post-1988 data for UK waters were summarised in Hedgecott and Lewis (1997). Most of the data are for estuarine and coastal waters, with xylenes apparently detected in relation to industrial releases of xylenes and releases during oil extraction and transport. None of the published values exceed the concentration of 30 Fg l^{-1} of total xylenes which has been proposed as the annual average EQS value.

B54.3 Fate and behaviour in the marine environment

Hedgecott and Lewis (1997) reviewed the fate and behaviour of xylenes.

Atmospheric xylenes are subject primarily to photo-enhanced oxidation by reaction with hydroxyl radicals, and this (and other reaction processes) is enhanced by nitric oxides and solids. Half-lives in the atmosphere have been variously estimated between 0.83 and 29 hours. Oxidation in water is considerably slower with estimated half-lives between 30 and 300 days. Hydrolysis is unlikely (Hedgecott and Lewis 1997).

Xylene molecules are relatively simple and biodegradation is widespread in environmental media, although o-xylene appears to be slightly more recalcitrant than the other isomers. Groundwater inocula have been reported to completely degrade low concentrations of xylenes in 2 to 20 days (varying with pre-exposure) under aerobic conditions (when dissolved oxygen levels are not limiting). Although anaerobic degradation has also been observed, this is somewhat slower. Typically there is a substantial lag period of around 30 (m- and p-) or >140 (o-) days before significant degradation in unacclimated aquifer material, but with pre-exposure and adaptation, degradation can be significant (>80%) after an additional 26 (m- and p-) to 100 (o-) days, although it may take longer (Hedgecott and Lewis 1997).

A moderate tendency to sorb to organic solids is suggested by the log Kow values of 2.77 to 3.20 and log Koc values of 2.1 to 2.5. Xylenes may sorb to aquatic sediments but higher proportions remain in solution; low sediment-water partition coefficients of 8.9 for o-xylene and 10.5 for p-xylene have been measured for the Tamar Estuary (Hedgecott and Lewis 1997).

Xylenes readily volatilise from water and this is probably the major single removal process in most surface waters, with a half-life of a few to tens of hours, depending on the degree of mixing (Hedgecott and Lewis 1997).

B54.4 Effects on the marine environment

B54.4.1 Toxicity to marine organisms

An exhaustive literature review on the toxicity of xylenes to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Hedgecott and Lewis 1997). The most sensitive groups of organisms have been identified.

Hedgecott and Lewis (1997) reviewed data on the aquatic toxicity of xylenes. A previous review (Hedgecott 1990) found saltwater data were limited to acute studies only, with the most sensitive of those species tested being the bay shrimp *Crago franciscorum* with 96 hour LC50s of 1.1, 3.2 and 1.7 mg l^{-1} for o-, m- and p-xylene, respectively (mean 2.0 mg l^{-1}). The most sensitive fish was the striped bass *Morone saxatilis*, with 96 hour LC50 values of 9.6, 7.9 and 1.7 mg l^{-1} for o-, m- and p-xylene respectively. These invertebrate and fish results are very similar to the lowest ones for comparable freshwater species.

Hedgecott and Lewis (1997) found few data had become available since the previous review (Hedgecott 1990), and again relate only to acute exposure. The lowest effect concentration is an EC50 for the Microtox bioassay (using *Vibrio fischeri*) of 8.5 mg l^{-1} mixed xylene (Calleja *et al.* 1994). This is similar to a 15 minute Microtox EC50 of 9.2 mg l^{-1} determined previously for p-xylene (Hedgecott 1990), and does not indicate greater sensitivity than previously determined for this or other saltwater species.

No data could be located for sediment-dwelling organisms.

B54.5 Bioaccumulation

Data summarised in (Hedgecott 1990) from fresh and saltwater studies indicated that bioaccumulation of xylenes was not significant, with BCF values ranging from 1 to 15 in freshwater fish and 1 to 24 in saltwater fish and invertebrates, and uptake and depuration both occurring rapidly. Hedgecott and Lewis (1997) found few additional bioaccumulation data had become available since the 1990 review; reported BCFs from a few freshwater test with algae are in excess of 200 but are based on dry algal weight (Herman *et al.* 1991b). Thus, the new data do not indicate higher bioaccumulation potential than that indicated previously.

Xylenes in marine fish in Japan have previously been implicated in tainting problems (Hedgecott 1990). Jardine and Hrudey (1988) determined a taste tainting threshold of 9 mg kg^{-1} for p-xylene spiked into a freshwater fish (the walleye, *Stizostedium vitreum*). Assuming a fish BCF of 15, this implies that a water concentration of 0.6 mg l^{-1} or above might lead to detectable tainting of edible fish.

B54.6 Potential effects on interest features of European marine sites

Potential effects include:

! toxicity of xylenes to invertebrates and fish at concentrations above the proposed EQS of 30 Fg l^{-1} (annual average) of total xylenes in the water column.

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B55. Radioactive substances

B55.1 Entry to the marine environment

Radioactive waste is divided into three broad categories:

1. High-level waste (HLW) - spent fuel or small volumes of highly active fission products from fuel reprocessing.

2. Intermediate-level waste (ILW) - waste products that require handling and shielding but which do not (unlike HLW) emit significant amounts of heat.

3. Low-level waste (LLW) - slightly contaminated waste that can be packaged and handled without special precautions. This includes low-level radioactive liquid effluent and the emission of low-level gaseous radioactivity to the atmosphere. In the UK, radioactive waste with up to $4x10^9$ Bq t^{-1} of alpha emitters and $12x10^9$ Bq t^{-1} of beta/gamma emitters is classified as LLW.

This section deals principally with the last category which is released into the environment.

There are five main sources of radioactivity to the environment and Table B55.1 summarises some of the most common radionuclides in relation to these sources.

Primordial and natural sources. The Earth’s crust contains primordial and natural radioisotopes, such as uranium and thorium, which may produce radioactive decay products. Cosmic radiation entering the Earth’s atmosphere replenishes the Earth’s supply of radionuclides (Kennedy *et al* 1988).

Nuclear weapons testing. Testing and use of nuclear weapons in the atmosphere has occurred since the Second World War. Nuclear explosions result in the presence of fission products, including man-made radioisotopes, in the atmosphere and on the Earth’s surface. Releases into the atmosphere have resulted in widespread contamination of the soils and oceans because of atmospheric circulation and fall-out.

Nuclear power generation. The generation of electricity from nuclear power stations results in low level discharges of radioactivity to the atmosphere, low level radioactive liquid effluent discharges to surface waters and the generation of solid radioactive waste from the normal functioning of the power stations. There is also the potential for uncontrolled releases of radioactivity from accidents, such as Chernobyl (1986).

Nuclear reprocessing industry. The use of nuclear fuel in power stations and in other uses generates spent nuclear fuel and solid radioactive waste that is stored or reprocessed at nuclear reprocessing installations. Two such installations exist in the UK: Sellafield (England) and Dounreay (Scotland). These installations also give rise to low level discharges of radioactivity to the atmosphere, low level liquid radioactive effluent discharges to surface (principally marine) waters and solid radioactive waste. There is also a risk of uncontrolled releases of radioactivity from accidents, such as at Windscale (Sellafield) during 1957.

Various military, industrial, medical and research establishments. Radioactivity is also released into the environment from various smaller sources in the form of low level atmospheric and liquid discharges and potentially from accidental releases. These include:

! Military establishments where nuclear weapons are located or nuclear powered vessels are based;

! industrial providers of radioisotopes for medical, industrial or research use (for example Amersham International plc in the UK), and users of radioisotopes including hospitals and research establishments.

With the exception of primordial and natural sources, all the above are point sources of radioactivity into the environment. However, in terms of entry to the aquatic ecosystem, there is a combination of point and diffuse sources. Discharges of low level liquid effluent discharges to surface waters can be considered as point sources. Discharges of low level discharges and accidental releases to the atmosphere can result in a widespread distribution due to atmospheric circulation, such that fall-out to the aquatic environment is effectively a diffuse source of contamination.

The principal diffuse source of radioactivity to the aquatic environment is from atmospheric fall-out and the main point source is from the nuclear reprocessing industry. Estuarine systems, in particular, are sinks for organic matter from both freshwater and marine origins and, as such, accumulate radionuclides that are associated with organic matter. They are also very productive and act as a nursery and feeding area for fish, birds and macro-crustaceans. As such, there is a pathway for accumulated radionuclides to enter the food web where potential impacts may occur and possibly result in the exposure of Mankind to this source of radioactivity.

B55.2 Recorded levels in the marine environment

The responsibility for monitoring levels of radioactivity in the marine environment lies with the Environment Agency in England and Wales, SEPA in Scotland and the Environment and Heritage Service in Northern Ireland. In addition, the competent authorities for food safety (MAFF, Scottish Executive and DANI) are responsible for monitoring radioactivity in food organisms (including algae, shellfish and fish). MAFF publish an annual report jointly with SEPA on ‘Radioactivity in food and the environment’ (i.e. MAFF 1998) that summarises the results of government surveillance. The main dischargers (i.e. British Nuclear Fuels at Sellafield) also monitor their own discharges and report the results annually (i.e. BNFL 1997).

Radionuclides are found in measurable quantities in the water column, suspended sediments, sea-bed sediments and the biota (Kershaw *et al* 1992).

Kennedy *et al* (1988) reported studies where detectable levels of ^{137}Cs were found in sand flats, *Arenicola* sand flats and coastal embayments and saltmarshes of the Solway estuary and levels of ^{137}Cs and ^{241}Am in the Ravenglass estuary (Table B55.2) .

Kershaw *et al* (1992) reported studies in the Esk estuary where detectable levels of ^{137} Cs, ^{144}Ce, ^{106}Ru, ^{95}Zr, ^{95}Nb and Pu were found. Radionuclides from Sellafield have also been found in the Wyre estuary and in the water column and sediment of the Ribble estuary (Kershaw *et al* 1992).

Table B55.1 Some of the most common radionuclides, with half-lives of greater than one day, from the main sources ofradioactivity to the environment (adapted from Kennedy *et al* 1988)

Element	Radionuclide	Source of radioactivity					
		Primordial or natural origin	**Fallout from nuclear weapon tests**	**Low level liquid discharges and emissions to atmosphere from nuclear reprocessing plants**	**Low level liquid discharges and emissions to atmosphere from nuclear power stations**	**Medical and scientific research**	**Additional radionuclides likely to be emitted from a nuclear power station or reprocessing plant in the event of uncontrolled explosion or fire**
Hydrogen	^{3}H	U	U	U	U	U	
Beryllium	^{7}Be	U					
Carbon	^{14}C	U	U	U	U	U	
Phosphorus	^{32}K				U	U	
Sulphur	^{35}S				U	U	
Potassium	^{40}K	U					
Calcium	^{45}Ca				U		
Chromium	^{51}Cr				U	U	
Manganese	^{54}Mn		U		U		
Iron	^{55}Fe		U		U		
	^{59}Fe				U		
Cobalt	^{58}Co				U		
	^{60}Co		U		U	U	
Nickel	^{63}Ni				U		
Zinc	^{65}Zn				U		
Arsenic	^{76}As				U		
Krypton	^{85}Kr	U	U	U			U
Strontium	^{89}Sr		U		U		
	^{90}Sr		U	U	U		
Yttrium	^{91}Y				U		
Zirconium	^{95}Zr		U	U	U		

Element	**Radionuclide**	**Source of radioactivity**					
		Primordial or natural origin	**Fallout from nuclear weapon tests**	**Low level liquid discharges and emissions to atmosphere from nuclear reprocessing plants**	**Low level liquid discharges and emissions to atmosphere from nuclear power stations**	**Medical and scientific research**	**Additional radionuclides likely to be emitted from a nuclear power station or reprocessing plant in the event of uncontrolled explosion or fire**
Niobium	^{95}Nb		U	U	U		
Technetium	^{95}Tc					U	
	^{99}Tc		U	U			U
Ruthenium	^{103}Ru		U				U
	^{106}Ru		U				U
Silver	^{110m}Ag				U		
Antimony	^{124}Sb				U		
	^{125}Sb				U		
Tellurium	^{125m}Te				U		
	^{132}Te						U
Iodine	^{129}I	U		U	U		
	^{131}I		U		U	U	
Xenon	^{131m}Xe						U
	^{133X}e						U
Caesium	^{134}Cs		U	U	U	U	
	^{136}Cs		U				
	^{137}Cs		U	U	U	U	
Barium	^{140}Ba		U				
Lanthanum	^{140}La		U				U
Cerium	^{141}Ce		U				U
	^{144}Ce		U	U			U
Promethium	^{147}Pm				U		
Neodymium	^{147}Nd		U				U
Europium	^{154}Eu				U		

Element	Radionuclide	Source of radioactivity					
		Primordial or natural origin	Fallout from nuclear weapon tests	Low level liquid discharges and emissions to atmosphere from nuclear reprocessing plants	Low level liquid discharges and emissions to atmosphere from nuclear power stations	Medical and scientific research	Additional radionuclides likely to be emitted from a nuclear power station or reprocessing plant in the event of uncontrolled explosion or fire
	^{155}Eu				U		
Thorium	^{232}Th	U					
Uranium	^{235}U	U					
	^{238}U	U					
Neptunium	^{237}Np		U	U			U
Plutonium	^{238}Pu		U	U			U
	^{239}Pu		U	U			U
	^{240}Pu		U	U			U
	^{241}Pu		U	U			U
	^{242}Pu			U			
Americium	^{241}Am		U	U			U
Curium	^{242}Cm			U			U
	^{243}Cm			U			U
	^{244}Cm			U			U

Table B55.2 Pre-Chernobyl radionuclide concentrations found in coastal sediments (Jones *et al* 1984, Horrill 1983 in Kennedy *et al* 1988)

	Solway Firth	Ravenglass Estuary	
	^{137}Cs (Bq kg^{-1})	^{137}Cs (Bq kg^{-1} dry wt)	^{241}Am (Bq kg^{-1} dry wt)
Fine sand	74-150		
Arenicola sand flats	220-440		
Coastal embayments/ saltmarshes	630-1,900	7,400-19,000	3,000-7,400

Radionuclide accumulation in saltmarshes is controlled principally by the physical processes associated with tidal flow and sediment deposition (Horrill 1983), but the type of vegetation present also has an effect on accumulation rates - vegetated areas accumulate radionuclides, such as americium, caesium and plutonium at faster rates than unvegetated areas. A large number of other factors can also affect accumulation rates, to the extent that variability within and between different saltmarshes can be wide. However, the relative stability and high biological productivity of saltmarsh sediments (away from tidal channels) favours the accumulation of plutonium and caesium isotopes, with highest activities often being associated with fine-grained mud flats, such as those in the Solway Firth (Kennedy *et al* 1988)

Some radionuclides have been found to accumulate in the biota. In particular, benthic algae, molluscs (mussels, winkles, limpets, whelks, scallops, queens), crustacea (crab, lobster, *Nephrops*, shrimps) and fish (including plaice, cod, flounder, herring) have been found to accumulate some radionuclides based on monitoring information collected by MAFF in the Irish Sea (Kershaw *et al* 1992). The principal concern has been to determine the risk to the human population and so the fish and shellfish species selected for monitoring have been commercially important ones. These species have been found to accumulate a number of radionuclides but the most important appear to be ^{106}Ru and ^{137}Cs. Both have been found to accumulate in fish muscle (plaice) and in crab *Cancer pagurus* hepatopancreas and muscle tissue. Crabs were found to accumulate ^{144}Ce and ^{95}Zr/^{95}Nb in addition to ^{106}Ru and ^{137} Cs. The most significant uptake route for these species is believed to be via the diet.

Table B55.3 summarises pre-Chernobyl levels of ^{137}Cs in birds collected from coastal sites in and around Cumbria.

The quantities of some of the shorter-lived fission product nuclides discharged to UK coastal waters, such as ^{95}Zr and ^{106}Ru, have declined since the early 1970s, whilst discharges of ^{134}Cs and the longer-lived ^{137}Cs reached peak values during 1974-1978, since when they too have declined. Discharges of ^{241}Am peaked between 1971 and 1975, and of ^{241}Pu between 1970 and 1980. Further reduction in Am and Pu discharges have occurred since 1994, in contrast to ^{99}Tc, ^{129}I, ^{60}Co and ^{14}C, the quantities of which have increased.

Table B55.3 Pre-Chernobyl levels of ^{137}Cs in birds collected from coastal sites in and around Cumbria (Lowe 1987)

Species	^{137}Cs concentration (Bq.kg^{-1} fresh wt)
Greylag goose (*Anser anser*)	58
Pinkfoot goose (*Anser brachyrhynchus*)	1.2
Shelduck (*Tadorna tadorna*)	290
Wigeon (*Anas penelope*)	160
Mallard (*Anas platyrhynchos*)	170
Merganser (*Mergus serrator*)	140
Blackheaded gull chicks (*Larus ridibundus*)	14
Herring gull (*Larvus argentatus)*	160
Curlew (*Numenius arquata*)	140
Bar-tailed godwit (*Limosa lapponica*)	480
Oystercatcher (*Haematopus ostralegus*)	610
Carrion crow (*Corvus cornoe*)	160

B55.3 Fate and behaviour in the marine environment

The fate and behaviour of radionuclides in the marine environment is determined by the fate and behaviour of the element concerned. For example, if an element is adsorbed to sediment particles, then the radionuclide of that element will behave in the same way.

The radioactive elements will not be destroyed in the environment and radioactivity will be emitted from whatever compounds are formed with the element. The duration that the energy will be emitted is governed by the half-life of the radionuclide which can range from hours to hundreds of years.

B55.4 Effects on the marine environment

There are a number of important factors that determine the environmental effects of radionuclides. Radioactivity is a form of energy released from radioactive elements and the potential for damage depends on the amount of energy absorbed by an organism. In radiation risk assessments, the amount of energy absorbed is termed the absorbed dose (measured in Grays (Gy)). Factors affecting the absorbed dose are the identity of the radionuclide, the type of radioactivity, the chemical form of the radionuclide, the exposure pathway to the organism and the biochemistry of the organism.

There are a number of different forms of radiation, including alpha and beta particles, gamma and x-rays each with different levels of energy. Radionuclides emit some of these forms of radiation in different proportions over different lengths of time (related to the half-life of the radionuclide. In order to compare the absorbed dose from different radionuclides, the estimate in Grays is commonly (though not always) converted by a quality factor to a dose equivalent (measured in sieverts (Sv)). Effectively, this takes into consideration the different biological effects of different types of radiation.

Polikarpov (1998) proposed a conceptual model of radiation effects in the environment, relating dose rates to effects at the individual, population and community level. The model comprises four zones:

! Radiation well-being zone: natural background levels of radiation up to a dose rate of 0.005 Gy yr^{-1};

! Physiological masking zone: where minor radiation effects at the individual level occur between 0.005 Gy yr^{-1} to 0.05 Gy yr^{-1}.

! Ecological masking zone: where effects of radiation at the population level have been detected between 0.05 Gy yr^{-1} and 4 Gy yr^{-1}.

! Damage to ecosystems zone: where community level effects (reduction in the number of organisms, elimination of radiosensitive species and impoverishment of communities) have been detected at concentrations above 4 Gy yr^{-1}.

This model is not confined to the marine environment but has been developed using responses in the marine, freshwater and terrestrial environments.

The most detailed study of potential environmental effects of radioactivity has been the investigations into the impacts of the Sellafield discharges on the marine environment (summarised up to 1992 by Kershaw *et al* 1992).

While it must be assumed that any exposure to radiation carries some risk of harm, for marine organisms, if the damage to individuals is not manifest at the population level, and does not damage the overall reproductive capacity of the population, then the effect may be regarded as being of little significance (Kershaw *et al* 1992). In a comprehensive review of radiation effects reported in Kershaw *et al* (1992), the lowest dose rate at which minor radiation induced disturbances of physiology or metabolism might be detectable was about 400 FSv hour^{-1}. The dose rates around Sellafield were at least an order of magnitude below those which would be expected to elicit effects under controlled laboratory conditions and about two orders of magnitude below those which might be expected to have an effect at the population level during the period of maximum discharges (Kershaw *et al* 1992). There have been no conclusively demonstrated effects at the population level of the radioactive discharges from Sellafield on the marine environment.

B55.4.1 Effects on marine organisms

An exhaustive literature review on the effects of radioactive substances on marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing review documents (Kershaw *et al* 1992 and Parrett 1998).

Parrett (1998) considered the following issues in a consideration of the effects of radioactivity on North Sea fish stocks:

! lethal effects;

! effects on reproductive success;

! genetic effects.

Studies reported in Parrett (1998) indicated that the range of lethal levels in adults of different species of fish was in the range 3.75 to 100 Gy, and for invertebrates ranging from 0.2 to above 500 Gy. Earlier developmental stages have been identified as more susceptible and mortality of fish embryos has been shown to occur at about 0.16 Gy.

The effects on reproductive success in fish that have been demonstrated include sterility, reduction in counts of primordial germ cells and reduced testicular weight. The lowest dose rate at which effects of chronic radiation exposure on fertility of aquatic invertebrates and fish were demonstrated was about 0.25 mGy hour^{-1} (Parrett 1998). The implied mechanism for these effects was damage to germ cells and the induction of dominant lethal mutations in gametes.

Mutation rates increase in relation to radiation exposure and so therefore does the chance of deleterious mutations occurring. While natural selection will act to keep these mutations at low level in the gene pool, some expression might occur in the short-term (in the form of sterility or dominant lethal mutations) or in the long term (in the form of ‘genetic disease.’)

Despite these types of effects being demonstrated in laboratory conditions, there is no evidence of the consequences of this expression at the population level in fish or macro-crustaceans. Dose rates in the order of 10 mGy hour^{-1} are considered acceptable for the protection of aquatic populations. This assumes some damage to individuals but not to the extent that this would affect the population as a whole (Parrett 1998).

B55.5 Bioaccumulation

Little is known of the processes involved in radionuclide uptake and retention to be able to predict those species which will be most efficient at accumulating environmental radioactivity. However, a number of generalisations can be made:

! Reproductive stages and growing tissues are the most sensitive to radioactivity, notably the eggs of marine fish (Kershaw *et al* 1992).

! Like more typical pollutants, such as persistent organics and heavy metals, radioactive isotopes can be bioaccumulated, both within primary producers and by uptake through the food chain.

! Bacteria, fungi and some lichens tend to be relatively tolerant to radioactivity.

! Amongst fauna, mammals appear to be the most sensitive, followed by birds, and then insects.

! Environmental radioactivity is not known to have produced deleterious effects in the growth patterns of plants and animals, so radioactive isotopes are probably less important than many of the other contaminants listed in this document.

The lowest dose rate at which minor radiation-induced disturbances in physiology or metabolism might be detectable is about 400 µSv.hour^{-1} (IAEA 1976), approximately an order of magnitude greater than the dose rates measured around Sellafield (Kershaw *et al* 1992) which is the largest radionuclide source in the British coastal environment. Despite this, wading birds and their prey are potential accumulators of radionuclides, so a precautionary approach is desirable. The following nuclide concentration factors have been estimated for a range of marine biota (Table B55.4. from Preston and Jeffries 1969):

Table B55.4 Estimated concentration factors for several fission product (from Preston and Jeffries 1969)

Biota	^{106}Ru	^{95}Zr/^{95}Nb	^{137}Cs	^{90}Sr
Fucus vesiculosus	330	1700	100	6
Porphyra	1800	420		1
Mussels	2000	950	15	8
Winkles	2000	1000	100	17
Limpets	1200	750	70	15
Lobster	25	10	25	
Shrimps	600	200	100	
Plaice	10		45	0.3
Skate	1		25	0.3

B55.6 Potential effects on interest features of European marine sites

Potential effects include:

! accumulation of radionuclides in sediments (particularly in estuaries) and in biota;

! exposure of organisms to ionising radiation at dose rates greater than background levels (if a precautionary approach is adopted).

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B56. Algal toxins and algae-related fish kills

B56.1 Entry to the marine environment

Algal toxins do not enter the marine environment from an external source but are generated during blooms of particular naturally occurring marine algal species. Such blooms have been referred to as toxic algal blooms, harmful algal blooms (HABs) and red tides. For example *Gyrodiunium aureolum* causes a red discolouration of the water (a red tide) and has been associated with shellfish and fish mortalities, particularly in marine fish farms. *Chaetoceros*, another alga, has spines which can physically clog and damage fish gills, leading to the death of cage-reared salmon and other species. Other algal species, such as *Alexandrium* and *Dinophysis* can cause poisoning through the food chain when shellfish ingest these algae (and their toxins) and are then subsequently consumed by fish, birds and potentially humans (Environment Agency 1998). The occurrence of blooms of these and other so-called toxic algae is perfectly natural but there are concerns that increases in the supply of essential nutrients (such as nitrogen (see Section C1), phosphorus (see Section C2)) to the marine environment as a result of Man's activities may be contributing to the increased frequency and magnitude of these events.

Algal toxins can give rise to a number of different poisoning syndromes:

- NSP - neurotoxic shellfish poisoning;
- PSP - paralytic shellfish poisoning;
- ASP - amnesic shellfish poisoning;
- DSP - diarrhoetic shellfish poisoning;

All are caused by toxins synthesized by dinoflagellates, except for ASP, which is produced by diatoms of the genus *Pseudonitzschia* (WHOI 1995). Some species of microflagellates may also produce toxins, e.g. *Chrysochromalina* sp. A fifth human illness, ciguatera fish poisoning (CFP), is caused by benthic dinoflagellate toxins in coral reef communities. However, this does not represent a problem in UK waters.

The principal concern about the effects of algal toxins in the environment has been the contamination of sea food for human consumption and consequently much of the research and monitoring is directed at protecting humans from these effects. There must also be concerns on the effects of these toxins on natural populations of consumers (fish, birds and marine mammals).

B56.2 Recorded levels in the marine environment

Monitoring for the occurrence of toxic algae and their effects is carried out routinely by the Centre for the Environment, Fisheries and Aquatic Sciences (CEFAS) on behalf of MAFF in England and Wales, by Fisheries Research Services in Aberdeen on behalf of SERAD in Scotland and by DANI in Northern Ireland. The results of this monitoring is reported annually (e.g. Howard and Kelly 1997 and MAFF 1998).

Monitoring takes the form of the analysis of water samples for the presence and concentration of toxic algal species and the measurement of concentrations of algal toxins in samples of shellfish flesh.

Standards for concentrations of algal toxins in shellfish flesh (so-called end product standards) have been set in The Food Safety (Fishery Products and Live Shellfish) Regulations 1998 as a requirement of the Shellfish (Hygiene) Directive. Breaches of these standards can result in the closure of a particular fishery for a period of time.

It is very difficult with current knowledge to determine the likelihood of toxic algal bloom occurrence, since bloom occurrence appears to be only loosely linked to nutrient levels (if at all), although it has been suggested by a number of authors that changes in salinity can stimulate either the growth or decline of toxic blooms. Other factors that have been cited for the reported increased occurrence of harmful algal blooms include increased awareness and monitoring (especially in relation to the effects on aquaculture), climate change and the transport of toxic algal species in the ballast tanks of vessels. Toxic dinoflagellate species also overwinter by forming spores which settle on the sea bed. These germinate and provide the inoculum for bloom development in future years. Consequently, once a toxic bloom has occurred for the first time, there is an increased risk of toxic bloom development at the same site in future years. Dinoflagellate spores remain viable for a relatively long period of time (certainly several, and perhaps tens, of years).

B56.3 Fate and behaviour in the marine environment

Algal toxins are naturally occurring compounds that are released into the environment, either when algal cells are ingested by filter feeding animals, or when algal cells are broken down after a bloom crashes. The fate and behaviour of these toxins in the marine environment is not well known but they will undergo microbial biodegradation when released into the environment.

Some dinoflagellate species of toxic algae form cysts that can accumulate in the sediment and act as an inoculum for a new population when conditions favour germination of the cysts.

B56.4 Effects on the marine environment

B56.4.1 Effects on marine organisms

An exhaustive literature review on the effects of algal toxins to marine organisms has not been carried out for the purposes of this profile. The information provided in this section is taken from existing general information and selected references.

The direct effects of blooms of toxic algae on marine organisms include:

! sub-lethal and lethal toxicity, especially to fish, birds and sea mammals;
physical damage to fish gills.

Toxic phytoplankton can be filtered from the water by shellfish, such as clams, mussels, oysters, or scallops, which then accumulate the algal toxins to levels which can be lethal to consumers, including humans (Shumway 1990, Ahmed 1991). Typically, the shellfish are only marginally affected, even though a single clam can sometimes contain sufficient toxin to kill a human. Fish and shellfish can also be subject to sub-lethal effects, including increased susceptibility to disease and reduced growth.

Fish can be affected by algal toxins, either by direct uptake from the water column (planktivorous fish) or by bioaccumulation through the food chain (zooplankton and macroinvertebrates). In turn, these fish can then endanger whales, porpoises, seabirds, and other animals.

In addition to toxin production, algae have also been implicated in fishkills by the following direct methods:

! Mechanical damage to gills by algal spines, notably the serrated spines of *Chaetoceros* spp. (e.g. Yang and Albright 1992).

! Irritation of gills resulting in over-production of mucilage within the gills leading to suffocation (WHOI 1995).

! Physical blocking of the secondary lamellae of fish gills (Jones and Rhodes 1994).

! Increased water viscosity due to the secretion of polysaccharides (e.g. Hallegraeff 1992).

The principal indirect effects arise from changes in the oxygen balance of the water column associated with the presence of the bloom during its growth phase (supersaturation with oxygen during the day and oxygen depletion during the night) and the decay of the algal cells when the bloom has crashed (oxygen depletion of parts of the water column and possibly the sediments).

Algae have been implicated in fishkills by the following indirect methods:

! Asphyxiation caused by oxygen depletion (e.g. Brooker *et al* 1977). This can occur as a result of the oxygen demand generated by a senescent bloom, or at night due to extreme diurnal fluctuations in dissolved oxygen levels which may occur during algal blooms.

! Gas bubble trauma from extreme oxygen supersaturation (Renfro 1963).

B56.5 Bioaccumulation

Many algal toxins readily bioaccumulate in marine animals and significantly biomagnify through food chains posing a hazard to consumers at higher trophic levels (fish, birds and sea mammals).

B56.6 Potential effects on interest features of European marine sites

Potential effects include:

! bioaccumulation and sub-lethal and lethal toxicity of a range of algal toxins to consumers at higher trophic levels (fish, birds and sea mammals). A precautionary approach to determining the scale of possible impacts of algal toxins should be adopted if the presence of toxic algal species or algal toxins is detected in a European marine site ;

! adverse physical effects on fish because of the presence of harmful algal blooms;

! hazards to all marine organisms resulting from changes to the oxygen balance of the water column, and potentially the sediments, both during and after a harmful algal bloom.

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B57. Microbial pathogens and toxins

B57.1 Entry to the marine environment

- introduction of infected alien species;
- Introduction of pathogens directly from ship ballast water;
- Effluent disposal;
- translocation/release of infected native species from other sites.
- Modes of action
- Direct infection by pathogenic bacteria present in the water or river sediments;
- Infection of stressed or debilitated animals by opportunistic pathogens in the water or sediments;
- Release of endo- or exotoxins by bacteria (see below).
- Bacterial toxins

Most bacterial toxins can be divided into two basic types (Todar 1997a,b):

- Proteins (exotoxins), which may be released into the environment by pathogenic bacteria.
- Lipopolysaccharides (endotoxins), which form part of the cell walls of Gram-negative bacteria.

Exotoxins

Most of the protein toxins are thought of as exotoxins, since they are released from bacteria and act on host cells at a distance (Topley and Wilson 1990). Typically, they are released during exponential growth, and are specific to a particular bacterial species.

Bacterial protein toxins are often very potent, retaining high activity at very high dilutions. The site of damage caused by the toxin usually indicates the location of the substrate for that toxin, but while some protein toxins have very specific cytotoxic activity, others (as produced by staphylococci, streptococci, clostridia, etc.) exhibit broader activity, being able to cause non-specific death of many cell types and tissues.

The group of filamentous bacteria, known as actinomycetes, contains a number of known exotoxin-producing genera, such as *Corynebacterium,* which do not need to be dominant members of the microbial community to have a toxic effect.

Endotoxins

Although the term endotoxin is occasionally used to refer to any cell-associated bacterial toxin, it should be (and is usually) reserved for the lipopolysaccharide (LPS) complex associated with the outer envelope of Gram-negative bacteria, such as *E. coli, Salmonella, Shigella* and *Pseudomonas* (Todar, 1997b, Topley and Wilson, 1990). LPSs can elicit a variety of inflammatory responses in animals (Todar, 1997b).

Gram-negative bacteria probably release minute amounts of endotoxin during growth. For example, it is known that small amounts of endotoxin may be released in a soluble form, especially by young cultures. However, for the most part, endotoxins remain associated with the cell wall until disintegration of the bacteria.

B57.2 Recorded levels in the marine environment

Microbial pathogens of humans are monitored in the marine environment by measuring indicators of human faecal contamination (e.g. faecal coliforms) in water and in biota (mainly shellfish) destined for human consumption. The presence of these indicator organisms is used to indicate the presence of other human derived microbial pathogens. The principal aim of the monitoring and the control mechanisms is to prevent humans coming into contact with these pathogens.

The principal monitoring of the marine environment for micro-organisms is associated with assessing compliance with standards laid down in the Bathing Waters Directive (see Section 5.4) and the Shellfish Waters Directive (see Section 5.3). This monitoring is limited to designated bathing waters in the bathing season and to designated shellfish waters (see Sections 2.2.2.6 and 2.2.2.4 respectively).

Microbial toxins are not routinely monitored in the marine environment.

B57.3 Fate and behaviour in the marine environment

The marine environment is hostile to most microbial pathogens and they will rapidly die off, especially in the presence of sunlight. They do become associated with suspended particles and can accumulate to some extent in sediments and survive for days or weeks. Microbial pathogens can accumulate in filter feeding organisms to levels that can be harmful to humans and perhaps other consumers (e.g. birds).

B57.4 Effects in the marine environment

In theory, almost any plant or animal is at risk from microbial pathogens, albeit that most attention has focused on the causes of fish kills and illnesses of marine mammals, although monitoring of shellfish populations means that more information probably exists about this group of organisms than any other collective group of marine fauna.

In marine waters, species of bacteria from the *Aeromonas, Alteromonas/Pseudomonas* and *Vibrio* groups have been detected in elevated numbers during fish kills associated with *Ptychodiscus brevis* red tides (Buck and Pierce 1989). Microbial pathogens are also regarded as a potential threat to bottlenose dolphins by Grellier *et al* (1995), while Thompson *et al* (1997) suggested that pathogens associated with the discharge of raw sewage from the town of Inverness could have been responsible for pathogenic infection of harbour seals.

B57.5 Potential effects on interest features of European marine sites

Potential effects include:

- potential for pathogenic infection of sea birds and Annex II sea mammals, resulting from exposure to microbial pathogens in food organisms or in the water column;

- potential for sub-lethal and lethal effects in marine organisms, resulting from exposure to microbial toxins.

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Appendix C. Non-toxic substance profiles

CONTENTS

C1. Nitrogen

The issues surrounding the potential effects of nutrients, including nitrogen, in relation to nature conservation in estuaries and coastal waters have been reviewed by Parr and Wheeler (1996), Scott *et al* (1999) and Parr *et al* (1999). The reader is referred to these documents for further details.

C1.1 Entry to the marine environment

Nitrogen (N) can enter the marine environment from a variety of point and diffuse sources (Table C1.1).

Table C1.1 Summary of point and diffuse sources of nitrogen to the marine environment

Point sources	Diffuse sources
Discharges of sewage effluent from sewage treatment works (STW)	Run-off/leaching from the land catchment to rivers and groundwaters or directly to estuaries and coastal waters
Discharges from some industrial processes	Atmospheric deposition
Cage fish farm installations	Off-shore waters
	Nitrogen fixation

Nitrogen in coastal waters is derived predominantly from land run-off and direct discharges of sewage effluent from sewage treatment works (STW), although in nutrient-poor marine and estuarine areas, atmospheric deposition of NO_X and NH_4 may make a large contribution. Of terrestrial sources, run-off/leaching of nitrogen from agricultural sources (livestock waste and inorganic fertiliser) represents the major source in most catchments, but it is possible for sewage effluent to be the major nitrogen source in highly urbanised catchments.

As atmospheric deposition is the major nitrogen source in oceanic waters, it is sometimes assumed that it will represent a major source in tidal waters. However, this is not usually the case. The following nitrogen budgets (Table C1.2) (Parr *et al* 1999) can be considered typical for many estuaries, with diffuse agricultural sources (livestock waste and inorganic fertiliser run-off) normally dominating the nitrogen inputs. Only in relatively small, highly urbanised catchments is the STW-derived nitrogen load likely to approach the diffuse source load. Nitrogen fixation by blue-green algae and bacteria in uncolonised sediment and saltmarsh typically accounts for a small proportion (typically <5%) of the N load to estuaries.

C1.2 Recorded levels in the marine environment

It is standard practice to monitor nitrate, nitrite and ammonium concentrations in tidal waters which, when added together, produce total inorganic nitrogen (TIN), an approximation of bioavailable nitrogen. However, some low molecular-weight organic nitrogen molecules, such as urea and some amino acids, are also taken up by algae and higher plants.

Table C1.2 Provisional nitrogen budget (tonne yr^{-1}) for estuaries in the Penllyn a'r Sarnau candidate SAC (from Parr *et al* 1999)

	Glaslyn/ Dwyryd Estuary	**% of input**	**Mawddach Estuary**	**% of input**	**Dyfi Estuary**	**% of input**
Atmospheric/background to land	67.2	12.7	76.3	14.9	133.5	12.6
Atmospheric to estuary	32.8	6.2	18.5	3.6	18.5	1.8
Livestock	208.2	39.4	236.4	46.2	513.6	48.7
Inorganic fertiliser	136.0	25.8	154.5	30.2	336.2	31.9
STWs	69.6	13.2	17.3	3.4	32.8	3.1
In-estuary N_2 fixation	14.0	2.7	8.6	1.7	20.9	2.0
Sub-total	527.8	100.0	511.6	100.0	1055.5	100.0
Loss via denitrification	47.5		35.8		73.9	
Total (input minus denitrification loss)	480.3		475.8		981.6	

A wide range of concentrations are reported, with mean coastal water concentrations in England and Wales ranging from 0.07 to 1.85 mg l^{-1} TIN (Parr *et al* 1999). Concentrations in the upper reaches of estuaries are similar to those found in river water, so concentrations here are often much higher, ranging from about 0.1 mg TIN l^{-1} to 10 - 15 mg TIN l^{-1}. However, annual means hide a great deal of variability, with peak estuary concentrations occurring during autumn/winter and peak coastal water concentrations during winter. Thus, it is winter samples which are normally used for temporal and spatial comparisons of tidal water TIN concentrations.

MPMMG (1998) reported concentrations of ammonia, nitrite and nitrate for National Monitoring Programme sites in estuaries and coastal waters throughout the UK.

Annual instream nitrogen loads calculated using flow/monitoring data are presented for all Harmonised Monitoring Sites by Parr *et al* (1999). However, the N load measured at Harmonised monitoring sites may constitute less than half of the land-derived load (to smaller estuaries in particular).

The Environment Agency commissioned WRc to derive a classification scheme for nutrients in estuaries and coastal waters as part of their General Quality Assessment (GQA) scheme (Gunby *et al* 1995). The proposed GQA methodology for classifying TIN levels allows comparisons to be made using samples collected from different regions (salinities) of different estuaries, or different areas within the same estuary. This is because the GQA methodology assumes conservative behaviour for TIN and a standard concentration in marine waters, which allows the TIN concentration in the freshwater input to be calculated, provided salinity data are available. Estuaries can then be grouped according to the following class boundaries:

Class	**Median projected TIN (mg l^{-1})**
A/B	5.3
B/C	8.1
C/D	11.1

For a range of estuaries in England, this provides the following projected median TIN concentration in freshwater and GQA TIN class (Table C1.3).

Different sources cite different nutrients as limiting in estuaries and coastal waters. Scott *et al* (1999) should be referred to for a more comprehensive review than is possible here.

As the freshwater input to estuaries from large lowland rivers usually has a nitrogen:phosphorus (N:P) ratio of >10, the water column is more likely to be P-limited than N-limited, particularly at the freshwater end of the estuary, but it appears that saltmarshes are usually N-limited. Although UK coastal waters have conventionally been described as nitrogen-limited, available data suggest that there are three major regions of coastline which are phosphorus-limited (i.e. the TIN:TRP ratio is >10; see Parr *et al* 1999). These regions extend from north of the Humber to the Essex estuaries, from the Solent to Dartmouth and around the Severn coastline from Padstow to Oxwich.

C1.3 Fate and behaviour in the marine environment

Nitrogen cycling in estuaries and coastal waters is a complex phenomenon and is outlined in Scott *et al* (1999) and in Parr *et al* (1999). Nitrogen is a major constituent of biota, so plants and animals (including plankton) are a sink for nitrogen. However, the largest sink for nitrogen remains the sediment, particularly in terms of organic nitrogen but, once in the sediment, this organic nitrogen can be broken down (mineralised) to produce bioavailable nitrogen, which is released back into the water column.

Nitrogen losses are achieved via denitrification (the conversion of nitrate to molecular nitrogen via ammonium). In estuarine and coastal shelf systems, this can amount to 7 - 54% of the total N or 11 - 57% of DIN (Dissolved Inorganic Nitrogen) (Nowicki *et al* 1997). The longer the residence time, the warmer the temperature and shallower the estuary, the greater N losses will be via denitrification.

C1.4 Effects on the marine environment

The effects of non-toxic substances, such as nitrogen, on the marine environment can be sub-divided into direct effects (those organisms directly affected by changes in the concentrations of nitrogen species) and secondary effects (those arising in the ecosystem as a result of the changes in the organisms directly affected).

The terms nutrient enrichment and hyper-nutrification are used to describe the increasing concentrations of nutrients, including nitrogen, in the aquatic environment but do not relate to the consequences or effects of the increasing nutrient levels. The term eutrophication has been defined by the Environment Agency (1998) as “the enrichment of waters by inorganic plant nutrients which results in the stimulation of an array of symptomatic changes. These include the increased production of algae and/or other aquatic plants, affecting the quality of the water and disturbing the balance of organisms present within it. Such changes may be undesirable and interfere with water uses.” As such, it encompasses both the increasing nutrient levels and the resulting direct and indirect effects.

Table C1.3 Classification of selected estuaries in England according to the GQA TIN projection methodology

Estuary	Projected median TIN concentration ($mg\ l^{-1}$) in freshwater	GQA TIN class
Blackwater	14.3	D
Camel	5.9	B
Carrick	5.4	B
Colne	12.7	D
Crouch	11.3	D
Dart	4.3	A
Deben	11.5	D
Exe	5.4	B
Fal	9.4	C
Fowey	4	A
Hamford Water	10	C
Helford	7.3	B
Humber	8.8	C
Itchen	5.6	B
Lynher	5.5	B
Medway	5.1	A
Mersey	7.1	B
Nene	15.1	D
Ore/Alde	9.5	C
Orwell	14	D
Ouse	12.2	D
Roach	11.9	D
Severn	7.6	B
Stour	13.3	D
Tamar	4.6	A
Test	6.3	B
Thames	12	D
Wash	13	D
Welland	13.1	D
Witham	21.9	D
Wyre	9	C
Yare	9.7	C
Yealm	5.9	B

Using the monitoring techniques currently employed, it is very difficult to unequivocally make a case for nutrient enrichment having a deleterious effect on the quality of tidal water ecosystems, because of the many confounding factors (e.g. see Parr and Wheeler 1996). In particular, because high nutrient loads are often associated with high organic loads, it is often very difficult to distinguish between the effects of these two parameters. More ecologically relevant methods of monitoring the trophic status of estuaries are discussed by Scott *et al* (1999) and Parr *et al* (1999). The adoption of some of these novel techniques should make the identification and formal legal control of eutrophication a simpler process.

C1.4.1 Direct effects

In the water column, the direct effects of increases in nitrogen compounds are the toxicity of ammonia (see Section B1) and the response of algae and other aquatic plant communities using nitrogen compounds as nutrients.

Increasing nitrogen concentrations have been shown to be related to increasing phytoplankton standing crops (reflected in increasing chlorophyll-a concentrations). Thus, a number of authors have modelled chlorophyll-a and nitrogen levels using linear regressions (e.g. Gowen *et al* 1992). The extent to which phytoplankton standing crops increase in relation to increasing nitrogen concentrations is limited by factors, such as the availability of other nutrients (phosphorus (see Section C2) and silicon, for diatoms, (see Section C3), the level of turbidity (see Section C9) and measures related to the time in which the increased nitrogen levels are available to the phytoplankton for growth. Consequently, relationships between nitrogen and chlorophyll-a concentrations are often weak, but may be improved by the use of correction factors to account for tidal flow/water velocity (e.g. Lack *et al* 1990). The use of similar factors to account for regional differences in turbidity around the UK coast (e.g. Parr *et al* 1998) could greatly increase the accuracy of such models.

Although it has been postulated that elevated nutrient levels are associated with increased occurrence of *Phaeocystis* (notably in the Adriatic, but also around the UK coast) and toxic dinoflagellate blooms (see Section B56), there is little evidence to support such a claim. The germination of spores lying on the sediment makes it much more likely that, following an initial bloom, blooms will reoccur in subsequent years.

Macroalgae found attached to hard surfaces in estuaries and coastal waters also respond to increasing concentrations of nitrogen in the water column, resulting in increased areal coverage and density. The most common macroalgal species involved are *Enteromorpha* spp. and *Ulva* spp.

Both nutrient and organic status influence the intertidal benthic diatom community, which may provide a good indicator of trophic status (e.g. Vos and de Wolf 1993, Parr *et al* 1999, Peletier 1996) - not in terms of biomass (chl-a), but rather in terms of species composition. However, the benthic diatom community consists of several sub-communities (those diatoms which live in interstitial water, those that are firmly attached to sediment granules, and those that live in frequently-desiccated areas of sediment). It is imperative that the same sub-community is monitored on all occasions. Epiphyte communities on macroalgae may similarly provide a sensitive indicator of trophic status.

C1.4.2 Indirect effects

The indirect effects of increased inputs of nitrogen are associated with changes in aquatic ecosystems resulting from the stimulation of algal and other plant communities in the water column and on the substratum.

While phytoplankton blooms are a natural occurrence, the nutrient enrichment of estuaries and coastal waters has been implicated in the more widespread occurrence and increased frequency and duration of such blooms. The plankton community includes consumers of phytoplankton, such as zooplankton which, in turn, are consumed by various metazoan animals (e.g. jellyfish and fish). The stimulation of phytoplankton will have knock-on effects for these consumers and change the community composition of the plankton with the possibility that biodiversity will be reduced.

Phytoplankton blooms can affect water quality during the growth and die-off phases. During the growth phase, the diurnal variation in dissolved oxygen can be exacerbated, such that, during the day, the water column can become supersaturated with oxygen as a result of the photosynthetic activity and, during the night, oxygen can become severely depleted due to respiration. Such fluctuations in dissolved oxygen can pose problems for invertebrates and fish and can lead to fish kills (see Section C5). During the die-off phase, the superabundance of phytoplankton cells in the water column and settling onto the substratum is a source of organic carbon for aerobic bacteria which rapidly decompose this material but, in doing so, can exert an oxygen demand on the water column and on the sediments resulting in severe oxygen depletion. This can lead to sublethal and lethal effects on invertebrates and fish. These changes in water quality are likely to be greatest in semi-enclosed bodies of water with long retention times and where stratification of the water column occurs (see Section 6).

Phytoplankton blooms can contribute to an increase in turbidity in the water column (see Section C9) which reduces the light availability to macroalgae and plants growing in the photic zone and resulting in a reduction in the depths of colonisation for several species (Parr *et al* 1998, Birkett *et al* 1998).

Repeated phytoplankton blooms can lead to severe degradation of the marine environment with potential adverse consequences for birds and sea mammals as the diversity and abundance of food organisms change.

The stimulation in the growth of macroalgae, particularly *Enteromorpha* and *Ulva*, in intertidal areas can result in the formation of an extensive cover of algal material (an algal mat) on the surface of exposed sediments. Above a critical standing crop, the increased amount of organic material and the reduced exchange of water between the sediment and the water column result in deoxygenation of the sediments. This can lead to a change in the infaunal benthic community and, in severe cases, the death of many benthic invertebrate species. Extensive coverage of intertidal sediments can severely diminish the feeding areas for fish and birds.

For a full range of possible direct and indirect effects of nutrient enrichment, the reader is referred to Scott *et al* 1999.

C1.5 Potential effects on interest features of European marine sites

Potential effects include:

- toxicity of ammonia to invertebrates and fish in the water column (see Section B1);
- stimulation of phytoplankton growth in the water column of estuaries and coastal waters;
- stimulation of macroalgae, particularly *Enteromorpha* and *Ulva* spp., on the substrata of estuaries and coastal waters;
- perturbation of the plankton community, including zooplankton, other invertebrates and fish, as a result of repeated phytoplankton blooms with the potential to reduce biodiversity;

- increased fluctuation is dissolved oxygen concentrations in the water column during the growth phase of a bloom with the potential for sub-lethal and lethal effects on invertebrates and fish;

- potential for depletion of oxygen concentrations in the water column and sediments as a result of the die-off of phytoplankton blooms with the potential for sub-lethal and lethal effects on invertebrates and fish;

- contribution to increased turbidity in the water column and reduction in light availability to macroalgae and other aquatic plants growing in the photic zone;

- reduction in oxygen availability in intertidal sediments under algal mats with the potential for sub-lethal and lethal effects on infaunal invertebrates and reduced feeding areas for fish and birds;

- potential for severe degradation of the ecosystem with adverse consequences for sea birds and Annex II sea mammals.

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C2. Phosphorus

The issues surrounding the potential effects of nutrients, including phosphorus, in relation to nature conservation in estuaries and coastal waters have been reviewed by Parr and Wheeler (1996), Scott *et al* (1999) and Parr *et al* (1999). The reader is referred to these documents for further details.

C2.1 Entry to the marine environment

Estuaries are the most difficult of all waterbodies on which to undertake source apportionment studies, although useful indicators of the relative importance of land-derived sources are provided by national studies. For example, the SDIA (1989) proposed that 20-25% of the phosphorus (P) in UK rivers is detergent-derived, with a similar proportion from human waste (faecal matter) and about 45% from agriculture. Giving more detail, the SDIA later attributed 3% of surface water phosphorus as being derived from direct industrial charges, 53% from sewage effluent, 25% from livestock, 2% from silage losses and 17% from soil run-off. Morse *et al.* (1993) produced similar values, albeit derived into different sources. They attributed 7% of the phosphorus in UK surface waters to background sources, with 17% derived from fertiliser, 10% from industry, 23% from detergents, 29% from human sources and 35% from livestock.

Estimating the marine-derived P load to estuaries and coastal waters is very much more difficult, but it should be remembered that estuaries are short-lived features (in geological terms) which, as you are reading this, are in-filling with deposited particulate matter from the fresh and marine water inputs. Suspended particulate matter contains phosphorus, so for estuaries that are rapidly in-filling (predominantly due to deposition of marine-derived particulate matter), this may account for a large proportion of the phosphorus budget. Thus, Parr *et al* (1999) calculated land and atmosphere-derived P budgets for the three estuaries within the Penllyn a'r Sarnau candidate SAC (Table C2.1), but based on sediment accumulation rates, predicted that P inputs to the estuaries may be doubled due to the load of suspended particulate matter from the marine environment.

Table C2.1. Provisional P budget for estuaries in the Penllyn a'r Sarnau candidate SAC (from Parr *et al* 1999)

	Glaslyn/ Dwyryd Estuary	% of total budget	Mawddach Estuary	% of total budget	Dyfi Estuary	% of total budget
Background from land	3.4	9.9	3.8	19.3	6.7	17.4
Atmospheric to estuary	0.6	1.8	0.4	1.8	0.6	1.5
Livestock	8.0	23.3	9.1	46.3	18.8	48.7
Inorganic fertiliser	1.0	3.0	1.2	6.0	2.6	6.8
STWs	21.3	61.9	5.2	26.6	9.9	25.6
Total	34.3	100.0	19.6	100.0	38.6	100.0

The estimation of land and atmosphere-derived nutrient inputs is discussed by Scott *et al* (1999), but more useful information is provided by Johnes *et al* (1994) and Mainstone *et al* (1996). Parr *et al* (1998) provided a useful worked example of N and P nutrient budgets/source apportionment for the upper reaches of the River Avon, Hampshire - exactly the same procedures can be used for tidal waters.

C2.2 Recorded levels in the marine environment

Phosphorus is present in the aquatic environment in both inorganic and organic forms. The principal inorganic form is orthophosphate which can be measured as dissolved orthophosphate (or soluble reactive phosphate SRP) by measuring phosphate in samples that have been filtered through a 0.45 mm mesh or as total reactive phosphate (TRP) by measuring phosphate in unfiltered samples.

Much of the monitoring undertaken by the Environment Agency in England and Wales involves the measurement of TRP, while the National Monitoring Programme uses SRP for sites in estuaries and coastal waters of the UK (MPMMG 1998).

Mean total reactive phosphate (TRP) (unfiltered orthophosphate) values in English and Welsh coastal waters range from 0.007 to 0.165 mg P l^{-1} (Parr *et al* 1999). Phosphorus was included in the proposed GQA scheme for nutrients in estuaries (Gunby *et al* 1995) which, as for nitrogen, utilises the estimated nutrient (TRP) concentration in freshwater as the classification statistic, according to the following class boundaries:

Class	Median projected TRP (mg l^{-1})
A/B	0.087
B/C	0.35
C/D	1.00

For some estuaries in England, this provides the range of values shown in Table C2.1.

As the freshwater input to estuaries from large lowland rivers usually has an N:P ratio of >10, the water column, particularly at the freshwater end of the estuary, is more likely to be P- than N-limited, but it appears that saltmarshes are usually N-limited. Although UK coastal waters have conventionally been described as nitrogen-limited, available data suggest that there are three major regions of coastline which are phosphorus-limited (i.e. the TIN:TRP ratio is >10; see Parr *et al* 1999). These regions extend from north of the Humber to the Essex estuaries, from the Solent to Dartmouth and around the Severn coastline (from Padstow to Oxwich).

C2.3 Fate and behaviour in the marine environment

The phosphorus cycle in estuaries and coastal waters has been summarised in Scott *et al* (1999) and Parr *et al* (1999).

Table C2.1 Classification of some estuaries in England according to the GQA phosphorus projection methodology

Estuary	Projected median TRP concentration (mg l^{-1}) in freshwater	GQA TRP class
Blackwater	6.8	D
Camel	0.4	C
Carrick	4.6	D
Colne	4.2	D
Crouch	5.3	D

Estuary	Projected median TRP concentration ($mg\ l^{-1}$) in freshwater	GQA TRP class
Dart	0.2	B
Deben	6.2	D
Exe	0.3	B
Fal	5.1	D
Fowey	0.1	A
Hamford Water	6.8	D
Helford	3.2	D
Humber	0.1	B
Itchen	0.3	B
Lynher	0.1	A
Medway	0.4	C
Mersey	0.4	C
Nene	0.9	C
Ore/Alde	-1.0*	A
Orwell	3.2	D
Ouse	0.8	C
Roach	11.4	D
Severn	0.5	C
Stour	2.5	D
Tamar	0.2	B
Test	0.3	B
Thames	2.4	D
Wash	1.5	D
Welland	0.4	C
Witham	0.5	C
Wyre	7.9	D
Yare	0.6	C
Yealm	4.2	D

The principal form of phosphate is orthophosphate which is assimilated by algae and converted to organic phosphate. After death of the algal cell, organic phosphate is released and converted into phosphate in dissolved inorganic, particulate and organic forms. Phosphate is associated with suspended particles in low salinity and high dissolved oxygen situations and, consequently, the concentrations of phosphate in the turbidity maximum of estuaries are large and the sediments are a significant sink for phosphorus. Sediments can also be a considerable source of phosphorus if the sediment becomes depleted in oxygen because, under these conditions, phosphate becomes desorbed and diffuses into the water column.

C2.4 Effects on the environment

The effects of non-toxic substances, such as phosphorus, on the marine environment can be sub-divided into direct effects (those organisms directly affected by changes in the concentrations of phosphorus) and secondary effects (those arising in the ecosystem as a result of the changes in the organisms directly affected).

The terms nutrient enrichment and hyper-nutrification are used to describe the increasing concentrations of nutrients, including phosphorus, in the aquatic environment but do not relate to the consequences or effects of the increasing nutrient levels. The term eutrophication has been defined by the Environment Agency (1998) as "the enrichment of waters by inorganic plant nutrients which results in the stimulation of an array of symptomatic changes. These include the increased production of algae and/or other aquatic plants, affecting the quality of the water and disturbing the balance of organisms present within it. Such changes may be undesirable and interfere with water uses." As such, it encompasses both the increasing nutrient levels and the resulting direct and indirect effects.

C2.4.1 Direct effects

The principal direct effect of increasing phosphorus concentrations in estuaries and coastal waters is its contribution, along with nitrogen, to stimulating productivity of phytoplankton in areas where primary productivity is not limited by light availability. Parr *et al* (1999) suggested that certain parts of the English and Welsh coast (north of the Humber to the Essex estuaries, Solent to Dartmouth and around the Severn coastline from Padstow to Oxwich) may be P- rather than N-limited and, in these areas, the consequences of increased phosphorus concentrations are likely to be more important.

As much of the phosphorus in the tidal environment becomes bound to particulate matter, the sediment tends to be highly enriched with phosphorus. Thus, the addition of more phosphorus should make relatively little difference to ecological communities within the sediment.

C2.4.1 Indirect effects

The indirect effects of increasing phosphorus concentrations are associated with the effects of eutrophication and are described with respect to nitrogen in Section C1. Reference should also be made to Scott *et al* 1999.

C2.5 Potential effects on interest features of European marine sites

Potential effects include:

- stimulation of phytoplankton growth in the water column of estuaries and coastal waters;

- perturbation of the plankton community, including zooplankton, other invertebrates and fish, as a result of repeated phytoplankton blooms with the potential to reduce biodiversity;

- increased fluctuation is dissolved oxygen concentrations in the water column during the growth phase of a bloom with the potential for sub-lethal and lethal effects on invertebrates and fish;

- potential for depletion of oxygen concentrations in the water column and sediments as a result of the die-off of phytoplankton blooms with the potential for sub-lethal and lethal effects on invertebrates and fish;

- contribution to increased turbidity in the water column and reduction in light availability to macroalgae and other aquatic plants growing in the photic zone;

- potential for severe degradation of the ecosystem with adverse consequences for sea birds and Annex II sea mammals.

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C3. Silicon

C3.1 Entry to the marine environment

Silicon is an essential nutrient for diatoms, radiolaria and sponges (Head 1985, Kennish 1986), but of these taxonomic groups, it is the diatoms which have the largest effect on Si cycling and levels, and which, conversely, are most affected by silicon, low levels of which are sometimes responsible for the crash of spring diatom blooms (Conley *et al* 1992).

Silicon in rivers is derived from the weathering of soils and rocks, primarily feldspars, but in marine waters, the main sources are dissolution of clay minerals and detrital quartz. However, the recycling rate of silicon is much slower than that of N and P

C3.2 Recorded levels in the marine environment

Silicon in tidal waters is derived overwhelmingly from natural sources, over which there is no effective control. Only in very rare cases does an anthropogenic source of Si (e.g. detergent manufacture) appear to make a large contribution to the Si budget of a localised tidal area.

Marine waters are always undersaturated with regard to silicon, with saturation levels of about 28 mg Si l^{-1} at 0°C and 69 mg Si l^{-1} at 25°C; reported concentrations range between 0 and 10 mg Si l^{-1} (Bruland 1983, Burton and Liss 1976, Riley and Chester 1971). MPMMG (1998) reported concentrations of silicate at estuarine and coastal waters sites around the UK as part of the National Monitoring Programme.

C3.3 Fate and behaviour in the marine environment

Cycling of silicate in the marine environment involves assimilation by diatoms where it is incorporated into the cell wall or frustule. When the diatom dies, the frustules are deposited onto the sediment and a proportion of the silicate is returned to the water column through a process of dissolution.

C3.4 Effects on the marine environment

The effects of non-toxic substances, such as silicon, on the marine environment can be sub-divided into direct effects (those organisms directly affected by changes in the concentrations of silicon) and secondary effects (those arising in the ecosystem as a result of changes in the organisms directly affected).

C3.4.1 Direct effects

For phytoplankton, the N:P:Si ratio principally controls what species grow, rather than how much. High silicon levels can be expected to result in prolonged or more severe spring diatom blooms than in otherwise similar waters and, conversely, reduced availability of silicon can reduce the abundance and productivity of diatoms. Some other phytoplankton species also require silicon as a macronutrient, notably some toxic dinoflagellates, but the availability of silicon for these species does not appear to be a limiting factor, since they do not usually bloom during spring (the only time of year when silicon is usually limiting to growth (due to uptake by diatoms)).

No information is available on the effects of elevated or reduced levels of silicon levels on benthic fauna or flora, but the relatively high levels of Si in interstitial water infer that lack of availability is unlikely to be a problem

C3.4.2 Indirect effects

The indirect effects of increasing silicon concentrations are associated with the effects of a bloom of diatoms in the spring or summer where productivity is not limited by light availability. Indirect consequences of the bloom are similar to those described for nitrogen (see Section C1) but are unlikely to be as severe due to the limited availability of silicon.

The diatom *Chaetoceros* has long spines and blooms of this genus can damage fish by physically clogging gills which has led to fish kills in cage-reared salmon and other species (Environment Agency 1998).

C3.5 Potential effects on interest features of European marine sites

Potential effects include:

! stimulation of diatom blooms where silicon concentrations are increasing and inhibition of diatom growth and productivity where silicon is limiting.

! blooms of *Chaetoceros* can result in damage to fish populations by clogging and damaging gills.

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C4. Organic carbon

C4.1 Entry to the marine environment

Organic carbon or organic matter enters the marine environment from allochthonous (external) and autochthonous (internal) sources.

Natural allochthonous sources include river-borne phytoplankton and organic detritus, and marginal vegetation. These natural sources are supplemented considerably by anthropogenic point sources including sewage effluent, some industrial effluents and cage fish farm installations. The activities of Man in river catchments can increase the export of organic detritus to rivers, estuaries and coastal waters.

Natural autochthonous sources include phytoplankton, marginal submerged vegetation, faunal faeces and pseudofaeces. The increase in loads of nutrients (nitrogen (see Section C1) and phosphorus (see Section C2)) to the marine environment as a result of Man's activities stimulates the production of autochthonous organic matter, principally in the form of phytoplankton and submerged marginal vegetation (macroalgae). For example, organic matter is derived from decaying seaweed (seasonal scouring of macroalgal, notably kelp communities, can result in large amounts of decaying seaweed being washed onto the shore - in some years more than 40,000 tonnes per year of stranded seaweed is removed from the beach at St Helier, Jersey (Parr *et al* 1996)). Deposits of organic matter in the marine environment can be redistributed by storm events.

C4.2 Recorded levels in the marine environment

Organic matter occurs in natural waters in dissolved (dissolved organic matter DOM) and particulate (particulate organic matter POM) forms. DOM is the organic matter passing through a 0.5 mm filter and POM is that retained by the filter.

The concentration of organic matter does not appear to be routinely measured in UK tidal waters, but the concentration is likely to vary enormously on both a temporal and spatial basis, depending on river flow, resuspension of sediment during windy/stormy weather. However, total suspended solids and ash-free suspended solids are monitored (subtracting the latter from former provides a measure of the particulate organic matter (POM) of water samples). While inorganic material comprises the majority of total suspended solids in English and Welsh coastal waters, along the Wash and North Norfolk coast, organic material is responsible for a greater proportion of total suspended solids (Parr *et al* 1998).

Total organic carbon (TOC) is frequently measured in sediments, particularly in monitoring programmes of sediment quality in relation to the disposal of organic wastes.

C4.3 Fate and behaviour in the marine environment

The fate and behaviour of organic matter in the marine environment is complex and is usefully reviewed for estuaries in Kennish (1986).

Dissolved organic matter (DOM) comprises substances from biological origins (e.g. polypeptides and polysaccharides) and from geological origins (e.g. humic substances). Much of the biological DOM is metabolised by heterotrophic bacteria, while most of the geological DOM is resistant to microbial breakdown. Some other animals can use biological DOM but are largely outcompeted by bacteria and the proportion they use is not nutritionally important for them.

Particulate organic matter (POM) is also metabolised by heterotrophic bacteria but is also used directly by a wide range of estuarine invertebrates both in the water column and in the sediment. POM can be suspended in the water column or be deposited onto sediments, depending on the size and density of particle and the current velocity.

Organic carbon is readily assimilated into the tissues of marine organisms, can be transformed from POM to DOM and is lost to the atmosphere as carbon dioxide by respiration.

The addition of large amounts of organic matter from anthropogenic sources can exceed the capacity of parts of the marine environment to process it, resulting in accumulation usually in the sediments.

C4.4 Effects on the marine environment

The effects of non-toxic substances, such as organic carbon, on the marine environment can be sub-divided into direct effects (those organisms directly affected by changes in the concentrations of organic carbon) and secondary effects (those arising in the ecosystem as a result of the changes in the organisms directly affected).

C4.4.1 Direct effects

The addition of organic matter (as DOM or POM) to the marine environment has the direct effect of stimulating heterotrophic bacterial production in the water column and in the sediments.

The addition of POM, in particular, stimulates the production of invertebrate detritivores in the water column. The response of benthic invertebrate communities to increasing inputs of organic material has been characterised by Pearson and Rosenberg (1978). There are two distinct phases in the response often referred to as organic enrichment and organic pollution.

Organic enrichment encourages the productivity of suspension and deposit feeding detritivores and allows other species to colonise the affected area to take advantage of the enhanced food supply. The benthic invertebrate community response is characterised by increasing numbers of species, total number of individuals and total biomass. This type of impact is typical of many modern sewage effluent discharges in the marine environment (e.g. O'Reilly *et al* 1998).

Organic pollution occurs when the rate of input of organic matter exceeds the capacity of the environment to process it. Commonly, there is an accumulation of organic matter on the sediment surface that smothers organisms, depletes the oxygen concentrations in the sediment and sometimes the overlying water which in turn changes the sediment geochemistry and increases the exposure of organisms to toxic substances associated with organic matter. The benthic invertebrate community response is characterised by decreasing numbers of species, total number of individuals and total biomass and dominance by a few pollution tolerant annelids. This type of impact is not common other than in localised areas in the estuaries and coastal waters of the UK but has recently been observed in relation to cage fish farm installations.

Eleftheriou *et al* (1982) showed that an organic loading rate of 2.1 g $C.m^{-2}.d^{-1}$ in a sea loch resulted in an enriched sediment fauna, while a loading rate of 4.1 g $C.m^{-2}.d^{-1}$ on marine mesocosms degraded the sediment community. Mesocosm studies at the University of Rhodes (Kelly and Nixon 1984, Frithsen *et al* 1987, Oviatt *et al* 1987 and Maughan and Oviatt 1993) showed that, while organic loading rates of 0.1 g $C.m^{-2}.d^{-1}$ had little effect on benthic community status, loading rates of 0.1-1.0 g $C.m^{-2}.d^{-1}$ produced an enriched community and rates in excess of 1.5 g $C.m^{-2}.d^{-1}$ degraded the benthos community.

Edwards and Jack (1994) suggested that the loading rates at which detrimental effects were reported varied so much between the mesocosm and sea loch studies because all of the organic matter applied in the mesocosms was deposited in the experimental system while in the sea loch study, a large proportion of the organic matter applied was probably lost from the immediate area being studied.

The model BenOss predicts the pattern of sedimentation and biological impact of organic matter around marine outfalls, relying on sedimentation coefficients for a range of particle sizes while taking account of dispersion by currents and turbulence. The model employs critical resuspension speed of 9.0 $cm.s^{-1}$ and a critical deposition speed of 4.5 $cm.s^{-1}$ (Cromey *et al* 1996). The model also predicts the effects of excess organic carbon from outfalls on the benthic faunal population.

Increasing amounts of both DOM and POM can contribute towards increased turbidity in the water column (see Section C9).

C4.4.2 Indirect effects

Stimulation of microbial degradation in the water column and sediments results in an increased oxygen demand and decrease in available oxygen for other organisms. Microbial degradation of organic matter also results in the mineralisation of nutrients (N and P) providing additional sources of these nutrients for phytoplankton and macroalgae (see Sections C1 and C2). The effects of eutrophication and organic enrichment are difficult, if not impossible, to distinguish. However, the distinction is only important when considering control mechanisms on the supply of nutrients (N and P) and organic matter.

The effects of increased oxygen demand in water and sediments are considered in more detail in Section C5. In the water column, reduced oxygen concentrations can result in dissolved oxygen sags (DO sags) in estuaries which can act as a barrier to migratory fish and damage estuarine fish communities. The combined effects of organic pollution by sewage, including the input of organic carbon and consequent depletion of dissolved oxygen in the water column, resulted in the eradication of the fish populations in the Thames estuary. Judicious management of water quality, including the artificial aeration of the water column, has allowed the fish populations to recover almost completely. Such a dramatic effect on the fish community must have had an equally dramatic effect on piscivorous birds using the estuary.

Organic enrichment of sediments in the marine environment can stimulate the production of benthic invertebrate communities which, while different in composition from pre-enrichment conditions, can provide significant food supplies for fish and birds. It has been suggested that some of the bird populations at European marine sites in estuaries are sustained by benthic invertebrate production resulting from anthropogenic sources of organic carbon, such as sewage (e.g. Pearce 1998). Concerns have been raised that current pollution control policy aimed at reducing the organic carbon content of sewage discharges might adversely affect these bird populations.

Organic pollution of the sediments tends to result in a reduction in biodiversity of benthic invertebrate communities and the dominance by relatively few taxa, usually annelid worms. While these taxa are of some importance to fish and birds as food items, the reduction in the variety of prey will result in a decrease in the variety of fish and bird predators.

The contribution of POM to turbidity in the water column can contribute to reduced production of phytoplankton, macroalgae and other plants (see Section C9).

C4.5 Potential effects on interest features of European marine sites

Potential effects include:

- stimulation of heterotrophic bacterial production in the water column and sediments;
- mineralisation of nutrients (N and P) from organic matter and contribution towards the effects of eutrophication;
- organic enrichment of the water column and sediment by stimulation of detritivore production, resulting in a change in community composition in favour of these animals and, possibly, their predators, including sea birds;
- organic pollution of the water column and sediment which can reduce the biodiversity of animal and plant communities with adverse consequences for fish and bird populations;
- increased oxygen demand in the water column that can have sub-lethal and lethal effects on fish populations, resulting in reductions in biodiversity with possible consequences for fish eating birds;
- contribution to turbidity in the water column with potential to suppress production of phytoplankton, macroalgae and other submerged aquatic plants.

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C5. Dissolved oxygen

C5.1 Entry to the marine environment

The primary sources of oxygen in the marine environment are atmospheric oxygen which enters the system via gaseous exchange across the air-sea surface interface and *in situ* production via photosynthesis of algae and other aquatic plants.

Of critical importance to marine organisms is the fate and behaviour of dissolved oxygen and the factors affecting fluctuations in dissolved (DO) levels. The principal anthropogenic activity resulting in changes in dissolved oxygen concentrations in the marine environment is the addition of organic matter (see Section C4).

C5.2 Recorded levels in the marine environment

DO is measured in estuaries and coastal waters in terms of either a concentration (mg l^{-1}) or as a percent saturation (%).

MPMMG (1998) reported summer and winter concentrations of DO at National Monitoring Programme sites in the UK in the range 4 to 11 mg l^{-1} expressed as a median, with lowest concentrations occurring in estuaries during the summer.

Many estuaries have intensive monitoring programmes for DO and data will be available from the Environment Agency, SEPA or the Environment and Heritage Service.

Oxygen demand is also routinely measured in effluents discharging to estuaries and coastal waters and is a common condition of discharge consents for effluents with a high organic content. Oxygen demand can be estimated as the Biochemical Oxygen Demand (BOD) or the Chemical Oxygen Demand (COD). The oxygen demand of the sediment can also be estimated as the Sediment Oxygen Demand (SOD).

BOD is a standard analytical procedure involving the incubation of a sample of water or effluent for a standard period of time (5 days) at a constant temperature (20 °C) and measuring the dissolved oxygen concentration at the beginning and end of the incubation period with the difference between the two measurements being the oxygen demand expressed in mg l^{-1}. The oxygen demand results principally from the microbial degradation of organic matter and from nitrification (see Section C5.3), although some chemical oxidation may also be taking place (hence biochemical oxygen demand). Commonly, the nitrification process is suppressed by adding allylthiourea (ATU) to the sample and then BOD is expressed as BOD_5 (ATU).

BOD_5 is a useful measure of oxygen demand for comparative purposes. However, if an estimate of ultimate oxygen consumption is required, a modified test over a longer period is required to better estimate the oxygen demand arising from the breakdown of compounds, such as lignin, which are not readily broken down by aerobic bacteria. In this context, BOD_5 is used as a measure of fast BOD and the longer-term test of slow BOD. The combination of fast and slow BOD represents an estimate of medium-long term oxygen demand which falls somewhere between BOD_5 results and those obtained using total oxygen demand or chemical oxygen demand (COD) results (see Comber and Gunn 1994).

COD is a standard analytical procedure involving the addition of a chemical oxidising agent (potassium permanganate or dichromate) to a sample of water or effluent for a standard period of time at a constant temperature and measuring dissolved oxygen concentrations as for BOD. COD provides a more complete oxidation of both organic and inorganic compounds than BOD (although both are erratic in their response to aromatic organics), so provides higher estimates of oxygen consumption rates. COD therefore provides a better indicator of medium to long-term oxygen demand. However, COD results are affected by the presence of chlorides (Sherrard *et al* 1979), which casts doubt over COD results from saline waters.

SOD can be measured by numerous methods (Nixon 1990). It is the result of all biological respiration and nitrification, which may be measured either *in situ* or *ex situ*, depending on the method chosen. As such, it is more akin to BOD. The results are usually expressed as oxygen removal over a 24 hour period per m^2 of sediment, usually standardised to a temperature of 20 °C. Because of the different timescales involved in measuring BOD and SOD, it may be difficult to relate the water column and sediment oxygen demands to each other, particularly when one (BOD) excludes oxygen demand due to nitrification, while the other includes it. The reason for this difference appears to be the close coupling of nitrification and denitrification in many sediments, but not in the estuarine water column.

C5.3 Fate and behaviour in the marine environment

The principal natural physical factors affecting the concentration of oxygen in the marine environment are temperature and salinity. DO concentrations decrease with increasing temperature and salinity. The other major factor controlling DO concentrations is biological activity: photosynthesis producing oxygen and respiration and nitrification consuming oxygen.

Photosynthesis occurs in aquatic plants in the presence of adequate supplies of carbon dioxide and light. Oxygen is released as a by-product. Blooms of phytoplankton in surface waters can supersaturate the water with dissolved oxygen during the day in the presence of adequate supplies of nutrients (see Sections C1, C2 and C3) and light.

Respiration consumes oxygen and occurs in all aerobic organisms. Blooms of phytoplankton in surface waters can deplete the water column of oxygen during the night in the presence of adequate supplies of nutrients (see Sections C1, C2 and C3). Microbial respiration can deplete the water column and sediments of dissolved oxygen in the presence of organic matter (see Section C4).

Nitrification (the conversion of ammonia to nitrate via nitrite) consumes oxygen, the process relying principally on two bacterial genera: *Nitrosomonas* and *Nitrobacter*. Except in regions with high ammonium concentrations, e.g. around sewage outfall discharges, nitrification in the water column of shallow marine and estuarine systems appears to be limited (Henriksen and Kemp 1988). However nitrification can constitute a large proportion of sediment oxygen demand (e.g. Rivsbech *et al* 1988). In estuaries such as the Tamar (Owens 1996), nitrification is closely coupled with the turbidity maximum, but in other estuaries (e.g. the Mersey, Reynolds *et al* 1994) nitrification rates may be greater in filtered than unfiltered samples.

Oxygen balance in estuaries was usefully reviewed by Nixon (1990).

C5.4 Effects on the marine environment

The effects of changes in dissolved oxygen concentration on the marine environment can be sub-divided into direct effects (those organisms directly affected by changes in dissolved oxygen concentration) and secondary effects (those arising in the ecosystem as a result of the changes in the organisms directly affected).

C5.4.1 Direct effects

The direct effects of changes in dissolved oxygen concentrations are primarily related to reduced DO levels and include:

! lethal and sub-lethal responses in marine organisms;

! release of nutrients;

! development of hypoxic and anoxic conditions.

The lethal and sub-lethal effects of reduced levels of dissolved oxygen were reviewed by Stiff *et al* (1992) for the purposes of EQS derivation. This review was updated by Nixon *et al* (1995) in order to derive a General Quality Assessment (GQA) scheme for dissolved oxygen and ammonia in estuaries for the Environment Agency in England and Wales. The reader is referred to these documents for a detailed assessment of the lethal and sub-lethal effects of dissolved oxygen on saltwater organisms.

The lethal and sub-lethal effects of reduced levels of dissolved oxygen are related to the concentration of dissolved oxygen and period of exposure of the reduced oxygen levels. A number of animals have behavioural strategies to survive periodic events of reduced dissolved oxygen. These include avoidance by mobile animals, such as fish and macrocrustaceans, shell closure and reduced metabolic rate in bivalve molluscs and either decreased burrowing depth or emergence from burrows for sediment dwelling crustaceans, molluscs and annelids.

Stiff *et al* (1992) and Nixon *et al* (1995) identified crustacea and fish as the most sensitive organisms to reduced DO levels with the early life stages of fish and migratory salmonids as particularly sensitive. For estuarine fish, Stiff *et al* (1992) suggested a minimum DO requirement of 3 to 5 mg l^{-1}. Based on the data in their review, EQSs for dissolved oxygen were proposed (Table C5.1).

Table C5.1 Recommended EQSs for dissolved oxygen in saline waters

Saltwater use	EQS	Compliance statistic	Notes
Designated shellfishery	70% saturation	50%ile, mandatory standard	EC Shellfish Water Directive
	60% saturation	Minimum, mandatory standard	
	80% saturation	95%ile, guideline value	
Saltwater life	5 mg l^{-1}	50%ile	
	2 mg l^{-1}	95%ile	
Sensitive saltwater life	9 mg l^{-1}	50%ile	
(e.g. fish nursery grounds)	5 mg l^{-1}	95%ile	
Migratory fish	5 mg l^{-1}	50%ile	Higher values may be required where fish have to traverse distances >10 km, or where high quality migratory fisheries are to be maintained
	3 mg l^{-1}	95%ile	

Nixon *et al* (1995) proposed the following class thresholds for exposure to levels of dissolved oxygen for a continuous period of greater than 1 hour in estuaries in England and Wales (Table C5.2). This scheme has not been implemented but the class thresholds are a useful indication of the levels of DO that are likely to cause effects if organisms are exposed for a continuous period of greater than one hour.

Table C5.2 Proposed GQA class thresholds for dissolved oxygen in estuaries in England and Wales (from Nixon *et al* 1995)

GQA class boundary	Threshold value of DO (mg l^{-1})
A/B	8 mg l^{-1}
B/C	4 mg l^{-1}
C/D	2 mg l^{-1}

Nixon *et al* (1995) reviewed information on reduced DO levels in bottom waters on benthic invertebrate communities. Josefson and Widbom (1988) investigated the response of benthic macro- and meiofauna to reduced DO levels in the bottom waters of a fjord. At DO concentrations of 0.21 mg l^{-1}, the macrofaunal community was eradicated and was not fully re-established 18 months after the hypoxic event. In contrast, the permanent meiofauna appeared unaffected. Jorgensen (1980) observed the response of macrofauna to reduced DO levels of 0.2 to 1 mg l^{-1} for a period of 3 to 4 weeks in an estuarine/marine area in Sweden by diving. Mussels *Mytilus edulis* were observed to first close their shells and survived for 1 to 2 weeks before dying. Crabs *Carcinus maenas* and shrimp *Crangon crangon* were amongst the first to die from lack of oxygen. *Hydrobia ulvae* were observed to die first in the hollows in the sediment surface and were observed congregating on the ridges to find more oxygen-rich water. Polychaetes were observed to come to the surface, small specimens first. *Hediste diversicolor* and *Lagis koreni* were observed limp and motionless on the surface but could be revived in 30 minutes by placing in oxygenated water. Burrowing bivalves were first observed to extend their siphons further into the water column but, as oxygen depletion continued, emerged from burrows and laid on the sediment surface. Sea anemones were the last animals to succumb but eventually they loosened their attachment and were found lying on the sediment surface.

Reduced levels of dissolved oxygen in the water column can result in the release of phosphate from suspended particles and the sediment (see Section C2).

Sustained reduction of dissolved oxygen can lead to hypoxic (reduced dissolved oxygen) and anoxic (extremely low or no dissolved oxygen) conditions. In anoxic environments, anaerobic bacteria proliferate, with nitrogenous oxide reducers absorbing oxygen by reducing nitrate to nitrite and forming ammonia or nitrogen gas. In addition, sulphate-reducing bacteria reduce sulphate to hydrogen sulphide which, when liberated, increases mortality of marine organisms and increases the BOD as it permeates through the water column (Kennish 1986). Such conditions can occur under a cage fish farm installation where release of hydrogen sulphide has caused fish kills and sediment can become covered in filamentous fungi, such as *Beggiatoa*.

C5.4.2 Indirect effects

The indirect effects of reduced dissolved oxygen concentrations depend on the severity of the direct effects which, in turn, depend on extent and duration of the oxygen depletion. Sustained or repeated episodes of reduced dissolved oxygen has the potential to severely degrade an ecosystem. Reduced DO levels contributed significantly to the reported elimination of the fish populations of the Thames estuary and its recovery has resulted from strict management of water quality, including inputs of organic matter and the artificial injection of oxygen into the water column during low DO events.

The consequences for seabirds and sea mammals of such ecosystem degradation are likely to be significant as the supply of food organisms is affected.

C5.5 Potential effects on interest features of European marine sites

Potential effects include:

- lethal and sub-lethal effects on marine organisms (in particular crustacea and fish) of reduced DO concentrations below the EQS values in Table C5.1;
- release of phosphate from suspended particles and sediment with potential contribution to the effects of eutrophication (see Section C2);
- establishment of anoxic conditions which can increase BOD, stimulate the release of ammonia and hydrogen sulphide which can be toxic to aquatic life;
- severe degradation of the ecosystem if reduced DO levels are sustained or repeated with potential adverse effects for sea birds and Annex II sea mammals.

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C6. pH

C6.1 Entry to the marine environment

Effluents containing acids and alkalis are discharged into the marine environment but generally the high buffering capacity of saline waters ensures that pH levels are returned to the normal range. Any variations arising from the discharge are likely to be local to the discharge point.

pH also varies naturally in the water column with maximum values occurring at or slightly after the time of maximum illumination with high values in the summer months. This is related to photosynthetic activity with bicarbonate used as a source of carbon dioxide. The degree of photosynthesis is affected by the supply of nutrients (see Section C1, C2 and C3), organic carbon (see Section C4) and turbidity (see Section C8).

C6.2 Recorded levels in the marine environment

Unlike freshwater, saline water has a high buffering capacity for pH, so any pH changes in marine waters tend to be small and localised around the source. The pH of oceanic water is fairly constant at about 8.2 pH units, but variations in seawater pH of a few tenths of a unit are possible, for example, on a diurnal scale associated with algal photosynthesis. As might be expected, buffering in estuarine waters is greater than that in freshwaters, but weaker than that in fully marine waters. Typical pH levels in UK estuaries range from 7.0 to 8.3 (Table C6.1).

Table C6.1 Reported pH levels in UK tidal waters (Wolff *et al* 1988)

Estuary @ location	pH (pH units)			Salinity (ppt)		
	Min	Mean	Max	Min	Mean	Max
Mersey @ Monks Hall	6.9	7.2	7.7	0.1	1.6	9.4
Mersey @ Eastham Ferry	7.2	7.6	7.9	21.7	25.7	28.8
Mersey @ Buoy C15	7.8	8.0	8.5	29.6	31.0	32.7
Ribble @ 1 Mile Post	7.2	8.0	9.0	0.1	3.9	20.2
Ribble @ 15 Mile Post	7.8	8.3	9.1	24.3	31.5	35.8
Usk d/s Newport Rd Bridge	7.6	7.9	8.1			
Ogmore @ Mouth	7.3	7.8	9.2	0.1	5.5	30.7
Afan @ Dock Entrance Port Talbot	6.7	7.6	8.1	0.1	10.8	33.3
Neath @ Monkstone Slip	6.7	8.0	8.6	0.4	14.9	32.8
Loughor @ Carmarthen Bay Power Stn	6.4	7.8	8.1	12.2	25.5	33.6
Tawe @ New Cut Bridge Swansea	6.7	7.7	8.4	0.1	5.3	24.8
Dee @ New Queensferry Bridge	6.7	7.5	8.7			
Conwy Mid-Channel	6.9	8.0	8.3	6.6	24.3	34.2
Menai Straits @ Beaumaris	6.5	8.1	8.7	20.6	29.5	35.2
Bann @ West Mole Leading Light	7.9	8.2	8.9	<0.1	8.2	34.3
Lagan @ Ormeau Bridge	7.3	7.8	8.1	<0.1	7.1	16.8
Belfast Lough below Queens Bridge	7.9	8.0	8.2	21.8	30.0	33.3
Belfast Lough Outer Channel	8.0	8.1	8.3	32.0	33.5	34.1
Tay @ Perth	6.7	7.2	8.5			
Tay @ Tayport Harbour	7.9	7.9	7.9			

Estuary @ location	pH (pH units)			Salinity (ppt)		
	Min	Mean	Max	Min	Mean	Max
Clyde @ Broomielaw	7.2	7.4	7.9			
Clyde @ Gourock	7.9	7.9	7.9			
Eye Harbour Mouth	7.7	7.9	8.2			
Itchen @ Kemps Boatyard	7.8	7.9	8.1	4.2	17.8	25.7
Test @ Dockhead	7.8	8.0	8.4	24.4	28.7	33.0
Tees @ Furness Yard	7.1	7.1	7.1	0.5	0.5	0.5
Tees @ Victoria Bridge	7.0	7.0	7.0	20.0	20.0	20.0
Tees @ Smiths Dock	7.2	7.2	7.2	30.0	30.0	30.0
Solent @ East Lepe Buoy	8.0	8.0	8.1	33.5	33.8	34.2
Solent @ N.E. Ryde Middle	8.0	8.1	8.1	33.6	34.1	35.0

C6.3 Effects in the marine environment

The effects of changes in pH on the marine environment can be sub-divided into direct effects (those organisms directly affected by changes in pH) and secondary effects (those arising in the ecosystem as a result of the changes in the organisms directly affected).

C6.3.1 Direct effects

The direct effects of a change in pH in the marine environment include:

! the potential for the release of $C0_2$ following the rapid release of acids;

! influence on the speciation and toxicity of substances, such as ammonia, silicate, phosphate, borate, some metals and some phenolic organic compounds;

! lethal and sub-lethal effects on marine organisms.

At pH 8, bicarbonate is the predominate carbonate species, but below pH 6, CO_2 predominates, so that the rapid discharge of acids to tidal waters may be able to liberate sufficient CO_2 to be lethal to aquatic life. pH affects the equilibrium position of other systems, such as that for silicate, phosphate and borate in a similar way.

pH affects the equilibrium for ammonia. At high pH the proportion of the toxic unionised form of ammonia increases and may cause water quality problems (see Section B1).

Low pH can increase the solubility of toxic metals, such as cadmium, copper, lead, aluminium, mercury and zinc but the degree of mobilisation in high alkalinity saline waters is less than that in freshwaters.

The quality of available data for the effects of pH on marine fish is questionable, since the effects of high CO_2 and low pH were not separated from each other until Brownell's (1980) study. However, LC50 values have been reported below 5.4, and above 9.0. Feeding of fish larvae appears to be affected at pHs below 6.0 and above 8.4. Some adult fish are reported to be to be unaffected at pH values above 9.0, but for the larval stage, a more appropriate standard appears to be 8.5 (Wolff *et al* 1988).

Data for bacteria appear to be sparse and difficult to interpret, particularly since different species have different media requirements for laboratory studies.

A wide range of tolerance exists for different marine algal species, with different optima for different physiological or reproductive processes, so that no overall trends or conclusions can be drawn. At low pH, the increased free CO_2/bicarbonate ratio may favour some species, but hinder growth/reproduction in others. Several species show reduced calcification as the pH is reduced towards 6.0 (Borowitzka and Larkum 1976, Paasche 1963, Smith and Roth 1979), and toxicity of copper may increase as pH is reduced (Sunda and Guillard 1976).

For molluscs, adverse effects are seen at pHs greater than 8.5 and less than 7.0, including shell dissolution at lower pH values (see Wolff *et al* 1988).

Some crustaceans (e.g. *Crangon crangon*) survive at well below pH 6.0, but others have LC50 values in the range pH 5.5-6.7 (e.g. *Pseudocalanus* sp., *Arcatia tonsa, Temora longicornis;* see Wolff *et al* 1988).

Wolff *et al* (1988) proposed an EQS for the protection of saltwater fish to be pH 6.0 - 8.5 as an annual average and for shellfish to be pH 7.0 to 8.5 as a 75 percentile.

C6.3.2 Indirect effects

The indirect effects of a change in pH in the marine environment are likely to be limited because the scale of the direct effects is limited by the buffering capacity of seawater. However, a precautionary approach should be adopted around known discharges of acids and alkalis to ensure that the direct effects are indeed minimal.

C6.4 Potential effects on interest features of European marine sites

Potential effects include:

- ! the potential for the release of $C0_2$ following the rapid release of acids which may be sufficient to be lethal to aquatic organisms;
- ! influence on the speciation and toxicity of substances, such as ammonia (see Section B1);
- ! lethal and sub-lethal effects on marine organisms and, in particular, to fish outside the EQS range of 6.0 - 8.5 (annual average) and to shellfish outside the EQS range of 7.0 -8.5 (75 percentile). No standard was proposed for the protection of all saltwater life.

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C7. Salinity

C7.1 Entry to the marine environment

Salinity is a major factor determining the distribution and composition of communities of marine organisms and variations in the salinity regime in estuaries are a characteristic feature defining these systems. The principal factors governing the temporal and spatial nature of the salinity regime in estuaries are the diurnal incursion of the tide and freshwater flow from the river(s). Any activity changing either of these factors can result in a change to the salinity regime.

Potential activities could include physical barriers to tidal incursions, including power generation (tidal) or amenity barrages (e.g. Cardiff Bay) or the consequences of flood defence works on longshore drift of sediment affecting natural bars or spits and physical barriers to freshwater discharge to estuaries such as weirs or other flood defence structures. Many estuaries have obstructions on either the main river channel or on creeks to prevent flooding of surrounding land at high tides. These structures have the effect of truncating the reduced salinity zone and the tidal freshwater zone which can be important for some plant (e.g. reeds) and animal communities.

Abstraction of freshwater from rivers and groundwater supplies in river catchments can reduce the total amount and the temporal pattern of the freshwater flow into an estuary and influence the salinity regime. This is perhaps the most important factor affecting the salinity regime in estuaries, especially in England. The pattern of development in the river catchment, and in particular development on floodplains, can also influence the magnitude of flood events and so produce large episodic changes to the salinity regime in receiving estuaries.

C7.2 Recorded levels in the marine environment

Concentrations in estuaries range between 0.5 and 35 ppt, with the salinity at individual sites changing with the tidal ebb and flow. Concentrations in marine waters are much less variable, typically ranging between 33 and 35 ppt. Salinity may vary with depth in poorly mixed estuaries, since fresh river water flows over the denser saline water, forming a so-called salt wedge. In tidal rock pools, salinities can increase well beyond 35 ppt on hot, sunny days as freshwater evaporates.

Many estuaries have intensive monitoring programmes that include measurements of salinity. Relevant data will be available from the Environment Agency, SEPA or the Environment and Heritage Service.

C7.3 Effects in the marine environment

The effects of changes to the salinity regime on the marine environment can be sub-divided into direct effects (those organisms directly affected by changes in the salinity regime) and secondary effects (those arising in the ecosystem as a result of the changes in the organisms directly affected).

C7.3.1 Direct effects

The direct effects of changes to the salinity regime include:

- changes to water column structure (e.g. stratification) and water chemistry (e.g. DO saturation and turbidity);

- lethal and sub-lethal effects on marine organisms;
- behavioural changes in fish and macrocrustacean populations.

Changes to the freshwater flow can have temporal and spatial effects on water column structure in estuaries as a result of differing degrees of salinity induced stratification. The precise consequences will be estuary specific but could have implications for water quality and for the distribution of organisms in the water column and sediments.

Dissolved oxygen is more soluble in freshwater than saline water at constant temperature (see Section C5) and, consequently, freshwater entering the estuary has the potential to have enhanced dissolved oxygen concentrations. Fluctuations in the salinity regime has the potential to influence dissolved oxygen concentrations. The distribution and transportation of suspended sediment and the deposition of fine grains in an estuary are driven by the mixing of seawater and freshwater. Any significant sustained changes to the freshwater flow have the potential to disrupt the cycles of deposition and erosion with the potential for adverse effects on certain habitats. For example, mudflats could have the supply of depositing material removed and begin to erode with a loss of associated benthic invertebrate communities and fish and bird feeding grounds.

All marine organisms have a range of tolerance to salinity which is related to their ability to regulate the osmotic balance of their individual cells and organs to maintain positive turgor pressure. Organisms are commonly classified in relation to their range of tolerance as:

- stenohaline (having a narrow range of tolerance) including most marine and freshwater organisms; and
- euryhaline (having a wide range of tolerance) including most truly estuarine species.

The reduction in the number of species with decreasing salinity in an estuary is a characteristic feature of these systems. For example, a typical marine rocky shore community may contain up to 100 macroalgal species, but at the freshwater end of an estuary, this may decrease to less than five macroalgal species. Benthic invertebrate communities also vary in response to salinity with diversity decreasing with decreasing salinity. Variations in salinity regime can modify community distribution and composition. This may be particularly evident at the head of an estuary where benthic invertebrate communities can vary between those typical of freshwater and those typical of an estuary, depending on the amount of freshwater flow entering the estuary during the summer.

Sub-lethal effects of changed salinity regimes (or salinity stress) can include modification of metabolic rate, change in activity patterns or alteration of growth rates (McLusky 1981).

Behavioural responses to changes in salinity regime can include avoidance by mobile animals, such as fish and macrocrustaceans, by moving away from adverse salinity and avoidance by sessile animals by reducing contact with the water by closing shells or by retreating deeper into sediments. The variations in salinity of interstitial waters within sediments are much less than in the water column. These responses are only successful for transient episodes of adverse salinity.

Salinity plays an important role in the cues for a number of migrations that take place within estuaries including those of crustaceans, such as shrimp and crabs, and of fish, such as salmon, flounder and smelt. Variations in freshwater flow within estuaries can determine the distribution of fish populations and potentially determine the success of a particular year class by affecting access to spawning or feeding grounds.

C7.3.2 Indirect effects

The principal indirect effect of changes in the salinity regime is a potential change in communities of secondary consumers (fish and birds) in response to changes in communities of benthic invertebrate and fish food organisms.

C7.4 Potential effects on interest features of European marine sites

Potential effects include:

- changes to water column structure (e.g. stratification) and water chemistry (e.g. DO saturation and turbidity);
- lethal and sub-lethal effects on marine organisms resulting in changes in community distribution and composition;
- behavioural changes in fish and macrocrustacean populations with the potential to impact adversely on feeding and spawning migrations within and through estuaries;
- potential change in communities of secondary consumers (fish and birds) in response to changes in communities of benthic invertebrate and fish food organisms.

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C8. Thermal discharges

Power station cooling water systems have a range of potential impacts on receiving environments including:

- the abstraction of large volumes of water,
- entrainment of organisms on intake screens,
- entrainment and passage of organisms through the cooling system,
- the addition of biocides to the cooling water to control biofouling (see Section B34), and
- the discharge and dispersal of the heated effluent.

These impacts are usefully reviewed by Langford (1990) and in relation to a specific power station in Milford Haven by Langford *et al* (1998). The information in this profile mainly covers the temperature effects associated with the discharge of the heated effluent.

C8.1 Entry to the marine environment

The primary source of thermal discharges to the marine/estuarine environment is power station cooling water discharges, although cooling-water from other industrial processes could be responsible for more localised temperature changes.

C8.2 Recorded levels in the marine environment

The ultimate temperature of any cooling-water discharge varies with a number of factors, including power station operating load, volume of cooling water used, design criteria for the station and the inlet water temperature. The optimum temperature rise for efficient power station operation is between 10 and 15 °C but rises of up to 30 °C have been recorded. The normal increase from inlet to outlet (DT) for British fossil fuelled power stations is 10-12 °C, although discharge temperatures at nuclear power stations can be up to 15 °C higher than inlet temperatures (Langford *et al* 1998).

The resulting temperature change in the receiving marine environment is very site specific and depends on many factors, including the hydrodynamics of the receiving system and the design and location of the discharge.

In the UK, 12 of the 155 estuaries included in the Estuaries Review (Davidson *et al* 1991) received thermal discharges from power stations facilities in 1989. Some estuaries received thermal effluents from a number of power stations located either directly on the estuary or upstream on the river system feeding the estuary. For example, the Humber has 3 power stations situated on the estuary (with a further 4 either under construction or planned) and 6 on river systems feeding into the estuary (Barne *et al* 1995).

C8.3 Fate and behaviour in the marine environment

The heat in a cooling-water discharge will dissipate in the marine environment as the plume mixes with the water column. Some energy may be lost to the atmosphere if the plume is buoyant. Similarly, some energy will be transferred to the sediments if the discharge passes over intertidal sediments at low tide or is entrained in lower layers of water. Continuous thermal discharges to semi-enclosed bodies of water such as estuaries can result in a net increase in temperature of the water column.

The rate of mixing of the discharge plume with the water column will determine the rate at which heat is dissipated. Discharges to estuaries are most likely to have reduced potential for complete mixing with heated effluent concentrated in a body of water that moves up and down the estuary with the ebb and flow of the tide. This can be exacerbated by stratification where heated effluents can be entrained in distinct layers in the water column. The heated effluent may reinforce stratification as the heated buoyant effluent is entrained in surface layers, increasing the temperature differential between the layers above and below the thermocline. In some situations, cooling-water discharges are of greater salinity than the receiving environment and become entrained in the lower layers of the water column.

C8.4 Effects in the marine environment

The effects of thermal discharges on the marine environment can be sub-divided into direct effects (those organisms directly affected by changes in the temperature regime) and secondary effects (those arising in the ecosystem as a result of the changes in the organisms directly affected).

C8.4.1 Direct effects

The direct effects of thermal discharges on the marine environment include:

- change to the temperature regime of the water column, and perhaps the sediment, of the receiving environment;
- lethal and sub-lethal responses of marine organisms to the change in temperature regime;
- stimulation in productivity in a range of organisms;
- reduction in the dissolved oxygen saturation.

Bamber (1995a cited in Langford *et al* 1998) identified three aspects in which changes to the temperature regime were important to the ecology of the receiving environment:

1. mean temperature (which varies with distance from the outfall and is crucial to understanding/predicting longer term effects);
2. maximum temperature (clearly important if it approaches the thermal lethal limit of an organism);
3. temperature fluctuation and rate of change (these can vary depending on controls within the heat source, tidal fluctuations altering the direction of the thermal plume, and tidal height altering the volume of water available to dilute and cool the discharge plume).

Examples of the upper temperature limits of seaweeds are shown in Table C8.1, with species, such as *Fucus* and *Ascophyllum* spp. declining in abundance where thermal discharges have resulted in temperature increases of 5-7°C above ambient (Langford 1990).

Table C8.1 Thermal tolerance data for selected seaweeds (Langford *et al* 1998)

Species	Lethal temperature (°C)	Upper reproduction limit temperature (°C)
Chondrus crispus	28	15
Cladophora spp.	30-35	25
Chorda filum	23	15
Laminaria digitata	23	10
Laminaria saccharina	23	15
Laminaria hyperborea	18	8
Dumononita contorta	24	12
Fucus serratus	28	
Lomentaria articulata	28	Gamete production limited above 15°C
Desmarestia aculeata	25	15

Some introduced invertebrates, including non-native oysters, may be able to reproduce and thrive in artificially heated regimes (Langford *et al* 1998) or affected populations may exhibit characteristics of more southerly populations, such as breeding earlier in the year (e.g. Bamber and Spencer 1984).

Temperature conditions before, during and after the spawning period appear to be important for the long-term variability (settlement and size) of *Tellina tenuis* (Barnett and Watson 1986). Likewise, high summer temperatures have been associated with dense settlements of the barnacle *Chthamalus* and the role of temperature on the seaweed-dwelling amphipod *Hyale nilsonni* has been demonstrated by Moore (1983). There are numerous other examples where increased temperatures have affected the growth and/or reproduction of invertebrates, such as the amphipods *Urothoe brevicornis* and *Corophium ascherusicum*, the harpacticoid crustacean *Asellopsid intermedia*, the isopod *Cyathura carinata* and the immigrant barnacles *Balanus amphrite* and *Elminius modestus* (see Langford *et al* 1998).

Behavioural effects are rarely reported in field studies, but the amphipod *Corophium volutator* has been reported to leave its burrow and enter the water column at temperatures over 25°C. Similar behaviour is shown by the burrowing bivalve *Donax serra* which leaves its burrow and lies on the sediment (sand) surface as temperature increases.

Ultimately, a long-term thermal discharge is likely to lead to a changed and thermally adapted community, more typical of that found in otherwise more southerly and warmer climates.

There have been a number of suggestions of potential effects on fish and macro-crustaceans ranging from a temperature related water quality barrier to the migration of salmon (NRA 1993) and the elimination of certain species on the boundaries of their geographic distribution to localised behavioural responses to individual discharges.

The evidence for temperature related water quality barriers is necessarily equivocal given the wide number of factors affecting salmon migration. Localised behavioural responses have been observed on a number of occasions where species, such as bass and mullet, have been attracted to these effluents at certain times of year. It is possible that they are exploiting additional food supplies but at the same time they can be exposed to additional predation from birds and anglers. Similarly, fish not suited to the localised increase in temperature/reduction in dissolved oxygen can avoid discharge plumes. Such behaviour has been termed behavioural thermoregulation.

Given the largely localised impacts of thermal pollution, it would appear that local changes in fish populations may be observed and idiosyncratic fisheries may be created. The overall impact on an estuarine fish community is likely to be limited.

In the Thames estuary, a set of quality objectives have been derived to ensure water quality is appropriate for the passage of migratory fish and to support fisheries consistent with the physical characteristics of the estuary. The objectives include a non-statutory temperature standard of a maximum temperature of 28 °C which is the EIFAC standard for cyprinid fish under EU Freshwater Fish Directive 78/659/EEC. The standard for migratory fish is 21.5 °C but it is recognised that this temperature would be exceeded under natural conditions in most summers. However, since 1989, all new discharges of cooling water are subject to a condition whereby when river/estuary temperatures exceed 21.5 °C, they have to switch to alternative methods of cooling (TEMP 1996).

Microbially-mediated processes, such as nitrification, denitrification and manganese oxidation, are all affected by thermal discharges, since every 8-10°C increase in temperature equates to a doubling of microbial activity. The same thermal relationship applies to phytoplankton productivity (providing no other factors, such as light and nutrient availability, are limiting). Thermal discharges are unlikely to have a substantial effect on planktonic populations where the residence time of water within the thermal plume is less than one week, although benthic diatoms are reported to be moribund in the near-field surrounding thermal discharges (Langford *et al* 1998). This observation is consistent with in with the 5-15°C optimal temperature range reported for a number of planktonic diatoms (freshwater and marine).

Changes to dissolved oxygen saturation potentially arise as a result of the reduction in solubility of oxygen in sea water with increasing temperature and as a consequence of the increased productivity of microbial communities in particular. The consequences of reduced dissolved oxygen are discussed in Section C5.

C8.4.2 Indirect effects

The indirect effects of thermal discharges on the marine environment include:

! changes in the distribution and composition of communities of marine organisms comprising European marine sites (particularly estuaries);

! localised changes in bird distributions usually in response to increased macroinvertebrate or fish food supplies close to thermal discharges.

C8.5 Potential effects on interest features of European marine sites

Potential effects include:

! change to the temperature regime of the water column, and perhaps the sediment, of the receiving environment;

- lethal and sub-lethal responses of marine organisms to the change in temperature regime;
- stimulation in productivity in a range of organisms;
- reduction in the dissolved oxygen saturation;
- changes in the distribution and composition of communities of marine organisms comprising European marine sites (particularly estuaries);
- localised changes in bird distributions usually in response to increased macroinvertebrate or fish food supplies close to thermal discharges.

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C9. Turbidity

The issues surrounding the potential effects of turbidity on nature conservation interests in the marine environment have been recently reviewed by Parr *et al* 1998. The reader is referred to this document for further details.

C9.1 Entry to the marine environment

Turbidity is a measure of the attentuation of light in the water column and can be caused by the light adsorption properties of the water, plankton, suspended particulate organic and inorganic matter and dissolved colour.

Turbidity can be measured in a variety of ways, the results of which are not usually inter-convertible:

- light transmission (transmissometers),
- light scattering (nephelometry),
- scattering and transmission (ratiometric turbidimeters),
- secchi disk, total suspended solids (sample filtered and dried at 105°C),
- ash-free suspended solids (sample filtered and dried at 500°C) and remote sensing.

In addition to the above, Parr *et al* (1998) also discussed the options for measuring the depth of macroalgal colonisation as a turbidity-monitoring tool, in combination with a measure of epiphyte density (which could itself be used as a measure of trophic status).

Turbidity is due primarily to suspended particulate matter, but a relatively minor contribution to light adsorption in the water column (less than in freshwaters) may be made by dissolved/colloidal humic substances, often referred to as gilvin (Kirk 1994).

Particulate matter can be derived from (Parr *et al* 1998):

- soil (land) erosion;
- coastal erosion;
- sediment resuspension (including dredging);
- suspended solids in discharge effluents;
- phytoplankton standing crop; and
- chemical flocculation at the freshwater/saltwater interface in estuaries.

Of the above, sediment resuspension represents the major source in most cases. The building of flood defence structures, such as sea walls, while preventing coastal erosion at the site itself, may transfer wave energy further along the coast, leading to erosion in another place. Dredging may make a large contribution to suspended solids, depending on tidal cycle. For example, in the Loire estuary during spring tides, dredging contributes about 5% of suspended particulate matter, but during neap tides, dredging may account for 20% (Sauriau *et al* 1994).

C9.2 Recorded levels in the environment

Parr *et al* (1998) quoted annual mean suspended solids (105°C) and ash-free suspended solids (levels 500°C) around the English and Welsh coast of 1 - 327 and 1 - 227 mg l^{-1} respectively. However, the extreme upper values disguise the fact that, at the majority of sites, annual mean levels are more typically 1 - 110 mg l^{-1} for both parameters. Higher levels are found in the mid/inner regions of the Firth of Severn (maximum values in the inner firth), around the Solway Firth (up to 20 mg l^{-1}) and along the East coast from Flamborough Head south to east Kent (30 - 100 mg l^{-1} at 13 sites and >100 mg l^{-1} at 2 sites).

In estuaries, turbidity levels are usually much higher than those in adjacent coastal waters, with peak levels confined to a discrete region (the turbidity maximum), usually in the upper-middle reaches, which moves up and down the estuary with the tidal ebb and flow. The level of suspended solids depends on a variety of factors including: substrate type, river flow, tidal height, water velocity, wind reach/speed and depth of water mixing (Parr *et al* 1998). The level of suspended solids can be enhanced by anthropogenic activities in the river catchment as well as within the river and the estuary. Changes in river flow as a result of abstraction can influence suspended solids concentrations reaching estuaries.

C9.3 Effects in the marine environment

The effects of non-toxic substances, such as turbidity, on the marine environment can be sub-divided into direct effects (those organisms directly affected by changes in turbidity) and secondary effects (those arising in the ecosystem as a result of changes in the organisms directly affected).

C9.4 Direct effects

The direct effects of high levels of turbidity in the water column include:

- a reduction in phytoplankton biomass in the presence of high concentrations of suspended particulate matter (especially in estuaries) because of the reduction of available light;

- a reduction in growth rates, areal coverage and depth of colonisation of macrophytes and macroalgae (including kelp) where turbidity is high;

- some evidence of adverse effects on zooplankton which can become associated with turbidity maxima in estuaries as a result of physical processes governing the movement of particles;

- turbidity or suspended solids can affect benthic invertebrate communities both when the particles are in suspension and when they are deposited;

- turbidity or suspended solids can directly affect fish populations.

In many coastal plain estuaries, light attentuation confines the photic zone to a fraction of the water column such that light availability is the limiting factor on phytoplankton productivity despite high nutrient levels in many cases (Parr *et al* 1998). However, high turbidity levels do not necessarily preclude high phytoplankton standing crops. Where rapid and complete mixing of the water column allows algal cells to have some exposure to light at the surface, phytoplankton biomass can increase where turbidity is high (Parr *et al* 1998).

Parr *et al* (1998) identified the effects of high turbidity on macrophytes, including *Zostera,* and on macroalgae, including *Laminaria* spp. and *Fucus vesiculosus.* Reduced growth rates, standing crop, areal coverage and depth of colonisation have been reported to be related to turbidity. Parr *et al* (1998) stressed the importance of the role of periphyton responding to increased nutrient concentrations in reducing the available light for these plants when attributing the observed effects to turbidity levels in the water column. The depth of colonisation of macroalgae is proposed as a biological measure of turbidity.

High zooplankton densities have been reported from areas of high turbidity in estuaries but it is unclear whether this is a natural physical phenomenon that benefits or harms zooplankton communities.

The effects of high turbidity or suspended solids on the benthos can occur through the concentration of particles in suspension (especially in the boundary layer between sediments and the water column) and through the deposition of particles onto sediments or hard surfaces.

Filter-feeding organisms entrain particles from the water column using a variety of feeding appendages. An increase in the concentration of suspended organic particles in the lower layers of the water column represents an increase in food supply and filter-feeding animals generally benefit. However, many toxic substances are associated with organic particles and an increase in supply of the latter may result in an increased exposure to the former. However, an increase in the concentration of inorganic particles could be detrimental because the organisms have to expend energy dealing with more particles of low nutritional value. Large increases in organic or inorganic particles tend to have detrimental effects by overloading feeding processes, damaging feeding structures or smothering organisms. The result is generally a shift in community structure away from filter-feeding animals in favour of deposit feeding animals.

Deposition of particles onto hard surfaces or sediments changes the physical nature of substratum for benthic organisms. Hard surfaces coated with fine particles are generally not as attractive to colonising organisms as clean surfaces and changes in community structure can occur. Deposition of organic particles onto sediments can change the particle size distribution of the sediment and therefore its physical properties and the composition of the benthic community. Perhaps more importantly, the biodegradation of the organic particles exerts an oxygen demand on the sediment reducing available oxygen to infaunal animals and changing many of the chemical processes within the sediment. Deposition of organic particles may also increase the load of toxic substances to the sediment because many substances are associated with organic particles. Deposition of inorganic particles changes the physical characteristics of the sediment and therefore the associated benthic fauna. In extreme cases, the deposition of organic and inorganic particles can result in the eradication of the benthic fauna. SOAEFD (1996) described the effects on the benthos of the deposition of dredged material at licensed disposal sites in the UK which included the effects of the deposition of inorganic particles.

There is some evidence to suggest that fish populations may be affected by changes in turbidity, the deleterious effects being reduced food availability for most fish species, and clogging of gillrakers and gill filaments by particulate matter. However, moderate turbidity levels may provide protection from predators (other fish and birds), and estuarine turbidity gradients may provide a navigational aid (Bruton 1985). Indeed, fish distribution in estuaries appears to be strongly linked to turbidity gradients, with different fish species favouring different turbidity waters (Cyrus and Blaber 1987a,b), and available evidence suggesting that the alteration in light availability has a greater effect on fish distribution than the concentration of suspended particulate matter (Cyrus 1983). However, most studies relating estuarine fish populations to turbidity have been undertaken in warmer climates than the UK (see Parr *et al* 1998), so few data are available for UK fish species.

C9.3.2 Indirect effects

The indirect effects of sustained increases in turbidity in the water column include:

! reduction in habitat complexity due to restrictions or removal of macroalgae/seagrass;

! resuspension of sediments results in associated effects of increased oxygen demand, release of nutrients and potentially toxic substances;

! fish feeding on benthic invertebrates may be adversely affected by a shift in the distribution and composition of benthic invertebrate communities;

! birds and sea mammals may be affected by a change in the supply of food organisms.

Macroalgae and other aquatic plant communities in the intertidal and the subtidal provide a very important habitat for invertebrate and fish communities. A reduction in the extent or the complete removal of these communities as a result of increased turbidity represents a significant impact on a European marine site.

Parr *et al* (1998) identified a prime cause of turbidity to be the resuspension of sediments. In estuaries, in particular, this can be exacerbated by encroachment of development onto the intertidal and increasing channelisation which prevents deposition of suspended material, maintains current speeds and increases resuspension. The associated effects of increased oxygen demand, release of nutrients and toxic substances are described in Sections C5, C1 and Appendix B respectively.

Benthic invertebrate communities can provide a significant proportion of the diet of some benthic fish with common prey items, including crustacea, siphons of suspension and surface deposit feeding bivalves and annelids. Changes in the community composition due to the deposition of organic and inorganic particles can result in a reduction in biodiversity and increasing dominance by annelid species. Such a change could adversely affect benthic feeding fish communities.

The combined effects of sustained increases in turbidity or an increase in the frequency episodes of increased turbidity have the potential to adversely affect communities of birds and sea mammals using the affected system.

C9.4 Potential effects on interest features of European marine sites

Potential effects include:

- a reduction in phytoplankton biomass in the presence of high concentrations of suspended particulate matter (especially in estuaries) because of the reduction of available light;

- a reduction in growth rates, areal coverage and depth of colonisation of macrophytes and macroalgae (including kelp) where turbidity is high;

- some evidence for adverse effects on zooplankton which can become associated with turbidity maxima in estuaries as a result of physical processes governing the movement of particles;

- turbidity or suspended solids can affect benthic invertebrate communities both when the particles are in suspension and when they are deposited;

- turbidity or suspended solids can directly affect fish populations;

- reduction in habitat complexity due to restrictions on or removal of communities of macroalgae and other aquatic plants;

- turbidity caused by resuspension of sediments results in associated effects of increased oxygen demand, release of nutrients and potentially toxic substances;

- fish feeding on benthic invertebrates may be adversely affected by a shift in the distribution and composition of benthic invertebrate communities;

- birds and sea mammals may be affected by a change in the supply of food organisms.

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Appendix D. Background levels of toxic substances

D1 Introduction

This Appendix is intended to provide some background information on concentrations found for some of the toxic substances considered in this report during systematic surveys undertaken in recent years. Other information on “typical” concentrations found for many contaminants is given in the individual profiles in Appendices B and C. However, this summary is not exhaustive and readers are advised to contact the Environment Agency/SEPA area or regional offices for advice on more recent survey information.

Two major reviews: ‘National Monitoring Programme. Survey of the Quality of UK Coastal Waters’ (prepared by the Marine Pollution Monitoring Management Group) (MPMMG 1998) and ‘Pesticides in the Aquatic Environment, 1995’ (prepared by the National Rivers Authority) (TAPS 1995) have been published which present summary information on the concentrations of various toxic chemicals in UK estuarine and coastal waters.

The National Monitoring Programme (NMP) was initiated in the late 1980s to co-ordinate marine monitoring in the UK between various regulatory organisations (and their predecessors). The results from the first phase of the NMP was intended to establish the spatial distribution of contaminants in UK marine waters and to define their biological status. A survey of 87 estuarine, intermediate and offshore sites was carried out between 1992 and 1995 to determine the distribution of contaminants (including metals and organic substances) in a range of matrices (water, sediments, shellfish and fish).

The report ‘Pesticides in the Aquatic Environment, 1995’ (prepared by the National Rivers Authority) (TAPS 1995) presents information on the concentration of various toxic substances in the estuarine and coastal waters of England and Wales. In 1995, the NRA monitored 101 pesticides and recorded almost 35,000 results in estuaries and coastal waters from 413 sites (TAPS 1995). The data were recorded as the number of samples that exceeded 0.1 μg l^{-1}, with no further information available on the highest concentrations reported.

A more recent report has been published (Environment Agency 1999) and readers are referred to this document for updated information on pesticides contamination of estuary and coastal waters.

D2 Water Column Concentrations

D2.1 Data summarised from National Rivers Authority Survey (TAPS 1995)

The information is presented in Table D1. The data were recorded as the number of samples that exceeded 0.1 μg l^{-1}, with no further information available on the highest concentrations reported. EQS exceedences were only seen infrequently with 6 sites (less than 2%) breaching relevant standards. Two EQS failures were reported for:

- **total HCH (lindane)** (EQS value = 0.02 μg l^{-1} as an annual average concentration);

- one for **azinphos-methyl** (EQS value = 0.01 μg l^{-1} as an annual average);

- one for **pp-DDT** (EQS value = 0.01 μg l^{-1} as an annual average);
- one for **endosulphan** (EQS value = 0.0003μg l^{-1} as an annual average);

! one for **chlorfenvinphos** (EQS value = 10 Fg l^{-1} as an annual average).

Data summarised from the ‘National Monitoring Programme Survey of the Quality of UK Coastal Waters’ (MPMMG 1998)

D2.2.1 Metals

Metal concentrations in estuaries were higher than at intermediate and offshore sites. This is interpreted as being a direct consequence of the proximity of estuarine sites to inputs, e.g. rivers. Within estuaries, there was also a general tendency for metal concentrations to decrease with increasing salinity. Where information is available, concentrations tended to be higher in those estuaries receiving inputs from industrial and/or domestic sources. Examples are cadmium (Severn), chromium (CIyde), lead (Tyne, Tees and Thames) and zinc (Tyne, Wear and Mersey).

Relative to metal concentrations in estuaries, those observed at intermediate and offshore sites were low and consequently of no real concern as regards compliance with EQSs. The data do, however, reveal some features of interest. Many of the metals included in the survey show higher concentrations in the southern rather than in the northern North Sea. This was attributed to the generally lower salinity in the southern North Sea, a consequence of the greater freshwater input from major rivers. A similar effect is evident for parts of the Irish Sea, where apparently high concentrations of metals can be attributed to the lower salinity of this area (CEFAS, 1997). Some metals are extremely particle-reactive, tending to be adsorbed onto suspended particles, with a consequent reduction in the dissolved phase concentration. Relatively high dissolved lead concentrations in the vicinity of Dogger Bank, observed in this and in other studies (Laslett, 1995), are attributed to the relatively clear waters of this area, where there is little removal onto particles.

Of all the median metal concentrations reported in the report, only two results (for zinc) exceeded the EQS for the metals included in the NMP survey (EQS values are: cadmium 2.5 Fg l^{-1}, copper 5 Fg l^{-1}, chromium 15 Fg l^{-1}, lead 25 Fg l^{-1}, mercury 0.3 Fg l^{-1}, nickel 30 Fg l^{-1} and zinc 40Fg l^{-1}, respectively).

Table D1 Pesticides exceeding 0.1 Fg l^{-1} in estuaries and coastal waters in England and Wales in 1995 (unless otherwise indicated) (TAPS 1995)

Pesticide	Total number of samples	Range of LOD Fg l^{-1}	% of samples >LOD	% of samples >0.1Fg l^{-1}
Diuron	69	0.02	86	58
Isoproturon	60	0.02	75	53
Mecoprop	58	0.02-0.1	74	21
Chlorotoluron	66	0.02-0.05	38	5
Linuron	65	0.02	25	3
Propetamphos	48	0.005-0.05	15	2
Simazine	501	0.01-0.3	14	1
Diazinon	103	0.005-0.2	16	1
Organotin	113	0.004-0.03	21	0.9
Atrazine	505	0.01-0.3	12	0.4
Dichlorvos	362	0.005-0.05	0.6	0.3
Pentachlorophenol	1307	0.05-1	0.4	0.2
Gamma HCH	1603	0.001-0.05	41	0.1

Pesticide	Total number of samples	Range of LOD Fg l^{-1}	% of samples >LOD	% of samples >0.1Fg l^{-1}
DDT op	1289	0.001-0.05	0.5	0.1
DDT pp	1208	0.001 - 0.05	1	0.1
TDE pp	1207	0.001-0.05	0.9	0.1
PCSD/eulan (1994)	-	-	-	9
Tributyltin (1994)	-	-	-	5
Methiocarb (1994)	-	-	-	2
Tetrabutyltin (1994)		-	-	0.5
Hexachlorobenzene (1994)	-	-	-	0.05
A HCH (1994)	-	-	-	0.05
Trifluralin (1993)	-	-	-	0.2
Dieldrin	-	-	-	0.1

D2.2.2 Organic Compounds

Organic compounds monitored as part of the NMP survey were:

PCB; alpha-HCH; beta-HCH; gamma-HCH (lindane); dieldrin; aldrin; endrin; isodrin; HCB; PCP; DDT; HCBD; PAHs; carbon tetrachloride; chloroform; trifluralin; endosulfan; simazine; atrazine; azinphos-methyl; azinphos-ethyl; dichlorvos; fenitrothion; fenthion; malathion; parathion; parathion-methyl; trichloroethylene; tetrachloroethylene; trichlorobenzene; 1,2-dichloroethane and trichloroethane.

However, with the exception of **HCH, atrazine, simazine, chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, trichloroethane and PCP**, the compounds were found at concentrations below analytical limits of detection. Insufficient positive results were available for analysis and therefore these data were not presented in the NMP report. However, the detection limits used are generally well below the EQS concentrations, indicating low background concentrations in UK marine waters.

Gamma-HCH (lindane)

Median concentrations of HCH were below the EQS concentration of 20 ng l^{-1} at all sites except the Thames at Woolwich. Individual results above EQS were found on the Tay, Ouse, Thames, Tamar, Mersey and Clyde. These elevated results were found in estuaries with either riverine sources (Ouse, Thames and Mersey) or in the vicinity of major urban conurbations which, in some cases, have known discharges (e.g. sewage discharges in the Thames and the combined effects of sewage and industrial discharges to the Clyde).

Generally, concentrations decline moving offshore, although concentrations in the outer Thames estuary off the East Anglian coast and south-eastern Irish Sea are higher than in the English Channel and Irish Sea off Northern Ireland. This may be due to transport of gamma-HCH on suspended particulate material.

Atrazine and Simazine

The NMP stated that no atrazine and simazine data were available for sites in Scotland, Northern Ireland or offshore sites.

All results for atrazine and simazine were significantly lower than the proposed EQS concentrations (statutory EQS of 2 µg l^{-1} (annual average) and a non-statutory EQS of 10µg l^{-1} (maximum allowable concentration) as the sum of atrazine and simazine). The highest median concentrations of atrazine and simazine were found in the Humber and Ouse estuaries respectively. Elevated concentrations were also found in the Thames, Tamar, Severn and Mersey, all of which have riverine sources. The ratio of atrazine to simazine was found to vary from estuary to estuary, probably because of variations in rates of application of these herbicides in the catchments.

Concentrations of atrazine and simazine found in this survey are comparable with earlier surveys (MAFF 1993, 1994). However, concentrations found in the NMP survey in the Thames, Tamar and Mersey are at the lower end of the range reported by Evans *et al* (1993) for surveys carried out in 1991 and 1992. This may be due to reductions in inputs of triazine herbicides to the marine environment resulting from the ban on non-agricultural use during the first year of the NMP survey. Evans *et al* (1993) stated that peak concentrations were found during periods of highest pesticides use or after rainfall. The timing of the surveys is likely to substantially affect observed estuarine concentrations.

Chloroform

Of the 44 sites with results available, 13 had results in which all values were below the detection limit. Median concentrations of chloroform were below the EQS of 12µg l^{-1} at all sites. Only one result (in the Wear estuary) was greater than the EQS. Elevated concentrations were also observed in the Tees and Mersey estuaries, which receive point source discharges of chloroform. The apparent elevated concentrations of chloroform in the Thames estuary, Solway Firth and off the Lune estuary are a consequence of relatively high limits of detection.

Carbon tetrachloride

Of the 44 sites with results available, 24 sites had results in which all values were below the limits of detection. Median concentrations of carbon tetrachloride at all sites were almost one tenth of the EQS concentration of 12 µg l^{-1}. Only one result, for a sample collected in the Wear, approached the EQS concentration. However, all North Sea states were obliged to discontinue production, consumption and import by 1 January 1996.

Trichloroethylene

Of the 30 sites with results available, 18 sites had results where all values were below the limits of detection. Median concentrations of trichloroethylene were all below the EQS of 10 µg l^{-1}. The highest individual concentration was found in the Wear estuary, which receives inputs of trichloroethylene from both river and point source discharges. Positive results were also recorded in the Severn and Mersey estuaries, which receive inputs of trichloroethylene from point source discharges and riverine sources.

Tetrachloroethylene

Of the 29 sites with results available, 18 had results in which all values were below limits of detection. All results were at most one tenth of the EQS concentration of 10 Fg l^{-1}. The highest median concentration was found in the Wear estuary which receives inputs of tetrachloroethylene. Positive results were recorded in the Humber, Severn and Mersey estuaries, all of which have point sources.

Trichloroethane

Of the 37 sites surveyed, 18 had results in which all values were below the limit of detection. All results were substantially below the proposed EQS of 100 Fg l^{-1} (annual average) for 1,1,1, trichloroethane. Positive results were recorded in the Tees, Severn and Mersey estuaries which receive inputs of trichloroethane from industrial point source discharges.

Pentachlorophenol (PCP)

The EQS for PCP is 2,000 ng l^{-1}. Of the 41 sites with results available, 29 had results in which all values were below the limit of detection. Median results at all sites were at most one tenth of the EQS. The NMP survey found it difficult to comment on spatial variability of PCP because few results above the limit of detection were recorded.

PAHs

The 10 PAH compounds for which data were considered within this assessment are a subset of those determined. The full data are presented elsewhere (Law *et al* 1997a).

The highest concentrations generally occur in major estuaries, particularly those of the Humber, Great Ouse, Thames and Tees. PAH concentrations at offshore sites were generally low or undetectable. Of the 39 samples taken at offshore locations (10 miles or more from the coast), only one (NMP station 245 off the River Tyne sampled in 1993) showed a significant concentration of PAH, and this was only for naphthalene (263 ng l^{-1}). Apart from this sample, PAHs were generally not detected in offshore waters. Higher concentrations were found in coastal and estuarine samples (although not in all), with total PAH concentrations ranging from none detected to 8.5 Fg l^{-1}. Total PAH concentrations greater than 1 Fg l^{-1} were found at 14 sites, in the estuaries of the Rivers Tees, Humber, Great Ouse, and Thames. Of these 14 sites, 10 were in the lower reaches of the River Tees estuary, and particularly high concentrations were observed in the vicinity of Redcar Jetty. The PAH profile observed in the five samples collected off Redcar Jetty was dominated by two- and three-ring PAHs, probably derived from an adjacent steel plant. The other data probably reflect inputs from a wide range of combustion processes, involving both industrial and domestic sources.

Comparison of samples for which duplicate filtered/ unfiltered concentrations were determined indicated that, for the lower molecular weight PAHs, the major portion was present in the dissolved phase (e.g. samples from the River Tees), while for the higher molecular weight PAHs the major portion was adsorbed onto particles.

While investigation in the NMP survey was only considered a ‘pilot’ study, the results obtained suggested that concentrations were low or undetectable at intermediate and offshore sites. However, significant concentrations of PAH have been found in a number of estuaries.

D3 Sediment Concentrations

D3.1 Data summarised from the 'National Monitoring Programme Survey of the Quality of UK Coastal Waters' (MPMMG 1998)

The results from this part of the survey have highlighted the major control that sediment characteristics, i.e. grain size and organic carbon, exert on observed contaminant concentrations. They concluded that the reported concentrations appeared to be typical background concentrations and were considerably lower than those reported for contaminated areas, such as some sewage sludge disposal sites.

Metals

Concentrations of all metals at offshore sites were relatively low, compared with those in estuaries. However, there were differences between estuaries, with a tendency for higher concentrations to be observed in those estuaries with either current or historical industrial inputs of metals. To some extent, these higher metal concentrations observed in estuaries stem from the presence of fine-grained sediment rich in clay minerals.

For example, relatively high mercury concentrations were observed in the Forth, Tees, Thames and Tamar. The Forth estuary has a history of mercury contamination, and although inputs have reduced dramatically, the turbid nature of the estuary has resulted in considerable retention of mercury in the system. Despite the known historical input of mercury to the Mersey estuary from chloralkali works, and the established contamination of the area, not all sediment samples contained high concentrations of mercury. In some industrialised estuaries, such as the Tees, concentrations of all metals were relatively high. Other estuaries, however, tended to have high concentrations of a smaller number of metals, e.g. Tyne (lead and zinc), Clyde (chromium and nickel) and Tamar (arsenic).

One difficulty in assessing these data is establishing the extent to which concentrations are determined by anthropogenic inputs or local geological sources. For example, the mineralised parts of the Pennines are likely to contribute to the relatively high lead concentrations observed in the Tyne and Tees estuaries. Metal concentrations in the Tamar estuary are also known to be influenced by mineralisation and historical mining activity within the catchment.

D3.1.2 Organic Compounds

The NMP determinands were 11 individual **polychlorinated biphenyl (PCB) congeners (PCBs 28, 52, 101, 105, 118, 128, 138, 153, 156, 170 and 180), dieldrin, aldrin** and **endrin, three DDT group compounds (pp-DDT, pp-TDE and pp-DDE)** and **hexachlorobenzene (HCB).** Organic contaminants are lipophilic and therefore have low water solubilities. They preferentially adsorb onto sediments, particularly where these are fine grained and/or contain a high proportion of organic carbon. Concentrations would, therefore, be expected to be inherently higher in areas with fine-grained organic rich sediments than in areas dominated by coarse sandy sediments.

PCB 153

Data for PCB 153 (a relatively abundant PCB congener) were used by the NMP to give an overall impression of contamination by PCBs.

Although data were presented for a total of 67 sites, very few sites yielded positive results. This was to be expected at some intermediate and most offshore sites, but previously published data suggest that PCB levels in some coastal and riverine sediments can be locally elevated, especially in areas of high industrial activity (CEFAS, 1997). However, two factors seem to have influenced the data set. Firstly the detection limits for many samples were inadequate to detect the very low background concentrations present. Secondly, many of the samples were sandy sediments, i.e. coarse particles with low organic carbon content. These comments are also applicable to many of the other organic contaminants discussed in this part of the report.

The highest reported levels of PCB 153, up to 25 Fg kg^{-1} median value, were reported at two sites in the Severn estuary; these are in the area of a site of historic manufacture of PCBs and were therefore not unexpected.

Dieldrin

The non-systemic insecticide dieldrin was commonly found at concentrations of 0.2-5 Fg kg^{-1} at estuarine and intermediate sites and these values represent typically background concentrations.

DDT group compounds

Although use of the insecticide DDT has ceased, its persistence means that it still occurs widely in the environment. In general, environmental levels of the parent compound are lower than its metabolites (ppTDE and pp-DDE). pp-DDT was rarely found, but pp-DDE and pp-TDE were more ubiquitous in their occurrence. Clear gradients of contamination were evident in the fine-grained sediments of the Forth and Clyde estuaries. In contrast, concentrations were very low in the coarse sandy sediments of the Tay estuary. Concentrations of compounds were low and often undetectable at most intermediate and offshore sites.

Hexachlorobenzene

Apart from the elevated levels from a known point source in the Forth, other positive values represent background concentrations.

PAHs

The NMP survey only carried out a ‘pilot’ study on the concentration of PAHs presented in the sediments of estuaries and offshore sites around the UK. Their findings are highlighted below.

Coverage of NMP stations in this pilot study of PAHs in sediments was not exhaustive, but a good spatial coverage was achieved and in some cases replicated over two years. These data suggest that concentrations are low or undetectable at most intermediate and offshore sites, and further work should be concentrated on fine sediments and depositional areas. Significant concentrations of PAH have been found in a number of estuaries. The conclusions of the NMP survey stated that the bioavailability of PAH and their uptake by shellfish (particularly bivalve molluscs) should also be evaluated in the next phase of the NMP programme, so that the significance of these compounds can be fully assessed for both marine animals and human consumers.

Total PAH concentrations ranged from not detected at some offshore sites with a sandy substrate to 35,400 Fg kg^{-1} dry weight in mud from the River Tyne at Hebburn. The samples from Scotland were at the lower end of this range, 27-488 Fg kg^{-1} dry weight, with the highest value in the Firth of Clyde. All of the highest concentrations (total PAH >10,000 Fg kg^{-1} dry weight) were found in the highly industrialised estuaries of north-east England, particularly in muddy sediments from the Rivers Tyne and Wear. Total PAH concentrations between 1,000 and 10,000 Fg kg^{-1} were found at sites in the Rivers Thames, Tamar and Severn and also at two offshore sites off the Tyne and off the Tees. Additional samples taken at non-NMP sites indicated that fine sediments from the Rivers Blyth and Tees also yielded total PAH concentrations above 10,000 Fg kg^{-1} dry weight, as did samples from a further site in the River Tyne at Tyne Bridge. One site within Millford Haven sampled in June 1996 yielded the highest recorded concentration of 93,000 Fg kg^{-1}. Millford Haven has been an oil terminal and refinery site since the 1960s and has been subject to discharges and numerous oil spills, the most recent being that from the Sea Empress in February 1996.

Total PAH concentrations between 1,000 and 10,000 Fg kg^{-1} were found at sites in Poole Harbour, the River Exe, Swansea Bay at Tenby and in the River Mersey. Nine sediments taken on a 3 x 3 grid in the Celtic Deep yielded total PAH concentrations of 366 to 786 Fg kg^{-1} dry weight, with both total and individual PAH concentrations varying by up to approximately a factor of two.

The highest concentrations of PAH recorded at NMP sites were:

! naphthalene 2,430 Fg kg^{-1};
! phenanthrene 6,220 Fg kg^{-1};
! anthracene 1,470 Fg kg^{-1};
! fluoranthene, 6,610 Fg kg^{-1};
! pyrene, 5,900 Fg kg^{-1};
! benz[a]anthracene, 4,130 Fg kg^{-1};
! chrysene, 3,410 Fg kg^{-1};
! benzo[e]pyrene 4,940 Fg kg^{-1};
! benzo[a]pyrene, 3,310 Fg kg^{-1};
! benzo[ghi]perylene, 1,930 Fg kg^{-1} dry weight.

The highest concentration of benzo[e]pyrene was found in the River Wear and of all the other PAH congeners at Hebburn in the River Tyne.

D4 Biota Concentrations

D4.1 Data summarised from the 'National Monitoring Programme Survey of the Quality of UK Coastal Waters' (MPMMG 1998))

D4.1.1 Metals in shellfish

Two shellfish species were specified for use in the NMP survey, the common mussel M*ytilus edulis* (L.) and the horse mussel *Modiolus modiolus*.

Data were submitted for metals in shellfish for 26 NMP sites around the UK coasts and estuaries. The NMP survey concluded that, while there were some gaps in the available dataset, on the basis of the available data, contamination by the metals examined was not a significant problem in UK estuaries.

Cadmium

Median cadmium concentrations ranged from 0.96 mg kg^{-1} dry weight at two sites on the Welsh side of the Dee estuary to 9.78 mg kg^{-1} dry weight in the Severn estuary. The range of median concentrations reported in the NMP survey was stated to be consistent with those previously reported for UK estuaries and coastal sites.

The Joint Monitoring Programme (JMP) of the Oslo and Paris Commissions has adopted arbitrary descriptive guidelines for cadmium in mussels of up to 2 mg kg^{-1} dry weight as in the "lower" level, between 2-5 mg kg^{-1} as the "medium" level, and >5 mg kg^{-1} as the "upper" level (MAFF, 1987). In this context, the highest cadmium concentrations reported for the UK NMP survey, in the Severn estuary, fall into the “upper" category. Results for one site in each of the Clyde, Mersey, and Severn estuaries fall into the "medium" category, while results for the remaining 11 sites are in the "lower" category.

In Scotland, a recommended standard of 15 mg kg^{-1} dry weight has been set for cadmium in mussels under the terms of the EC Shellfish Growing Waters Directive, specifically to ensure that "the concentration in the shellfish water or in the flesh must not reach or exceed a level which gives rise to harmful effects on the shellfish or their larvae" (ADRIS, 1982). The NMP survey concluded that the results presented by the NMP survey suggested that harmful effects due to cadmium contamination were unlikely in any of the UK estuaries surveyed.

Mercury

Median mercury concentrations ranged from 0.084 mg kg^{-1} dry weight in Southampton Water to 0.804 mg kg^{-1} at the intermediate site off the Lune and Wyre estuaries. These concentrations are lower than levels reported for contaminated estuaries elsewhere in the UK (0. 12-2.3 mg kg^{-1}) and for European shores (0.012-1.02 mg kg^{-1}), but similar to levels found at UK coastal sites (0.11-0.38 mg kg^{-1}).

The ADRIS (Association of Directors and River Inspectors in Scotland) recommended standard set under the EC Shellfish Growing Waters Directive is 3 mg kg^{-1}, well above the highest reported concentration. The NMP survey concluded from the results presented that harmful effects on mussels from mercury contamination were unlikely.

Lead

Median lead concentrations ranged from 3.01 mg kg^{-1} dry weight at the intermediate site in the Firth of Clyde to 13.5 mg kg^{-1} at Broughty Castle near Dundee in the Tay estuary. The elevated concentrations in the Tay estuary mussels were said to be consistent with high lead levels reported for sediments collected at the mid-channel NMP site off Broughty Castle. Concentrations above 10 mg kg^{-1} were also recorded for one site in each of the Forth and Clyde estuaries, which have been subject to historical industrial contamination.

Lead levels at the NMP sites were found to be slightly lower than median concentrations previously reported for contaminated estuaries in the UK (3.5-39 mg kg^{-1}) but similar to levels reported for UK coastal sites (<3.0-29 mg kg^{-1}) and European shores (0.6-27.6 mg kg^{-1}). Standards are not available for lead in mussels, although the ADRIS recommended standard for shellfish growing waters has been set at 50 mg kg^{-1} dry weight which the NHP survey suggests /indicates that shellfish are not at risk.

Zinc

Median zinc concentrations ranged from 84-90 mg kg^{-1} dry weight at Selsey Bill and in the Solent to 204-209 mg kg^{-1} at the outer most sites in the Tyne and Humber estuaries. The NMP survey reports these to be broadly similar to levels reported at coastal sites in the UK (58-303 mg kg^{-1}) and Europe (55-294 mg kg^{-1}), and to results for UK estuaries (91-330 mg kg^{-1}).

The NMP survey suggests that the high concentrations reported for mussels in the Mersey should be investigated since they approach the ADRIS recommended level of 500 mg kg^{-1} set under the terms of the EC Directive on Shellfish Growing Waters to protect shellfish and their larvae.

D4.1.2 Metals in fish

The NMP determinands were mercury and arsenic in fish muscle tissue and cadmium and lead in fish liver. The coverage achieved in the survey, particularly for intermediate and offshore sites, was considered to represent the best attempt to date to obtain a synoptic survey across the whole of the UK. Only in some estuaries are there significant gaps.

The NMP survey states that the results are reassuring in that they generally confirm those from previous surveys, which have demonstrated that contamination is confined to a few well known geographical locations.

Mercury in fish muscle

Results were generally as would have been expected from previous surveys, with highest concentrations found in Liverpool Bay and Morecambe Bay, areas that have been subject to considerable inputs of mercury via discharges from the chloro-alkali industry. The results presented confirm those from more specific local studies, e.g. the Mersey.

Levels were relatively high in some other inshore areas, e.g. the Thames estuary, with an observed general reduction in concentrations offshore. One unexpected result was the mercury concentrations in dab from inshore Cardigan Bay, which were relatively high in both CEFAS and Environment Agency samples.

Concentrations were generally low around the coast of Scotland, with only one value, from the Minches, exceeding 0.1 mg kg^{-1} wet weight. This was for megrim, which cannot be compared directly with other species. Plaice from the same station contained low concentrations of mercury (0.03 mg kg^{-1}).

Median mercury concentrations in dab ranged from 0.01- 0.02 mg kg^{-1} in Dundrum Bay and off the Tamar in the English Channel, to 0.26 mg kg^{-1} in the Burbo Bight off the Mersey. No median values therefore fell in the "higher" level category (>0.3 mg kg^{-1}) designated by the Joint Monitoring Group of the Oslo and Paris Commissions and virtually all were 50% or less of the maximum limits for mercury in fishery products (0.5 mg kg^{-1}) designated in European Community Commission Decision 93/351/EEC.

The range of the mean concentrations of mercury in those dab samples collected from North Sea NMP stations during the present survey was 0.03-0.11 mg kg^{-1} wet weight, generally similar to that (0.05-0.12 mg kg^{-1}) found in dab samples collected in the 1989-91 period under the Monitoring Master Plan designed to provide data for the North Sea Quality Status Report.

Median concentrations in the essentially estuarine samples of flounder ranged from <0.01 to 0.08 mg kg^{-1}.

Arsenic in fish muscle

There appeared to be little obvious spatial pattern in the concentrations observed. The highest levels in dab (~20 mg kg^{-1}) were found off the Tees, Tay and Forth estuaries. However, concentrations were almost as great in the Moray Firth area, indicating that the levels found are not likely to be entirely due to anthropogenic inputs. The highest arsenic concentration found in fish muscle was in the Minches, which would be expected to be relatively free of anthropogenic contamination. This was, however, in non-recommended species, megrim, and it is known that very considerable differences occur between species in the accumulation of arsenic in fish (Falconer *et al.,* 1983*)*.

Concentrations of arsenic in flounder were relatively low, with a maximum concentration of ~6 mg kg^{-1}.

Unfortunately, arsenic has not yet been included in most international programmes, so data for comparison purposes from previous monitoring are limited.

Cadmium in fish liver

Concentrations appear to be highest off the east coast of Scotland, with a maximum median of around 0.8 mg kg^{-1} wet weight off the Tay. The maximum median concentration in English waters (0.37 mg kg^{-1}) was offshore of the Tyne-Humber , previously identified in the sampling carried out under the North Sea Monitoring Master Plan as an area where cadmium concentrations were above the upper quartile of the survey results.

The maximum values found in the earlier North Sea survey was 0.96 mg kg^{-1} cadmium, with the median concentration 0.18 mg kg^{-1}.

Cadmium concentrations were relatively low in the Northern Irish samples and in all samples of flounder.

Lead in fish liver

The range of concentrations of lead found in dab liver was relatively small, from 0.03 mg kg^{-1} in the Moray Firth to a maximum of 0.58 mg kg^{-1} off the coast of Northern Ireland. Generally low concentrations were recorded in dab taken from Scotland, but plaice taken off the Tay had the highest level for all the fish sampled 0.62 mg kg^{-1}.

There are unfortunately few earlier data that could be used for comparative purposes, since in previous years, the methods generally employed were rarely able to provide low enough detection limits to yield positive results. In the early 1990s, for example, concentrations in dab liver in the samples collected under the North Sea Monitoring Master Plan were all <0.6-< 1.0 mg kg^{-1}.

D4.1.3 Organochlorines in shellfish

Drins

NMP specified the determination of dieldrin, aldrin, endrin and isodrin. The most common compound in biological samples is dieldrin. Other drins tend to revert to dieldrin in the natural environment and are unlikely to be found unless the organism has been recently exposed.

Only data for dieldrin were reported at concentrations greater than the limit of detection. Dieldrin was detected at five sites at concentrations ranging from 0.006 to 2 Fg kg^{-1}. All data were below the ADRIS "no harmful effects" concentration of 100 Fg kg^{-1}.

DDTs

More than half the data reported for pp-DDT was below the limit of detection of the analysis. Positive data for pp-TDE were reported at both sites in the Forth and one site in the Humber. The concentration found in the Forth is approximately an order of magnitude less than that found in the Humber. Data for pp-DDE were reported at eight sites at concentrations ranging from 0.007-6.5 Fg kg^{-1}. All data were below the ADRIS "no harmful effects" concentration of 100 Fg kg^{-1}.

HCH

Data greater than the limit of detection were reported at five sites for gamma-HCH . Concentrations were low (0.25-5.5 Fg kg^{-1}) and well below the ADRIS "no harmful effects" concentration of 30 Fg kg^{-1}. Positive data for % -HCH were reported at only one site (Selsey Bill).

PCBs

NMP specified a range of congeners for analysis. Data are presented for PCB 153 as this is the congener for which most data were available. Positive data were reported at seven sites, two in the Forth, two in the Humber and three in Belfast Lough. The highest concentrations occurred in the Humber (maximum 12.8 Fg kg^{-1}). Concentrations reported in Belfast Lough (0.006 Fg kg^{-1}) were below the limit of detection of all other sites. Belfast Lough and the Forth samples fall into the lower contamination range for PCBs in molluscs (JMP guideline values) whereas the Humber sites fall into the medium range.

HCB

Positive data were only reported in the Humber (26.9 Fg kg^{-1}) and the Forth (0.31 Fg kg^{-1}). The sediments of the Forth have been shown to be contaminated with HCB as a result of past discharges (Harper *et al,* 1992) and provide a source of HCB to the resident biota.

PCP

Only two sets of data were returned for PCP and both sets had more than 50% of data less than the limit of detection. PCP is known to metabolise rapidly and is consequently difficult to analyse for in mussels.

D4.1.4 Organochlorines in fish liver

The NMP determinands were 11 individual polychlorinated biphenyl congeners (PCBs 28, 52, 101, 105, 118, 128, 138, 153, 156, 170 and 180), dieldrin, aldrin and endrin and three DDT group compounds (pp-DDT, pp-TDE and pp-DDE). As with the metals the first choice species was dab with flounder as an alternative.

PCB 153

PCB 153 (2,2',4,4',5,5'- hexachlorobiphenyl) is generally considered to be highly persistent in marine biota and therefore is most often the dominant congener in a typical chlorobiphenyl profile. This, coupled with the relative ease of measurement, results in it often being used as an indicator chlorobiphenyl and this is the case for the purposes of the NMP report.

PCB 153 was detected at more than 90'% of the 39 stations for which data were presented, with more than 50% of the stations having values exceeding 20 Fg kg^{-1}. Seven stations exceeded 50 Fg kg^{-1}, while the highest median values (in excess of 100 Fg kg^{-1}) were reported for the three stations; the Forth at Kingston Hudds Liverpool Bay at Burbo Bight and Liverpool Bay, offshore with values of 120, 160 and 170 Fg kg^{-1} respectively. The last two values are consistent with previous data that have put contamination in the medium and upper categories of the JMP guideline levels for PCBs in fish tissue. Although concentrations generally declined offshore, PCB 153 was present at all stations. The relatively high levels in Liverpool Bay are consistent with the results of more localised studies in that area.

Dieldrin

Dieldrin was detected in more than 90% of the stations for which data were reported. Highest median values were reported for Liverpool Bay; Off Lune/ Wyre ; Thames and offshore Moray Firth, with median values of 35, 22, 50 and 72 Fg kg^{-1} respectively

Aldrin

The results for the nine stations for which data were presented were all less than the limit of detection, which is not surprising as aldrin is readily converted to dieldrin in many environmental compartments.

Endrin

The coverage for endrin was wider than for aldrin, with data for 13 stations being produced. However, only two stations, Moray Firth and Belfast Lough yielded positive results, with median values of 5 and 6 Fg kg^{-1} respectively . Although endrin is highly toxic, it is much less persistent than dieldrin and its occurrence was not expected to be widespread.

DDT group compounds

Three DDT compounds were required to be determined, namely, pp-DDE , pp-TDE and pp-DDT. The highest median level concentrations for all three compounds were found at the sites off the north-west of England with median values of 15-91 Fg kg^{-1} for pp-DDE; 23-130 Fg kg^{-1} for pp-TDE and 13-28 Fg kg^{-1} for pp-DDT. These values are within the "expected range" for these compounds in fish liver, with the stable metabolite pp-DDE being the dominant component. The concentrations of these compounds generally decreased at offshore sites, with stations off Wales and the south-west coast of England being close to or below the limit of detection. The concentration patterns were similar for pp-DDE and pp-TDE. However, four stations off the east coast of England appear to have higher levels with median values ranging from 6.5 to 20 Fg kg^{-1} for pp-DDT. No corresponding data were presented for the estuarine sites in this area.

D4.1.5 Organochlorines and mercury in gannet eggs

During 1971-1997, eggs have been obtained from up to eight different gannet colonies around Britain and Ireland as part of an on-going monitoring programme funded by the Joint Nature Conservation Committee (JNCC). Although residues of DDE, HEOD and PCB have generally declined, some sites have shown an increase in residues, particularly of PCBs and mercury, at least over part of this period (Newton *et al* 1999).

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