Characterisation of European Marine sites

The Exe Estuary

Special Protection Area

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Cover photograph:
The Exe Estuary from the air
Graham Ward

Site Characterisation of the South West European Marine Sites

Exe Estuary SPA

W.J. Langston*[1], B.S.Chesman[1], G.R.Burt[1], S.J. Hawkins[1], J.Readman[2], and P.Worsfold[3]

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A study carried out on behalf of the Environment Agency and English Nature

by the Plymouth Marine Science Partnership

* [1](and address for correspondence): Marine Biological Association, Citadel Hill, Plymouth PL1 2PB (email: wjl@mba.ac.uk): [2]Plymouth Marine Laboratory, Prospect Place, Plymouth; [3]PERC, Plymouth University, Drakes Circus, Plymouth

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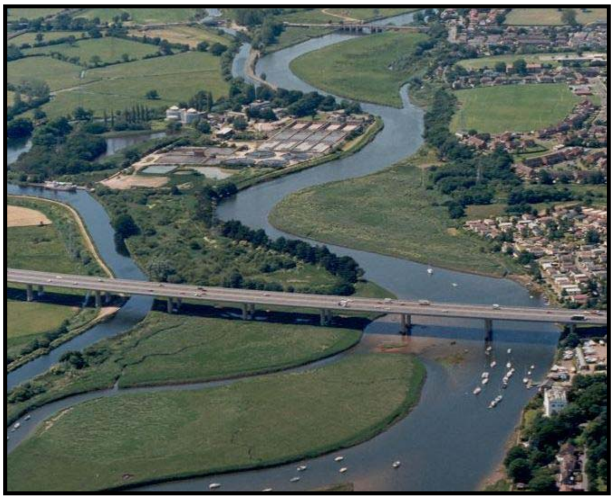
Plate 1: Some of the operations/activities which may cause disturbance or deterioration to key interest features of the Exe Estuary SPA



1: Countess Wear STW and the M5 motorway

2: Agricultural land bordering the freshwater River Exe

3: Embankments border the Estuary on both sides

Photographs:
1: Graham Ward **2:** Steve Johnson (Cyberheritage)
3: MBA

Plate 2: Some of the Interest Features and habitats of the Exe Estuary SPA

Annex 1 bird species:

1: Avocet (*Recurvirostra avosetta*)

2: Slavonian Grebe (*Podiceps auritus*)

3: (above) Atlantic 'Salt Meadows' opposite Topsham

4: (above right) Salt marsh and mudflats at Turf Locks

5: (right) Sandflats, Exe Estuary (Lympstone)

Photographs:
Plate 1:Eric Isley **Plate 2**: Keith Regan
Plates 3-5: MBA

1. EXECUTIVE SUMMARY

The Environment Agency and English Nature are currently undertaking investigative work in order to review permissions required under regulation 50 of the Conservation (Natural Habitats &c.) Regulations, 1994. Phase 1 of this exercise is the characterisation of designated European marine sites. In the South-West these sites include the marine areas of the Exe Estuary Special Protection Area (SPA).

This project, undertaken by the Plymouth Marine Science Partnership (PMSP), (comprising Marine Biological Association (MBA), University of Plymouth (UoP) and Plymouth Marine Laboratory (PML)), has two main objectives. Firstly, to characterise the site in terms of water quality over recent years (up to 2002), and to identify areas where conditions might result in effects on habitats and species for which the site was designated. Secondly, to consider permissions, activities and sources, either alone or in combination which have, or are likely to have, a significant effect on the site.

Site characterisation has been accomplished by review of published literature and unpublished reports, together with interrogation of raw data sets, notably that of the EA (this does not include recent compliance data and other forms of self-monitoring for Integrated Pollution Control sites, which was not available). Some of the key findings are as follows:

There may have been a long-term decline in the diversity of algal species and in the extent seagrass beds in the estuary, although it is difficult to speculate on the exact causes of the change.

The intertidal sediments and fauna of the Exe remained relatively unchanged for much of the 20th century. Composition of the sediment-dwelling species appears to differ in different parts of the estuary, determined largely by natural environmental conditions. Highest numbers of infaunal species have been recorded at Exmouth and Shutterton, although diversity at these sites have been reported as relatively low compared with similar locations elsewhere. Nevertheless, infaunal diversity indices indicated that the majority of the estuary was completely undisturbed and relatively unaffected by unnatural disturbance such as chemical pollution, organic enrichment from sewage and frequent bait digging.

British Trust for Ornithology (BTO) observations on bird populations have indicated declines for Widgeon, Dark-bellied Brent Goose, Oystercatcher and Avocet at various times over the last 25 years, though these are not considered cause for concern.

The review of toxic contaminants reveals little direct threat to biota across most of the estuary, though for many chemicals the data are not sufficiently robust to provide detailed analysis.

Rivers entering the Exe Estuary are unlikely to cause problems with regard to metals though elevated levels are reported near the head of the estuary at Countess Wear, most notably for Zn. Metal concentrations in sediments are also highest in the upper estuary (due to proximity to STW, and to enriched organic and oxyhydroxide coatings which sequester metals). The only metal above sediment ‘probable effects levels’ here, was Zn, though Cd, Hg, Pb, Cu and As exceeded the lower guideline value. Concentrations of most elements decrease to background levels towards the mouth of the estuary. Based on available evidence it is only in the region of Countess Wear near the tidal limit of the estuary, that deterioration due to metals could be expected.

Apart from slight enrichment in Ag, Cd, Hg, Sn and Pb there is little significant bioaccumulation above normal in the estuary. Elevated burdens in mussels close to Exmouth Dock appear to be a localised phenomenon. Shellfish from commercial beds display little evidence of contamination except perhaps, slightly, for Pb. Recent bioaccumulation data for the Exe would be useful to confirm trends.

Most organic compounds are below detection limits, appear to comply with EQS standards and, in designated shellfish areas at least, are generally considered of little toxicological importance. However, data on some compounds such as TBT, though indicating little threat, are probably not adequate for an accurate appraisal. STW and diffuse agricultural inputs along the estuary have contributed reckonable loadings of γ-HCH (and probably other pesticides and herbicides) to the estuary in the recent past and concentrations in estuarine sediments in the early 1990s were above the PEL. However, inputs now appear to be declining substantially. Also, small PCB loadings appear to have originated from the river in the past, carried into the estuary in particulate form and concentrated at the turbidity maximum. Occasional irregular localised sources of PCB within the estuary may have been superimposed on the main input(s) from the River Exe. Some of these sediment values approach or exceed quality guidelines and PEL, and are therefore of possible biological significance, however more recent EA data do not corroborate this contention. Concentrations of PAHs in the upper estuary are naturally ‘concentrated’ due to the high levels of suspended solids, and decrease towards the mouth of the estuary. Thus, concentrations are moderately high in sediments upstream, occasionally exceeding, by a small margin, ecotoxicological guideline values for ΣPAH and some individual PAHs.

In general, any effects due to metals or organic contaminants, if they occur, are likely to be chronic rather than acute and restricted to sites towards the head of the estuary, rather than in sandier sediments further downstream.

It is evident that the Exe Estuary is exhibiting symptoms of eutrophication. Although the River Exe appears to be the source of the majority of nutrients in the estuary (introducing contributions from agricultural run-off and sewage discharges higher up in the system) sewage discharges direct to the estuary constitute additional loading and result in chronic contamination of the affected areas. Countess Wear STW is implicated as the major point source. Additional diffuse inputs from tributary rivers and streams may also be important, in combination. Elevated BOD and nutrient levels in the estuary were noted in the late 1980’s and appear to be increasing over recent years. Phytoplankton blooms have occurred within the estuary and, although these have not been persistent due to the efficient tidal flushing characteristics of the estuary, are a symptom of eutrophication. However, ammonia concentrations in tidal waters are of immediate concern for biota as toxic levels have been recorded. These manifestations lead to the Exe being investigated as a Sensitive Area (Eutrophic) during 2001. Designation could have facilitated significant reductions in nutrient loadings. However, it was not put forward to DEFRA due to the rapid flushing rate and lack of evidence, therefore it will not be designated in the foreseeable future.

These principal findings are discussed in detail in the following report, together with implications for key habitats and species. A major challenge for the future is to establish a more reliable integrated means of assessing changes in the biology and chemistry of the marine site. Recommendations are made which may improve understanding of the system and assist Regulatory Authorities in their statutory responsibilities to ensure the favourable condition of the site and its features.

CONTENTS

2. INTRODUCTION

This review considers the characteristics of the marine areas of the EXE ESTUARY SPA and how the status of the site is influenced by existing permissions and activities, either alone or in combination. Also considered are possible impacts from other factors such as unconsented activities, diffuse sources and natural processes. This includes activities and consents outside the site itself. The purpose is thus to collate and interpret information relevant to the assessment of water quality impacts and risks to the marine component of the SPA, to ensure that EA and EN are fully informed when making decisions in relation to the scope of appropriate assessment. The opinions expressed are made on the basis of available information (up to 2002). We have emphasised areas where information is lacking, or where we see an opportunity to improve implementation and monitoring to comply with the requirements of the Habitats Directive and to provide a better means of establishing the status of the site.

To achieve this goal, specific objectives were:

- To prepare comprehensive reference lists of previous investigations and existing datasets, including published research and unpublished reports, relevant to an assessment of the effects of water quality on the marine sites and interest features identified.
- To review the existing information, pinpoint key studies, collate and summarize their findings.
- To identify site-specific models predicting pollutant concentrations and their links to impact.
- To prepare a summary of existing datasets (spatial and temporal) on water and sediment quality (e.g. determinands and summary statistics where available).
- To integrate and evaluate biological information, with specific reference to water/sediment quality.
- To conclude if there is any evidence that existing water (or sediment) quality is causing impact and highlight limitations of the available data.
- To identify and recommend further research which will address the limitations of current information and establish cause/effect relationships.

English Nature has provided advice on the Exe Estuary SPA, given under Regulation 33(2) of the Conservation Regulations 1994 (English Nature, 2001). A summary of the interest (or qualifying) features, and conservation objectives, for the site is given in Annex 1. The table below is a summary of the operations which, in the opinion of English Nature, may cause disturbance or deterioration to these interest features. In terms of the current project's emphasis on consents, we will focus on the vulnerability to toxic contamination and non-toxic contamination unless any of the other threats are seen as highly relevant.

Table 1. Summary of the operations, which, in ENs opinion may cause disturbance or deterioration to key interest features of the Exe Estuary SPA. Toxic and non-toxic contamination are the principal threats considered in the current project. (Table adapted from English Nature, 2001)*

Standard list of operations which may cause deterioration or disturbance	INTEREST FEATURES*	
	Internationally important populations of regularly occurring Annex 1 birds	Internationally important assemblage of waterfowl, including the internationally important population of regularly occurring migratory species
Physical loss		
Removal (e.g. harvesting, coastal development)	✔	✔
Smothering (e.g. artificial structures, disposal of dredge spoil)	✔	✔
Physical damage		
Siltation (e.g. run-off, channel dredging, outfalls)	✔	✔
Abrasion (e.g. boating, anchoring, trampling)	✔	✔
Selective extraction (e.g. aggregate dredging,)		
Non-physical disturbance		
Noise (e.g.boat activity)	✔	✔
Visual presence(e.g. recreational activity)	✔	✔
Toxic contamination		
Introduction of synthetic compounds (e.g. TBT, PCB's,)	✔	✔
Introduction of non-synthetic compounds (e.g. heavy metals, hydrocarbons)	✔	✔
Non-toxic contamination		
Changes in nutrient loading (e.g. agricultural run-off, outfalls)	✔	✔
Changes in organic loading (e.g. mariculture, outfalls)	✔	✔
Changes in thermal regime (e.g. power station)		
Changes in turbidity (e.g. run-off, dredging)		
Changes in salinity (e.g. water abstraction, outfalls)		
Biological disturbance		
Introduction of microbial pathogens		
Introduction of non-native species and translocation		
Selective extraction of species (e.g. bait digging, wildfowl, commercial and recreational fishing)	✔	✔

***Note: Key habitats (subfeatures) of the site which support these internationally important birds include shallow inshore waters (including lagoons), intertidal sediment communities, saltmarsh communities and reedbeds. See Annex 1 for more detailed descriptions.**

The key questions, which we have tried to incorporate into our considerations of site characteristics are in line with the Agency's Management System i.e.

- Is there a potential hazard mechanism by which the consent/activity could affect the interest features of the site (directly or indirectly)?
- Is there a probability that the consent/activity could affect the interest features of the site (directly or indirectly)?
- Is the scale and magnitude of any effect likely to be significant[1]?

Clearly if the answer to all three questions is positive a more detailed assessment is likely to be required.

We have also kept in mind similar criteria which EA/EN may need to apply during the review process as outlined in their *Guidance for the Review of Environment Agency Permissions: Determining Relevant Permissions and 'significant effect'* (March 1999):

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.

[1] Examples of 'significant' effects criteria:
- Causing change to coherence of the site
- Causing reduction in area of the habitat
- Causing change to the physical quality and hydrology
- Altering community structure (species composition)
- Causing ongoing disturbance to qualifying species or habitats
- Causing damage to size, characteristics or reproductive ability of qualifying species (or species on which they depend)
- Altering exposure to other impacts
- Causing a reduction in resilience against other anthropogenic or natural changes
- Changing stability of the site/feature
- Affecting a conservation objective

3. REFERENCE LISTS AND SOURCES OF INFORMATION

- A full list of publications in the open literature has been assembled using the Aquatic Sciences and Fisheries Abstracts (ASFA) and Web of Science information retrieval systems. The NMBL in-house data base ISIS has provided additional listings (see accompanying electronic database).

- Unpublished reports and data-bases: Environment Agency, Joint Nature Conservancy Council (JNCC) Coastal Directories Reports, Centre for Environment, Fisheries and Aquaculture Science (CEFAS); (see accompanying electronic database).

- Information, monitoring data and summary statistics provided by the Environment Agency up to 2002, extracted from WIMS (this does not include recent compliance data and other forms of self-monitoring for Integrated Pollution Control sites, which was not available).

- The Plymouth Marine Science Partnership (PMSP) laboratories (MBA, PML, and UoP) have already undertaken a small number of studies in the Exe system on bioaccumulation of metals, TBT, modelling and ecology of benthic organisms. Comparative data for other UK estuaries, including south-west marine sites (e.g. Severn, Tamar, Poole, Fal) have been used to draw comparisons.

Section 4 of this report describes the main physical, chemical and biological features which shape the character of the site and summarises some of the perceived threats to its favourable status. Studies which describe the biology and ecology of benthic communities within the site, many of which support the bird populations for which the site is designated, are discussed in **Section 5.**

Section 6 discusses published information on toxic contamination (metals, TBT, petrochemicals, pesticides, PCBs, volatile organics) and non-toxic contamination (nutrients, turbidity, dissolved oxygen). Section 6 also presents summary statistics of previously unpublished water quality data, in relation to Environmental Quality Standards and guidelines (listed in Annexes 2-5). This draws on available information provided by the Environment Agency (extracted from WIMS).

A synthesis of available information on sediment quality, based mainly on MBA metals data and mapping routines, together with limited data on organic contaminants from WIMS is given in **Section 7.**

A brief description of modelling exercises of direct relevance to the environmental quality status of the site is provided in **section 8**.

Concluding remarks (**section 9**) include a summary of evidence for impact in the Exe Estuary marine site, together with recommendations for future monitoring and research requirements.

4. THE SITE: FEATURES AND THREATS

In addition to its SPA status under the European Commission Directive on the Conservation of Wild Birds (79/409/EEC) the Exe Estuary is designated as an SSSI in the British context for its biological, geomorphological and geological interest.

The Exe Estuary was also listed as a Ramsar site under the International Convention on Wetlands of International Importance in 1992. The Ramsar margins encompass the waters, foreshore, low-lying land, three marshes (the largest of which is Exminster) the sand dunes of Dawlish Warren and the double spit across the mouth of the estuary. There are also several Local Nature Reserves (LNRs). The boundaries of the Exe Estuary Marine site, which essentially incorporate the entire marine component of the SPA, are shown in figure 1. Detailed maps of communities and features within the site can be found in greater detail elsewhere (English Nature, 2001).

The estuary opens into the western side of Lyme Bay and was formed through the drowning of the lower Exe River valley, during the post-glacial rise in sea level. The tidal estuary now occupies a basin of about 15km long and 1-2km wide, and is situated in Permian deposits (Dawlish Sandstones, Exe and Langstone Breccias, and Exmouth Mudstones) between the Cretaceous Greensand of the Haldon Hills to the west and the Pebble bed ridge of Budleigh Salterton and Woodbury to the east.

The mean tidal range at Exmouth is 3.8m for spring tides, and 1.5m for neaps. Admiralty tide tables indicate a similar range at Topsham, diminishing to 1m at the A38 Countess Wear Road Bridge, near the head of the estuary. For hydrographic purposes the latter is usually taken to be St James Weir, though the normal tidal limit is about 1km below this and the saline intrusion somewhat lower still (McCandlish, 1980).

The Exe is unusual in that it has a double spit across its mouth. The dunes of Dawlish Warren, and Pole Sand (an area of shoaling sediment) on the western side restrict sea access to a long narrow channel. This results in very strong tidal currents in this area, particularly on the ebb tide (Thomas, 1980), when speeds of up to 4.5 knots have been reported in the narrows between Warren Point and Bull Hill[1] (Dixon, 1986). At low tide, much of the estuary dries, exposing a narrow channel (~500m wide) which winds along the estuary (mainly on the west side) between extensive intertidal mud and sand flats. There is a significant deflection to the east at Powderham sands. Numerous small channels drain the flats and minor streams, with more sizeable channels which run towards Lympstone and Starcross. The greater part of the main channel has a depth of less than 1-2m below chart datum (BCD), although depths of up to 5m BCD occur in isolated spots. Estimated residence (flushing) time for the estuary is 6 days (Uncles *et al.,* 2002).

To a large extent, the site is protected from the excesses of the prevailing southwesterly wind and wave action by the western side of Lyme Bay, and the western spit, although southeasterly gales can result in large swells and occasional embankment damage. Generally however, the importance of waves in the shallow estuary lies in the maintenance of suspended sediments and water column mixing

[1] Bull Hill is an almost semicircular bank northeast of Exmouth Harbour, and is a delta formed by sediment swept in on the flood tide (Thomas, 1980).

(Thomas, 1980). The lower estuary is characterised as being well mixed whilst the upper reaches are partially stratified, particularly at neap tides, though in winter there is a tendency for the latter to become better mixed also. Thus, the greatest salinity variations occur along the longitudinal axis rather than with depth, most notably as the river water moves seaward behind the ebbing tide. Salinity variations also tend to be greatest in the main channel – turbulence over the shallow banks promotes more thorough mixing (Atkins, 1988). Suspended solids levels at spring tides may exceed 25 g l^{-1} in the region of Starcross due to a combination of high current speeds, limited water depth and river and sewage discharges. This pattern increases up the estuary.

Much of the western shore of the estuary basin is formed by the embankment of the main Exeter to Plymouth railway. Similarly, the Exeter to Exmouth line runs along the eastern side, its embankment often on the foreshore.

There are no natural rocky shores within the estuary, and the little alternative hard substrata present consists of stones and small boulders concentrated around the high water mark, and the areas where the stone-faced railway embankments fall within the upper intertidal zone. Subtidally, habitats are also primarily sedimentary, ranging from mud at the head of the estuary to sand, stones and boulders at the mouth, with occasional outcrops of flat bedrock in the narrow channel entrance. Because of the lack of stable hard substrata, epifaunal and algal diversity tends to be somewhat limited, although in heterogeneous muddy and sand areas, infaunal populations may be less sparse. Benthic communities are discussed in greater detail in section 5.

By and large then, the character of the bed sediment is fairly homogeneous throughout much of the length of the Exe Estuary, with a median grainsize diameter between 10 and 100μm. Low energy environments (in the upper estuary, mainly, and behind Dawlish Warren) encourage the deposition of finer fractions which may be enhanced by local sewage discharges. Some organic enrichment has also been observed at Exton in the past, attributable to local inputs of untreated sewage (Atkins, 1988), although these discharges are being improved (see annex 7).

There are two major urban areas, Exeter, at the head of the estuary, and Exmouth, on the eastern banks of the estuary mouth. Several smaller settlements lie along its banks; Topsham (at the head of the estuary below Exeter), Lympstone and Exton on the Eastern shore, and Starcross, Cockwood and Dawlish Warren on the western shore.

In spite of its historical role in national and international trading routes, development of the region (and the Exe in particular) - in terms of port facilities, industry and population - did not occur during the industrial revolution. This was partly due to the relative isolation of the southwest peninsular, and partly because of the lack of important resources such as coal and iron. Consequently, the catchment has retained its predominantly rural nature and supports dairy and mixed farming, and market gardening, accounting for ~80% of land use (EA, 2001a).

As a whole, the Exe Estuary supports important numbers of Avocet, Slavonian Grebe and waterfowl assemblages, hence its designation as an SPA (see annex 1). Nationally-important aquatic species include the polychaete worm *Ophelia bicornis*; the Exe Estuary is one of the few known British locations for this species, and also the tentacled lagoon worm *Alkmaria romijni.* Pink sea fan *Eunicella verrucosa* is found on near-shore reefs close to Exmouth. Elsewhere within the Exe, several areas support regionally important habitats, such as eelgrass *Zostera spp,* and saltmarsh, part of which is a cordgrass (*Spartina. spp*) monoculture.

Rivers

Freshwater draining from three catchments, the Exe, the Creedy and the Culm (totaling 1462km^2), meets north of Exeter and flows into the estuary as the River Exe. The River Clyst drains a further sub-catchment and joins the Exe Estuary to the northeast at Topsham

Flow-rates entering the Exe Estuary from the River Exe amount to an average of (23 m^3 s^{-1*}), and are supplemented by much smaller inputs from the Clyst (1.4 m^3 s^{-1}), River Kenn (0.5 m^3 s^{-1}), Polly Brook (0.4 m^3 s^{-1}) and a number of smaller tributaries such as Shutterton Brook and Alphin Brook (figure 1). The banks of the rivers and streams support grazing marsh that contributes to the importance of the SPA for wintering birds.

The River Exe rises on Exmoor at a height of 450m above sea-level and descends 87.2km to the tidal limit of the estuary at St James Weir. Total catchment area is of the order of 1100km^2. Analysis of the flow record at Thorverton (figure 1) shows a mean daily flow of 15.89m^3 s^{-1} with a Q95 (95th percentile) that is 12% of this indicating a relatively 'flashy' flow regime compared to the rest of England[2].

The Exeter Canal, which is the oldest canal with locks in the country, stretches from Exeter Quay to Turf Locks, a distance of five and half miles, and runs parallel to the Exe behind the west bank of the upper estuary. It was built to enable navigation after the Exe became impassable to ships due to the building of a weir by the (then) Countess of Devon around 1400. The opening of the canal in 1566 re-established the link between the city and the estuary, and the port trade (which was predominantly in wool) began to prosper once more.

Up until EU legislation prevented it in 1998, sewage sludge was carried twice weekly by SWW's vessel, from the Countess Wear STW down the Exeter canal, through the estuary, to be dumped five miles off Exmouth. The canal is now used principally for recreation purposes.

Threats

Salt works which were constructed in the salt marshes near Topsham in the 18th and early 19th century, together with the building of the Exeter Canal, construction of railway embankments along both sides of the estuary and marsh reclamation (for agricultural purposes) has considerably reduced the original area of saltmarsh (Parkinson, 1980) and changed the nature of the shoreline (Dixon, 1986). Although these are not recent events, the physical loss would have reduced the availability of intertidal habitats, and roosting habitats and food supply for birds and waterfowl.

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[*] These are relative ratios scaled using micro-low flow means (Murdoch, 2001). Total mean river flow for 1984 ~25 m^{3}s^{-1} (Dixon, 1986)

[2] Environmental Change Network (ECN) website

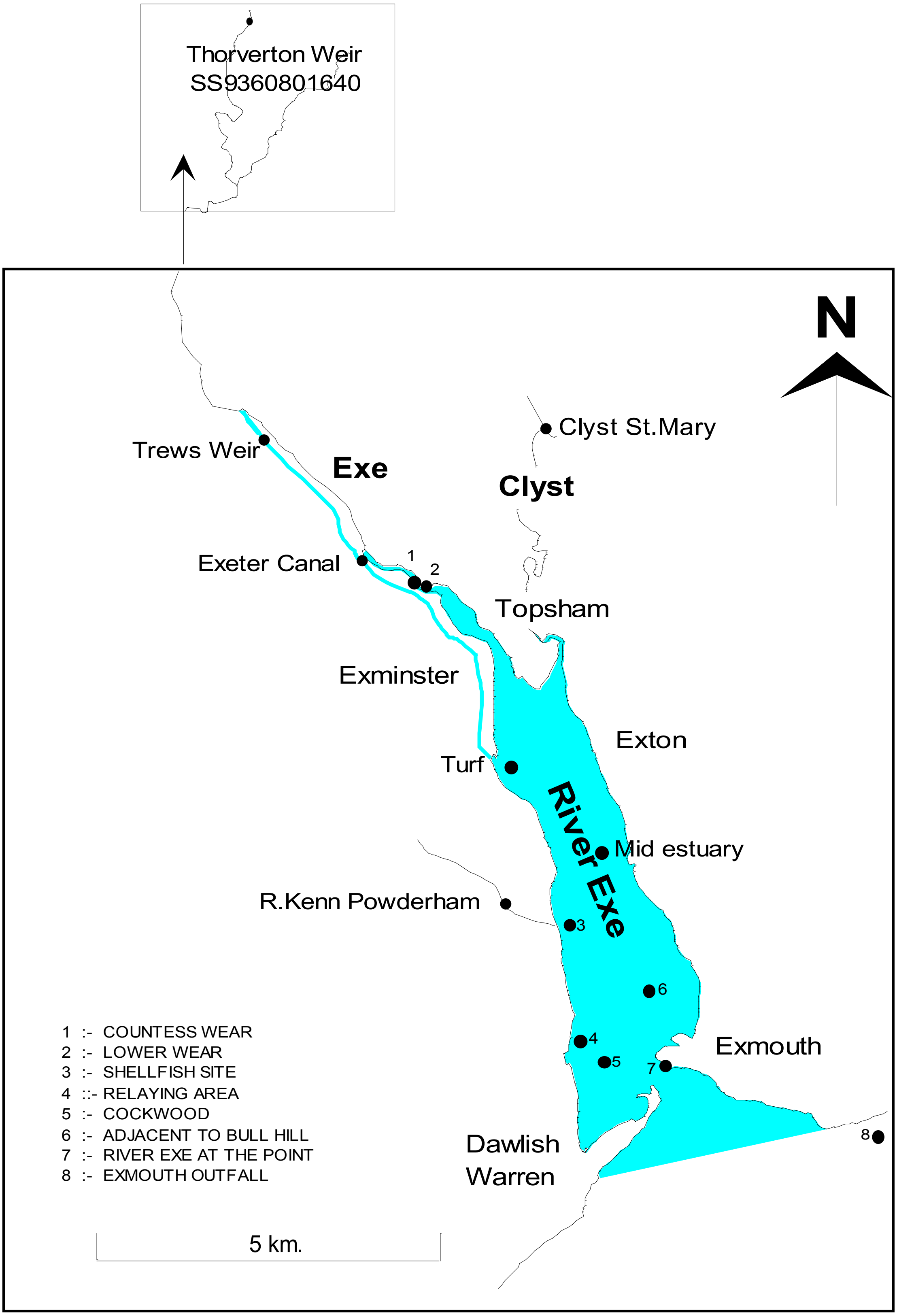


Figure 1: The Exe Estuary SPA showing boundaries of the marine site and EA sampling sites in tidal waters

Commercial boating activity on the Estuary itself is limited to a number of boat building companies and the operation of passenger services. Dock facilities at Exeter and Topsham have not been used commercially for several decades, although Exmouth Dock was still in commercial use until 1989 and handled 100000 to 125000 tonnes of shipping annually in the 1970s (Devon County Council, 1975).

The area is used intensively for recreation, including most water sports, chiefly between April and September. There are over 1600 moorings based at Topsham, Lympstone, Cockwood, Exmouth and Starcross, but the highest concentrations of boats are near the main deep-water river channel at Cockwood, in the lower estuary. Potential threats associated with leisure usage to SPA features include disturbance, waste (sewage and domestic) and the effects of antifouling compounds.

Near Exton, there is some limited military use of the estuary including a small arms range at Straight Point.

Bathing Beaches

Of the five designated beaches in the Exe Estuary region, four were classified as excellent in 2001 (Dawlish Warren, Dawlish - Coryton Cove, Exmouth and Sandy Bay) and one as good (Dawlish Town). All passed the mandatory standard (for total and faecal coliforms and three physico-chemical parameters) (see annex 4), and with the exception of Dawlish Town, additionally achieved the more stringent guideline standard (for total and faecal coliforms and faecal streptococci), necessary for a Blue Flag (DEFRA website).

Fisheries

Shellfish farming is the largest single commercial fishery on the Exe. Under the Shellfish Harvesting classifications for 2002, all western beds in the estuary were designated as class B bivalve production areas for Pacific oysters and mussels. Sandy Bay, just outside the estuary mouth was classified as a provisional class B for *Spisula solida*, the thick trough shell.

Mussel beds in the Exe, particularly on Bull Hill (figure 1), traditionally provided a source of raw material for the stocking of beds in the neighbouring Teign Estuary. However, the growing exploitation of an apparently free resource during times of economic recession has led directly to the Devon Sea Fisheries Committee, the body which regulates all shell and sea fisheries on the Estuary, placing an emergency prohibition order on the Bull Hill shellfish beds (Exe Estuary Project, 1998).

Fixed netting is banned in the estuary. The river Exe and upper areas of the estuary provide an important salmon fishery both by rod, and, on a restricted scale, by commercial draft nets. Netting for migratory species of salmonid fish and eels is conducted on a seasonal basis and controlled by the Environment Agency. Outside the salmon season, there is also a small fishery, drift netting for marine species such as bass, mullet, herring and mackerel. The whole Estuary has been designated a Bass Nursery Area indicating its national importance for this species

Several areas of the intertidal mudflats are used by bait diggers, and sheltering tiles and pipes are used to catch peeler crabs. The latter practice has increased over recent years, and there are indications that this has led to a decrease in both the number and size of crabs.

Disturbances through bait digging and fishing are potentially damaging to feeding birds, however there is little quantitative information on these threats.

Pollution

There were concerns during the early 1970s about the condition of the tidal Exe when, primarily due to sewage discharges, it was classed as 'a river of poor quality requiring improvement as a matter of urgency'. The situation is reported to have significantly improved with the commissioning of the STW at Countess Wear (McCandlish, 1980). However, recent investigations indicate that the estuary may be, or is at risk of, suffering from eutrophication once again (EA, 2001b).

Diffuse sources: Diffuse pollution, particularly from agricultural land run-off, is seen as an important issue in the South West Area. Intensive agricultural practices are susceptible to soil erosion. Resultant run-off from eroded land can lead to water quality problems (siltation, eutrophication, pesticide residues and River Quality Objectives compliance issues). Increased run-off may also reduce infiltration to ground, compounding low flow problems. Farm animal waste is a significant potential source of pollution to rivers feeding the Exe Estuary SPA and although there have been significant improvements in farming practice, and an overall improvement in water quality over the last decade, there is a need for further improvement (EA, 2001a). The area around Dawlish has recently been designated as a Nitrate Vulnerable Zone (NVZ) to help address the problem of diffuse source pollution.

Point sources: Siting of some of the more important (by volume) discharge consents to the site are shown in figure 2. Consented sewage discharges (which may contain some trade wastes) are moderate, amounting to roughly 107754 m^3d^{-1} (DWF) for the SPA as a whole (not including inputs upstream of the tidal limits).

One of the most significant and sensitive discharges arises from the STW at Countess Weir (40486 m^3d^{-1} dry weather flow). Other water company STWs are Exton (North and South), Kenton & Starcross, Exmouth, and Dawlish. Sewage from Lympstone and the new Ebdon works are pumped to Exmouth and Countess Wear, respectively. Countess Wear and Kenton & Starcross are the principal STWs discharging directly to the marine site.

There are no major industrial activities which discharge aqueous effluents into the estuary directly. Discharges from the trading/industrial estates of Marsh Barton and Sowton are directed through Countess Wear STW.

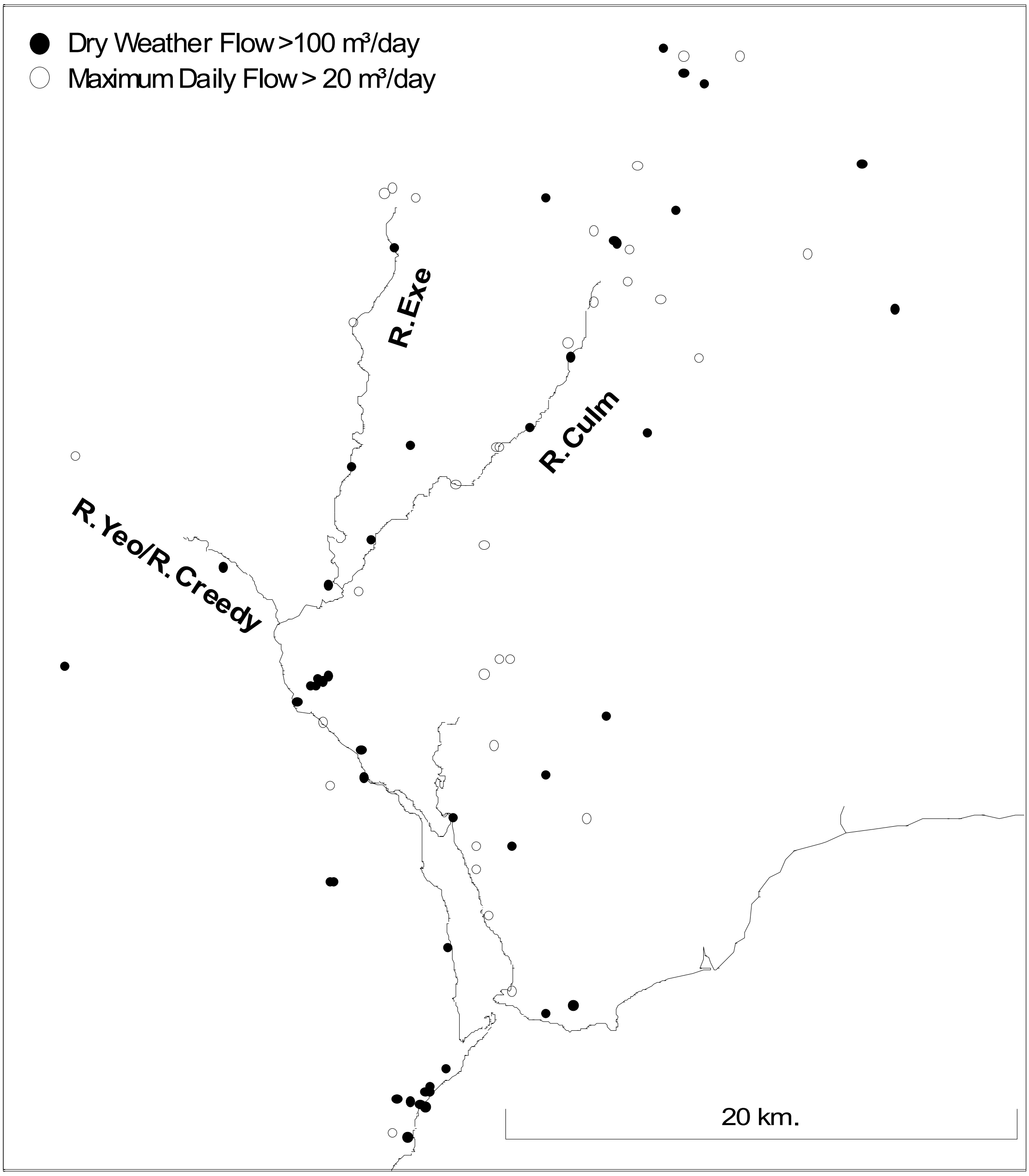


Figure 2. Locations of some of the larger discharge consents to the Exe Estuary Catchment. Consents for the discharge of sewage are based on Dry Weather Flow (values > 100 m^3/d shown). Trade consents, and miscellaneous sources of effluents are expressed as Maximum Daily Flows (values >20 m^3/d shown). (From data supplied by the Environment Agency, South West Region).
NB No distinction has been made between continuous and intermittent discharges. Details of specific discharges should be clarified with the Environment Agency

Surveys by W.S. Atkins in 1987 demonstrated that the BOD of water in the Exe Estuary increased upstream from the mouth towards the Countess Wear STW discharge, and then fell somewhat, further upstream. Failure of the STW during the survey period may have exaggerated this trend, however (Atkins, 1988). Nutrients (phosphate, nitrate, nitrite and ammonia) also increased towards Countess Wear but, unlike BOD, continued to increase upstream, demonstrating that river water was a further significant source. Nevertheless, the relatively high concentrations of ammonia observed throughout the Exe Estuary were a clear marker of sewage input. Above Topsham these levels were regarded as toxic and would prevent passage of migratory fish (Atkins, 1988). Elevated levels of primary productivity were also observed in the upper estuary, indicative of eutrophication. Associated high levels of photosynthetically produced DO were evident in daylight hours, though the situation over-night was not monitored at that time.

The Exe Estuary has been nominated as a candidate for Sensitive Waters (eutrophic) although no designation has been made. Recent Agency investigations show that the marine site is at risk of eutrophication and describe the estuary as 'eutrophic now'. This does not correspond with the rejection of the estuary as a Sensitive Area (Eutrophic), which appears to due to the rapid flushing rate and lack of evidence.

Sewage outfalls have had important influences on numbers of total and faecal coliforms in the upper estuary which, in the past, may have reflected local inputs at Topsham, Exton and Lympstone, as well as the main input at Countess Wear (Atkins, 1988). Bacterial counts dropped significantly in mid estuary during rising neap tides, though inputs from coastal outfalls (e.g. Exmouth, Dawlish, Maer Rock) have tended to contribute to contamination during springs (enforcing the requirement to cleanse shellfish before consumption). Installation of the long outfall at Exmouth in the mid 1990s, and other measures, have presumably helped to reduce this problem, as indicated by recent the bathing water classifications, described above. Prior to this, failure to meet bacterial guidelines were frequent, particularly at beaches to the east of Exmouth. Improvements to treatment of wastes under the Urban Waste Water Treatment (UWWT), Shellfish and Bathing Water Directives are an on-going process.

Water company improvements include, or will include, addition of UV disinfection to the secondary treatment at Exmouth, Dawlish, Kenton and Starcross and Countess Wear, and secondary treatment at Exton North and Exton South STW's by 2005. At present Exton (N) discharges crude sewage and discharge from Exton (S) is subject to primary treatment. Approximately 35 intermittent discharges in the Exe catchment are due to be improved by 2005 (see annex 7).

There are several abstraction points, mainly on the upper Exe, to take water for domestic, agricultural and industrial (fish farming, textile manufacture) purposes, much of the abstracted water is treated and returned to the river after use. SWW also temporarily (April 2001-end 2002) abstract water at Exebridge to supplement the flow of the Taw in north Devon. The abstraction of water can have an unacceptable environmental impact on wildlife and amenity by reducing river flows and may compound eutrophication problems during periods of low flow.

5. STUDIES ON BIOLOGICAL COMMUNITIES

'The Fauna of the Exe Estuary' (Allen and Todd, 1902) provides an early description of the macrofauna at different locations of the estuary, and includes habitat details for sites visited. Later, the proceedings of a symposium on the Exe published in 1980 (Boalch, 1980), included essays on many aspects of the estuary (its physical characteristics, vegetation, Foraminifera, intertidal fauna of Bull Hill, and the ecology of mussels and oystercatchers).

More recently, Dixon (1986) provided useful background information on the SPA, including a full list of habitats, communities and a comprehensive site-by-site species guide to the estuary. Further information on studies relating to key organisms, or groups of organisms are reviewed below.

Saltmarsh

There are three main areas of saltmarsh within the estuary. The largest of these lies in the shelter of the western spit at Dawlish Warren, and there is a further smaller patch behind the point at Exmouth. A second area stretches up the west shore from Turf locks to Lower Wear in the upper estuary (Exminster Marshes), and on the eastern shore, salt marsh extends from Exton to the River Clyst. Parkinson (1980) detailed the loss of large areas of the estuary's saltmarsh habitat due to land reclamation, industry and embankment building over several centuries, and estimated that of the original 2110 acres, only 2.4% remained in 1980, of which more than half was *Spartina* monoculture.

Spartina anglica is a hybrid resulting from a crossing of *S. alterniflora*, an introduced American species, with the native small cord-grass *S. maritima*. *S. anglica* is now the most widespread *Spartina* species in the UK (Davidson *et al.,* 1991) and owes its success in this country to a suite of biological properties related to its hybrid origin, and notably, its occupancy of a formerly vacant niche on intertidal mudflats to seaward of the previous limit of perennial vegetation (Gray, 1986).

Proctor (1980) gave a comprehensive account of the Exe estuary saltmarsh. Briefly: *S. anglica* was deliberately introduced into the estuary in 1935, when 1000 setts from Poole Harbour were planted in the Dawlish Warren saltmarsh. A second transplantation was made in the 1950's by British Railways, presumably to stabilise the spit and protect the embankment in the estuary. Subsequently, *S. anglica* became the most common plant in the estuary and now dominates the low/mid-shore of saltmarsh areas. Just above the high water mark of spring tides, there is a belt of the sea couch grass *Agropyron pungens* interspersed with *Atriplex riuscula,* and here and there low sandy ridges stretch out into the saltmarsh. These are dominated by sea purslane *Halimione portulacoides*, and a number of associated saltmarsh species characteristic of British saltmarsh environments (including grass *Puccinellia maritima,*sea lavender *Limonium vulgare,* sea plantain *Plantago maritima,* spurrey *Spergularia media* and sea arrowgrass *Triglochin maritima*). Succulents *Salicornia* spp and *Suadeda maritima* occur in localised patches on sandflats near Warren Point and mudflats of the upper estuary.

Vigorous reedbeds of *Phragmites communis* and *P. australis* also occur in the upper estuarine saltmarsh where salinity is reduced, particularly on the western shore.

For the Exe Estuary, there are no records to indicate the extensive sediment accumulation, or release, that the 'spectacular' spread, and subsequent 'dieback' of *Spartina* has given rise to in other UK estuaries, e.g. Poole Harbour (Raybould, 2000). However, Proctor (1980) noted that although *Spartina* was still spreading vigorously in the upper estuary, some areas behind Dawlish Warren were showing signs of decline and stunted growth similar to that observed in Southampton Water and Poole. Unfortunately no recent accounts of the saltmarsh areas of the Exe are available to establish whether this decline, which has implications for the ecology of the estuary (Raybould, 2000), has continued.

Zostera

Eelgrass beds occur in estuaries, on the open coast and in saline lagoons. There are three species of *Zostera* in the UK, all of which are considered nationally scarce. All three occur in the Exe. The rhizomes of the plants stabilise the substratum, and the leaves are an important source of organic matter and a rich source of food, particularly for wildfowl (wigeon, Brent goose). Eelgrass beds also provide shelter and surface attachment for many species, such as fish (flatfish, cuttlefish, squid) and molluscs (*Rissoa membranacea, Akera bullata*) as well as algae, diatoms, anemones and stalked jellyfish (*Haliclystus auricula*).

There are two main areas of *Zostera* in the Exe Estuary. At Dawlish Warren a large, roughly triangular bed lies in the lee of the western spit, and on the eastern side a more extensive area stretches between Exmouth and Lympstone (figure 3). The eastern bed appears to be patchier in the Exmouth area. The beds consist principally of the narrow-leaved eelgrass *Z. angustifolia* (Proctor, 1980) which generally occupies a mid to low shore position, and the dwarf eelgrass *Z. noltii*, predominantly found highest on the shore and often adjacent to lower saltmarsh communities, is also recorded in the estuary near Exmouth (Dixon, 1986).

Zostera is reported to have once been more widespread in the Exe Estuary, particularly on the eastern side of the estuary. Allen and Todd (1902) noted an extensive *Zostera* bed on Greenland Bank, off the village of Exton. Later, Lympstone was given as the northernmost extent of this *Zostera* bed (Gilham, 1957), and in 1980, Proctor reported that the eastern beds of *Z. angustifolia* extended from the point at Exmouth to 0.5mile south of Lympstone (Proctor, 1980). Dixon (1986) recorded a similar distribution and commented on the loss at the northern edge of the bed. The current distribution, shown in figure 3, indicates the patchiness of the *Zostera* bed around Exmouth which had not been previously noted, and may be a further sign that *Zostera* is declining in the estuary.

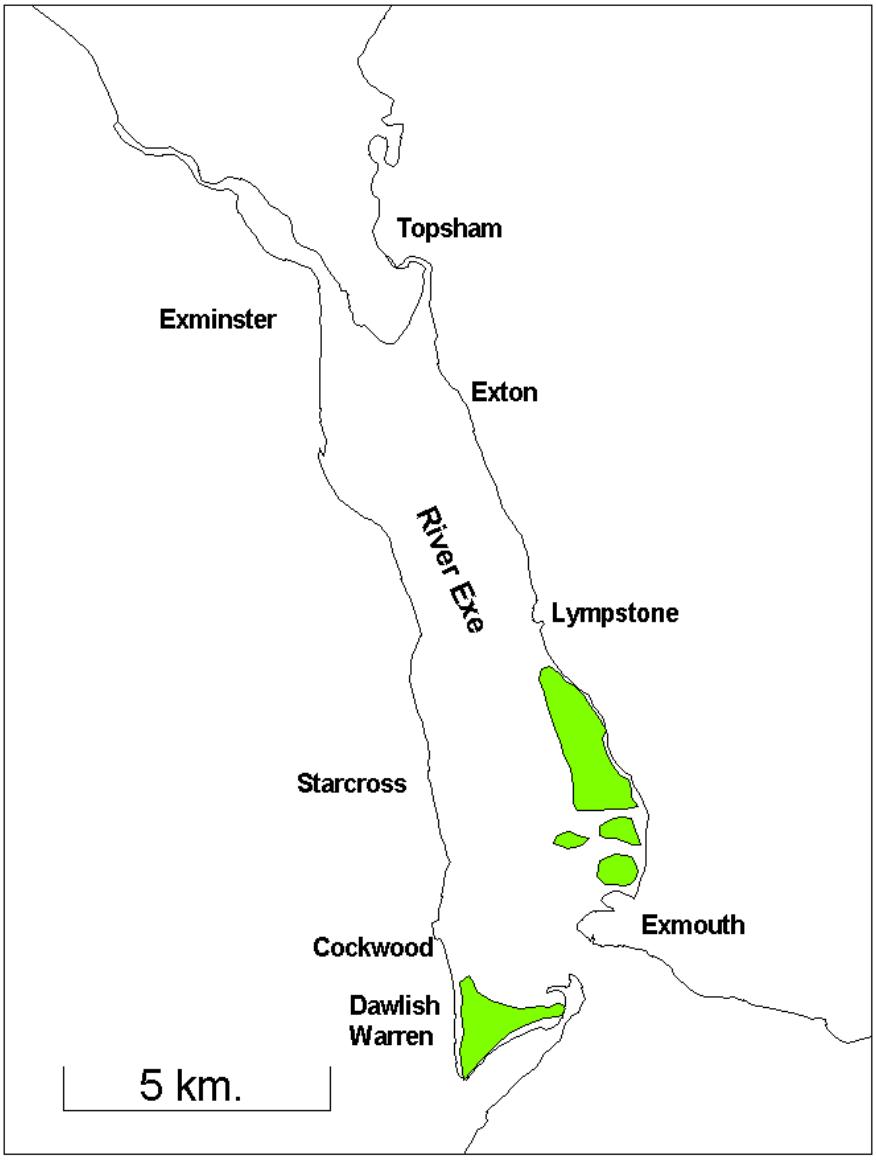


Figure 3. Seagrass (*Zostera*) beds in the Exe estuary. From EN, 2001a.

Since the sparse evidence suggests that seagrass beds in the estuary are declining, an ongoing programme to survey, map and monitor the extent of these important features would seem prudent. A reduction in the biomass is an early indication of stress in seagrass beds and it is important to identify possible stressors in the vicinity of seagrass beds. Its decline nationally may have serious consequences for the rich and diverse fauna, often associated with beds of *Zostera* and fine algae, and for the waders and wildfowl which feed amongst the beds. This is particularly relevant in SPAs and SACs, where rare and nationally important species occur. Davison and Hughes (1998) have produced a comprehensive overview of dynamics and sensitivity characteristics of *Zostera* in UK SACs, and although it is difficult to speculate on the exact cause of the decline, table 2 summarises natural events and human activities which may be contributing factors.

Table 2. Natural events and human activities which may be contributing factors to the decline of *Zostera spp.* (adapted from Davison and Hughes (1998)

Natural events -*Zostera* beds are spatially dynamic, and subject to a number of naturally-occurring factors which can cause changes in coverage at a range of scales.
• Extreme weather conditions such as violent storms or heavy floods can denude eelgrass beds over wide areas. Plants can also be killed or damaged by severe frosts. • Wasting disease is the most important factor observed to cause long-lasting declines in the number and extent of *Zostera* beds. The most severe outbreak of this disease took place in the early 1930s, and recovery from this is still incomplete. The disease-causing agent is the fungus *Labyrinthula macrocystis*. This is probably continually present at low levels, but undergoes occasional epidemic outbreaks for reasons which are not fully understood. *Labyrinthula* does not appear to cause disease if salinity is low, so that the intertidal/estuarine *Zostera* species (*Z. angustifolia* and Z. *noltii*) are much less susceptible than *Z. marina*, which prefers subtidal marine conditions. • Wildfowl grazing can remove a high proportion of the available *Zostera* biomass (over 90% in some cases), but beds can normally withstand this grazing pressure unless under stress from some other factor. • Declines in populations of epiphyte grazers can indirectly affect the health of *Zostera* beds by allowing increased growth of fouling algae. Nutrient enrichment or other forms of anthropogenic pollution are the factors most likely to bring about such changes.

Human activities - A large proportion of the UK's population lives on or adjacent to the coast. As a result, pollution, development and recreation pressures are increasingly affecting the coastal environment, and their impacts can be especially acute in the shallow bays, estuaries and lagoons where *Zostera* biotopes most commonly occur.
• Coastal development can have adverse effects on *Zostera* beds by causing increased sediment erosion or accretion (depending on the nature of development), and by causing increases in water turbidity. • There is little evidence of harm caused by heavy metals or antifoulants, but runoff of terrestrial herbicides has been shown to affect growth and survival of *Zostera* plants. • Eelgrass beds are not highly sensitive to chronic oil pollution (eg. refinery effluent). However, when exposed to major oil spillages, the associated fauna appear to be more susceptible to damage than the *Zostera* itself. The chemical dispersants used to control oil spills are more harmful to *Zostera* than the oil alone, and should not be used in these biotopes. • Excessive nutrient enrichment can cause damage to eelgrass beds by a variety of mechanisms, the most important of which are metabolic imbalance, proliferation of phytoplankton, epiphytic or blanketing algae, and increased susceptibility to wasting disease. • Eelgrass beds are not physically robust biotopes, and can be degraded by trampling, mechanical bivalve harvesting, dredging and other forms of disturbance. • Two non-indigenous plants, the cord-grass *Spartina anglica* and the brown alga *Sargassum muticum* have colonized eelgrass beds in the UK, mainly in the south of England. To date, there is no firm evidence of either species competing significantly with *Zostera* or displacing it in the absence of other adverse environmental factors. • Disturbance by wildfowlers may cause local increases in numbers of ducks and geese on *Zostera* beds, and hence higher grazing pressure on the eelgrass. • Human-induced climate change may have significant long-term effects on the distribution and extent of *Zostera* beds. Possible significant effects include higher temperatures and increased frequency and severity of storms.

Although *Zostera* species are fast-growing and relatively short-lived, they can take a considerable time to recover from damaging impacts - if recovery is possible at all. Holt *et al.,* (1997) estimated that *Zostera* species recoverability is within the range of five to ten years but, in many cases, recovery may take longer. This is borne out by the slow or apparent lack of recovery from the 1920s to mid-1930s wasting disease epidemic. Table 3 summarises the key factors which may limit or facilitate seagrass bed recovery in marine SACs and elsewhere.

Table 3. Summary of major factors believed to influence the capacity of *Zostera* beds to recover after disturbance or destruction (from Davison and Hughes 1998).

Factors that may limit bed recovery	Factors that may facilitate bed recovery
Removal of habitat	Artificial transplantation
Unstable substrata	Stable substrata
Fragmenting and destabilized *Zostera* beds, caused by factors such as changes to coastal processes, physical damage or stochastic weather events	Stable *Zostera* beds
Reduced rhizome growth, seed production, germling success and seedling development into patches	Increased rhizome growth, seed production, germling success and seedling development into patches
Reduced light penetration, caused by increased turbidity, eutrophication, some forms of pollution, or epiphyte smothering	Improvements in light penetration, caused by reductions in turbidity, eutrophication, pollution, epiphyte and algal smothering
Nutrient enrichment	Reductions of, or limited increases to, nutrient inputs
Declines in epiphyte grazer populations Unusual increases in wildfowl grazing pressure	Healthy and stable epiphyte grazer populations Wildfowl grazing activities may prevent excessive sediment build up in *Zostera* beds
Competition with non-native species, *Spartina* sp. and *Sargassum muticum*	Absence of non-native species, *Spartina* sp. and *Sargassum muticum*
Environmental stress, (e.g. extreme temperatures or pollutants), which may increase the susceptibility to wasting disease infection	Absence of environmental stresses and low populations of *L. macrocystis*, the causative fungal pathogen for wasting disease

Macroalgae

Dixon, (1986) reported on algal communities in the marine site and noted that within the estuary, suitable substrata for algal colonisation is scarce. In the mouth of the estuary, at Maer Rocks and Orcombe Point, *Laminaria digitata* and *L. saccharina* was recorded although the algal community was dominated by *Enteromorpha spp., Rhodochorton floridulum* and *Audouiella sp.* The invasive species *Sargassum muticum* was also recorded from rock pools on Maer Rocks.

Since it was first discovered on the Isle of Wight in 1973, *S. muticum* has spread along the south coast to the Isles of Scilly and along the north Cornish coast to Lundy. The northern range of *Sargassum* in the UK appears to be extending as populations have also become established in Strangford Lough in Northern Ireland. It is now common on the South coast of England, dominating low shores with a broken stone or boulder substratum.

Perhaps the most relevant threat of *Sargassum* in the Exe Estuary is due to its rapid growth and reproductive capacity, which enables competition with native estuarine species such as *Zostera*. As a fouling organism, *S. muticum* may also have economic impacts: it is reported to interfere with recreational use of waterways, particularly when it becomes detached from holdfasts and floats off forming large masses (Dyrynda, 1987: Farnham *et al.,* 1981). It can block propellers and intakes of boats and is a nuisance to commercial fisheries: *Sargassum* can proliferate on shellfish beds obstructing dredges and can even attach to live oysters and 'steal' them by floatation and tidal transport. The long fronds can also foul fishing nets (Critchley *et al.,*1983, 1986).

Further into the estuary, *Enteromorpha* and *Ulva* species were the most widespread attached algae, together with the fucoids *Fucus vesiculosus* and *F.spiralis* which predominated in the outer estuary but were replaced north of Powderham by the brackish water species *F. ceranoides*. Rhodophycaeae were represented by *Gracilaria verrucosa, Cryptopleura ramosa, Chondrus crispus, Porphyra* spp. *Ceramium* spp. and *Polysiphonia* spp.

Overall, Dixon (1986) observed a lower diversity of algal species than previously reported (Gilham, 1957: Proctor, 1980). Notable changes were the absence of *Pelvetia canaliculata* and *Ascophyllum nodosum*, both of which had previously been reported as far north in the estuary as Lympstone. Several species, *Palmaria palmata, Hypoglossum woodwardii, Catenella caespitosa* and *Audouinalla* spp, which had been reported by Gilham (1957) as far north as Exton were recorded only on the open rocky coast.

In a study of the invertebrate community structure of Bull Hill, Harris (1980) noted extensive beds of *Enteromorpha linza* which formed blanket-like cover of the sand in much of the area. This could have serious implications for *Zostera* in the Estuary as elsewhere, green algal blooms are implicated in its decline: a thick blanket of *Enteromorpha* is considered to have eradicated *Zostera* in Langstone Harbour further along the south coast (den Hartog,1994).

Macrofauna

Warwick *et al.,* (1989) conducted a comprehensive infaunal survey in the Exe Estuary, sampling nine sites between Topsham and the estuary mouth as part of a comparative study of the intertidal benthic invertebrate communities of 7 southwest estuaries. Findings are principally discussed in the context of relevance to the Severn, although the report includes full species lists for the Exe and other estuaries, and diversity indices (discussed in section 9). Looking at environmental variables, the authors note that abundance and biomass of the ragworm *Nereis diversicolor* is closely related to grain size in the Exe, and that for a given sediment organic (carbon) content, densities of *Nereis* are higher in the Exe than the Severn (probably reflecting major differences in tidal regime, turbidity, and the greater sediment stability of the

Exe). An inverse linear relationship was found between the abundance of cockles and the nitrogen content of Exe sediments, though it is not known if this is a cause-effect relationship or a co-incidental trend (see section 9.1). The burrowing amphipod crustacean *Corophium volutator* was significantly heavier (for a given length) from the Exe Estuary than those sampled in other southwest estuaries although no potential explanations for this phenomenon are given.

Harris (1980) described the invertebrate community structure of five areas on, and near Bull Hill. Each area provided a distinctive substratum and was reported to support a clearly defined faunistic association. A large component of the estuarine sand fauna was made up of worms and worm-like animals including *Arenicola marina, Nerine cirratulus, Scoloplos armiger, Capitella capitata, Lanice conchilega, Cirraforma tentaculata* and *Glycera alba*.

Harris (1980) also recorded *Ophelia bicornis* in both sandy, and well-scoured areas of Bull Hill and reported that its distribution throughout the estuary was patchy. Speculating on reasons for its limited occurrence, Harris discussed several reports on the subject and concluded that no single factor could be identified, rather a combination including sediment characteristics and food availability (meiobenthos), which in turn may be linked to oxygen tension in the interstices.

Hydrobia ulvae and *Littorina littorea* were the dominant grazers on fine mud and sand where grazing activities were thought to be linked to populations of diatoms. Bivalves *Scrobicularia plana* and *Spisula solida* were found in the deeper layers of fine mud and sand, together with *Corophium volutator* which can tolerate almost anaerobic conditions (Gamble, 1970). Extensive colonies of the hydroid cnidarian *Dynamena argentea* were found attached to stones and shells in the mussel beds, and numbers of polychaete *Eunereis longissimia* also occurred in the muddy gravel and amongst the clusters of mussels. Both of these areas also contained large populations of the scavenging shore crab *Carcinus maenus. Pomatoceros triqueter* was abundant on stony ground on the margins of the mussel beds. The most numerous of estuarine macrofauna were filter feeders *Cerastoderma edule* and *Mytilus edulis,* although the slipper limpet *Crepidula fornicata* was also recorded in large numbers amongst the mussel beds.

The gastropod mollusc *Crepidula fornicata* is known to have been introduced to the UK between 1887 and 1890 from North America, in association with the American oyster *Crassostrea gigas* (Crouch, 1894, 1895; Fretter and Graham, 1981) and spread fairly rapidly (Franklin and Pickett, 1974). Its success in this country is probably due to a lack of predators and the unusual method of reproduction (which relies upon individuals settling upon each other to form breeding ‘stacks’ as they develop from males to females). A pelagic larval stage aids the spread of the species, once introduced. Reports suggest that high densities of *C. fornicata* can modify the nature and texture of sediments in some bays (Ehrhold *et al.,* 1998) and where *Crepidula* stacks are abundant, few other bivalves or other filter-feeding invertebrates can live amongst them. This is due to spatial competition, trophic competition and alteration of the substratum.

However, reports of subsequent surveys (Warwick *et al* , 1989: Baker, 1993) do not indicate that *Crepidula* has become a problem in the estuary, although with the trend of rising temperatures this species could become more widespread; Minchin *et al.,* (1995) indicate that temperatures may be an important limiting factor in its ability to develop extensive populations.

The early work of Allen and Todd (1902) enable comparisons with subsequent surveys to be made and therefore determine the extent of any changes in faunal composition. Dixon (1986) considered that the intertidal sediments and fauna appeared to have remained relatively unchanged over the eighty year period. There was a similar graduation down the estuary from sheltered *Nereis/Scrobicularia* dominated mud, through mixed sediments with populations of *Arenicola*, *Pygospio elegans, Scolopos armiger* and *Cerastoderma* to clean tidally swept sand with communities of *Nephtys cirrosa, Bathyporeia sarsi* and *Ophelia bicornis*.

In addition to the reduction of *Zostera* and algal diversity (see above), Dixon (1986) also noted the following changes to infaunal species in the Exe Estuary:

- The disappearance of carpet shell *Venerupis decussatus* which had previously been 'moderately common'.
- The ampharetid polychaete *Melinna palmata,* previously recorded in muddy sediments, was no longer present.
- A few specimens of polychaete *Ampharete grubei* and the tentacled lagoon worm *Alkmaria romijni* were found in 1985 although neither species had been previously recorded.
- High numbers of the isopod *Cyathura carinata* were found at muddy sites north of Powderham but had not been previously recorded.

In the mouth of the estuary at Maer Rock and Orcombe Point, there was also some evidence of species change:

- The reef-building polychaete *Sabellaria alveolata,* which was once common, had disappeared.
- Bivalves *Barnea parva* and *Pholas dactylus* had been common at this site in 1901 but no evidence, holes or valves, was found in 1985.
- Dog whelk *Nucella lapillus,* once 'very common' had disappeared.
- The sea squirts *Clavelina lepadiformis* and *Morchellium argus* were present when Allen and Todd (1902) had specifically noted their absence at this site.

Dixon (1986) considered that in some cases, the observed discrepancies could reflect sampling differences. However, suggested causes regarding the disappearance of *N. lapillus,* which had been noted elsewhere in southwest England, included organotin compounds and dinoflagellate blooms. For *Sabellaria,* Dixon (1986) commented that population fluctuations had been known to occur at the site for a number of years, but the cold winter of 1962/3 and possibly trampling pressure may have contributed to its disappearance. Neither *N. lapillus* or *S. alveolata* have been recorded in subsequent surveys (Hooper, 1988: Baker, 1993).

Non-native species recorded by Dixon (1986) in the Exe Estuary included *C. fornicata*, barnacle *Elminius modestus, S. muticum* (see above) and the Manila clam *Tapes philippinarium (=Venerupis semidecussata). T. philippinarium* was restricted to a mesh enclosure behind Dawlish Warren.

Concerns about a possible threat to the natural ecology of British coastal waters posed by the introduction and aquaculture of non-native *T. philippinarium*, led to a long-term experiment in the Exe. This was set up to monitor environmental changes associated with harvesting cultivated Manila clams and the effects and changes to the infauna and sediment composition during the early and later ongrowing phases of cultivation (Spencer *et al.,* 1998; MAFF, 1996). At the time the experiment began (November, 1991) it was said that the Exe estuary was not used for cultivation of Manila clams (though *T. philippinarium (=Venerupis semidecussata)* had been collected from within a mesh enclosure according to Dixon in 1986). The MAFF study began with the intertidal seeding of the clams in the lee of Dawlish Warren and continued through ongrowing and finally harvesting, a period of about $2^{1}/_{2}$ years.

Results showed that intertidal plots covered with netting encouraged a proliferation of deposit-feeding worms (*Ampharete, Nephtys, Pygospio* and cirratulid spp) irrespective of the presence of clams. The increase of these species persisted throughout the cultivation cycle. There was a small increase in the organic content of the sediment and in one component of sediment particle size (the proportion of silt). These changes may have been partly influenced by the presence of the green alga *Enteromorpha* which grew on the netting from May to October (necessitating periodic clearing) and the associated feeding activity of periwinkles.

The immediate effects of harvesting by hand-raking caused a reduction in invertebrate species (and numbers) of 50% compared to control plots. Where suction dredge harvesting was used, reduction was >90% (MAFF, 1996). The animal community recovered slowly at first but complete infaunal recolonisation had occurred one year after harvesting (Spencer *et al.,*1998).

On a cautionary note, it is interesting that in recommending management procedures for clam farming, the authors (MAFF, 1996) recommend keeping nets in good order to prevent the escape of non-native species. Although British waters are considered too cold at present for spawning and reproduction in *T. philippinarium*, it is unlikely that nets would prove an effective barrier should such an event occur. Possible impacts are illustrated in Italy, where the Manila clam was intentionally introduced in the beginning of the 1980s and has almost completely taken the place of the native clam species along the Italian coast (Coffey, 2001).

A study of the environmental effects associated with the trestle cultivation of Pacific oysters, *Crassostrea gigas*, was also conducted in the Exe estuary, at a commercial cultivation site (Nugues *et al.*, 1996). Small, but significant, changes were detected in the macrofaunal community, sampled beneath oyster trestles, compared with that found in adjacent uncultivated areas. These changes were associated with an increase in organic and silt composition and a reduction in the depth of the oxygenated layer of the sediment beneath the trestles. Water velocity was decreased by the presence of the trestles which probably led to an increase in sedimentation rate, which was observed beneath them. Although biological and physical changes were observed, they were relatively minor compared with the extreme environmental changes associated with suspended culture techniques used for other bivalve species and fishes. However, the authors note that oyster cultivation is relatively small-scale on the Exe, and other studies suggest that the environmental effects associated with oyster cultivation become more severe in areas of large-scale (hectares) cultivation (e.g. Castel *et al.,* 1989).

Atkins (1988) recorded ten species of fish in the estuary during a 1987 survey. They were said to be typical estuarine species and characteristic of estuaries such as the Exe. Sand gobies *Pomatoschistus minutus* and juvenile plaice *Pleuronectes platessa* were common in all areas, although the absence of flounder *Platichthyes flesus* was noted. Common eel *Anguilla anguilla,* sole *Solea solea,* pipefish *Syngnathus acus,* pout *Trisopterus luscus,* dab *Limanda limanda,*, sand eel *Hyperoplus lanceolatus* and hooknose were listed. There was a reduction in species number towards the upper estuary reflecting their predominantly marine origin.

Migratory fish including salmon *Salmo salmar* also pass through the estuary. Other species recorded in the estuary are bass *Morone labrax*, (the whole estuary is designated a Bass nursery area) mullet *Mugil labrosus*, herring *Clupea harengus* and mackerel *Scomber scomber.*

Meiofauna

Early studies of littoral ecology tended to exclude the interstitial fauna, or meiofauna. Thorson, (1966) described some aspects of the meiobenthos and emphasised the vital role that it plays in the ecology of benthic communities. The meiofauna (and flora) are considered an important food source for estuarine macrofauna, particularly as much of the meiobenthos of intertidal mudflats is confined to the top 0.5mm (Barnett, 1968).

Meiofauna are sensitive to subtle changes in the nature of their environment, therefore factors such as oxygen tension are of prime importance, and may be a determining factor in the biology and distribution of meiobenthos. This in turn can have repercussions upon the faunal community in general (Harris, 1980). Their vast abundance and ubiquitous distribution render meiofauna a likely food source for a variety of macrofauna (endobenthic annelids, bivalves, crustaceans and juvenile fish). However, internal predation amongst the meiofauna may mean that they represent a non-interactive component of the food web (McIntyre, 1971).

Kennedy (1993) studied predation upon meiofauna by endobenthic macrofauna in the Exe Estuary. The importance of the meiofauna-macrofauna trophic link was investigated using four species, representing the main estuarine feeding modes (*Cerastoderma edule* - suspension feeder*; Nereis diversicolor* - omnivore/scavenger; *Ophelia bicornis* - sand-ingestor*; Scrobicularia plana* - deposit feeder). Results indicated that in the Exe, meiofauna was of little importance in the diet of these four species. However, Kennedy (1993) acknowledges the limitations of the enclosure method used and also notes that the experiments would not detect subtle predation acting at lower taxonomic levels. Previously, Gee (1987) had analysed gut-contents of a variety of epibenthic macrofauna in the Exe estuary and showed that many positively select the harpacticoid copepod *Asellopsis intermedia* as food in preference to other meiofauna.

The role of meiofauna in estuarine and marine trophic systems continues to be a subject of considerable controversy.

The meiofauna of the Exe Estuary is reported to be rich in harpacticoid copepods and nematodes, particularly in the mud and sand sediments of Bull Hill where harpacticoid copepods dominate the meiobenthos (Harris, 1980). An early account of the meiofaunal copepod community is given by Wells (1963). Warwick (1971) described nematode associations in the Exe estuary and reported a rich community. Full species lists for the different habitats are included in this report. Coarse littoral sands in the lower estuary, with a low organic content and a more or less permanently high salinity water table, were the most species-rich habitat. Coarse sands around Lympstone and Shelly Bank contained the least number of species; the interstitial salinity of these areas was very low due to seepage of coastal sub-soil water. There was a dominance of predatory species in sandy sediments and greater numbers of deposit feeders in mud, reflecting the amount and type of food present. Joint *et al.,* (1982) related the vertical distribution of nematodes and harpacticoid copepods in Cockle Sands to that of benthic algae and bacteria.

Schratzberger and Warwick (1999) conducted a series of microcosm experiments using intertidal sediments, with their natural meiofaunal communities to evaluate the responses of intertidal nematode assemblages to treatments of physical and biological disturbance and organic enrichment. Assemblages from an exposed sandy estuarine site poor in organic matter on the Exe (Cockle Sands), and from a sheltered muddy estuary rich in organic matter (the Lynher) were compared. Results generally suggested that nematode assemblages exhibited various characteristic changes when exposed to different types of disturbances. Changes depended on the type of disturbance, the initial structure of the assemblage and the morphological and physiological adaptations of the species. For both assemblages, biological disturbance caused the least severe changes in assemblage structure. Notably, for the sand nematodes of the Exe, most extreme changes were the result of organic enrichment, while mud nematodes showed the most intense response to treatments of physical disturbance. Not unexpectedly, the authors conclude that meiobenthic assemblages are most affected by the type of disturbances that they do not normally experience naturally.

Birds

Recently the British Trust for Ornithology has carried out a review of species trends in SPAs over the last 5, 10 and 25 year time periods using data collected as part of the Wetland Bird Survey (WeBS). SPAs where species have declined by > 25% over a specified time period, when the larger-scale regional or national trends indicate stable or increasing population sizes, are targeted as being of concern. Population declines of between 25% and 50% are flagged as 'Medium Alerts' and declines of greater than 50% as 'High Alerts'. Alerts are intended as advisory measures triggering further investigation. The report, produced for the Environment Agency, English Nature and the Countryside Council for Wales summarises statistics for nine Evaluated Species in the Exe SPA: Cormorant, Dark-bellied Brent Goose, Wigeon, Red-breasted Merganser, Oystercatcher, Avocet, Grey Plover, Dunlin, Black-tailed Godwit (Armitage *et al* 2002).

A ‘high alert’ was triggered for Widgeon over the 25 year period though the most recent trends (5 and 10 year) signify partial recovery. ‘Medium alerts’ were triggered for the Dark-bellied Brent Goose, Oystercatcher (5 and 10 year trends) and Avocet. The decline in the Avocet (a species of national importance) is for the last five-year period only and set against a fluctuating trend is considered to be of only limited cause for concern. Possible adverse factors reported at the site include habitat loss due to dredging, fishing and aquaculture, changes in water quality resultant from improvements to waste water discharges, and recreational disturbance (Armitage *et al.*, 2002). On balance however, the trends in bird numbers were not considered sufficiently important to trigger further investigations into the causes of population changes (‘Level 2’ assessment).

The Centre for Ecology and Hydrology (CEH) has carried out research on the Exe Estuary focussing on mathematical models of wading birds and wildfowl that spend the winter on the estuary. The models predict how many birds will survive the winter in good condition if various activities are carried out on and around the estuary, such as cycling, bait digging, dog walking. The models also predict the effect of climate change and sea level rise on the birds and can be used to evaluate the effectiveness of current and proposed measures aimed at helping the birds, such as limiting access by people to certain areas and providing new mudflats to compensate for coastal squeeze.

This work extends a model of oystercatchers feeding on the mussel beds of the Exe estuary, which was developed during the 1990s, to all the common species of wading birds (eg. godwits, plovers, dunlin) and wildfowl. The model for oystercatchers showed that neither mussel fishing or disturbance from the general public at their present levels are likely to have a harmful effect on these birds (see Models, section 8).

6. TOXIC AND NON-TOXIC CONTAMINANTS

Overview of contaminant loadings and sources

There are relatively few published statistics available as to the relative contributions from different sources into the SPA itself. Where published information exists (mainly for nutrients) this is included in the relevant sections on individual contaminants.

The Agency provides data for OSPAR on a regional basis. The returns for the region encompass the South Devon coastline between Seaton and Dartmouth and do not present loadings for the Exe separately. Figure 4 distils the information for 1999 as to the relative contributions to the seas arising from rivers and sewage. No separate figures for industrial discharges are entered[1]. Principal sources for most of the determinands considered are rivers, though there are sizeable proportions from sewage for suspended particulate matter, Zn and Cd. Notably, the most significant source of orthophosphate for this region is sewage (55% of the total load), whilst total nitrogen from sewage represents only 14% of the total load. Contributions of Hg, Pb and γHCH (lindane) from sewage appear to be negligible.

There are very few specific studies on contaminant loadings in the Exe. Interestingly, however, Walling and Webb (1985) describe some of the principal problems associated with the estimation of annual contaminant loads (particularly those associated with particulates) in a detailed study at Thorverton HMP on the Exe. By continuously monitoring suspended solid concentrations and flow rates over a 2-year period they were able to arrive at an accurate picture of particulate loadings and compare this with values derived by various methods of estimation, based on samples taken at intervals (as is the case for most monitoring programmes). Infrequent sampling can, for example, miss the rare flood-type events which account for major transport of contaminants. Similarly, intermittent sampling of discharges or use of inappropriate detection limits can compound errors when calculating loads based on the product of flow and concentration: using time-averaged data for suspended solids (e.g. the product of annual average flow and annual average concentration, collected by monthly sampling) it is possible to underestimate actual suspended solids loads by some 75%. Attempting to incorporate flow-rated values (matching concentration with measured flow) can, if repeated sufficiently (n=50) arrive at a calculated mean value close to the true mean, though individual estimates could vary from less than 10% to more than 300% of the actual load. This study highlights the caution with which load estimates in general should be viewed.

[1] The Agency website 'Whats in your backyard' lists only one IPC authorisation in the region: HOWMET LTD, (Non Ferrous Metals) Sowton Industrial Estate. Grid Ref X296250 Y92020

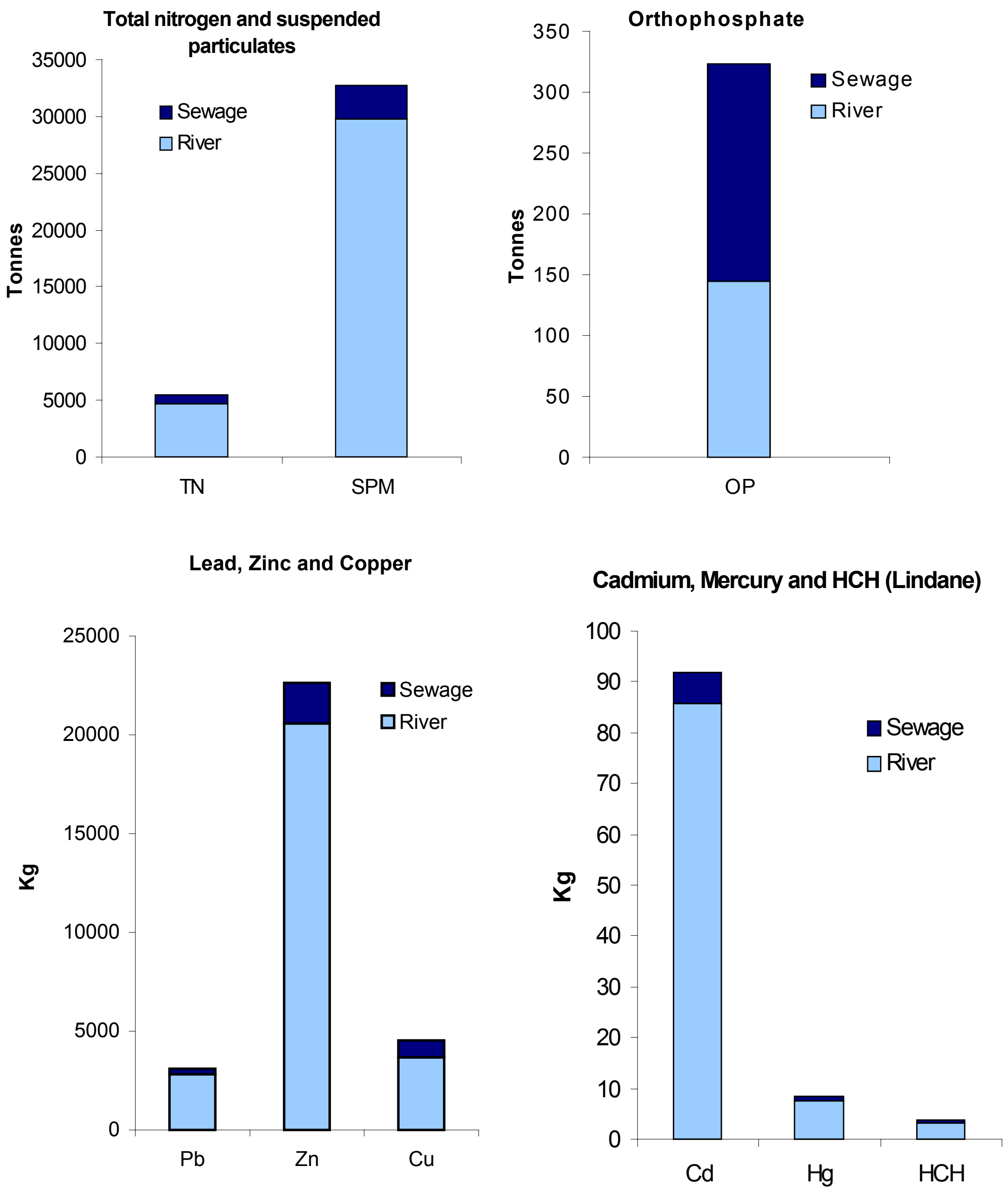


Figure 4 Relative loadings for OSPAR determinands from rivers and sewage discharging to the sea between Seaton and Dartmouth, 1999. NB Highest values have been used where there is a choice. Data source EA.

NB Principal rivers are sampled just upstream of their tidal limits to assess freshwater discharges into marine waters therefore riverine sources may also contain an indirect sewage and industrial component.

In sections 6.1 and 6.2, below, we discuss published and unpublished information for the Exe Estuary on toxic- and non-toxic contaminants, respectively. Before doing so, however, we outline briefly the rationale and limitations of the current assessment of environmental quality in the SPA.

Water quality and environmental standards

Because of the paucity of contaminant studies on the Exe Estuary the assessment of environmental quality status draws heavily on data for key determinands supplied by

EA, in the context of statutory standards and non-statutory guidelines. Summary statistics have been drawn up by the EA (based on monitoring since 1990), and the raw data analysed in an attempt to establish further evidence as to whether or not existing water quality is likely to cause impact. Where relevant, temporal trends are discussed - otherwise only the most recent data is shown.

It should be noted that much of the data from monitoring surveys is often several years old, and may be for the purpose of compliance monitoring only. Detection limits are often set with that specific intention in mind, such that the data may be of limited value for environmental behaviour studies. Nevertheless (half) detection limits have usually been included in summary statistics since it allows at least a crude assessment of water quality issues. These statistics are broken down in to:

1) **Discharges** – to gauge the importance of specific point sources (mainly STWs). Calculation of fluxes is beyond the scope of the current project, therefore only available concentration data is discussed for most contaminants (with regard to potential threat to the site).
2) **Harmonised monitoring points** (HMP) or the equivalent freshwater site immediately above the tidal limit (to characterise riverine input). Again data is not always available at each site – the majority of information relates to the River Exe, the major source of freshwater to the Exe Estuary, together with limited data for the River Kenn, Clyst and, occasionally other small tributaries (figure 1).
3) **Tidal waters** – a review of data within the Exe Estuary itself and adjacent tidal waters. Because the EA data set does not contain widespread information on contemporary values, entries recorded over the last ten years have been summarised to provide a more integrated picture of water quality issues, and to make comparisons with Environmental Quality Standards.

The majority of List I and List II (Dangerous Substances) determinands have been screened here, together with other water quality parameters such as nutrients and DO. In the absence of extensive site-specific biological effects information, comparisons of water-monitoring results with Environmental Quality Standards (EQS) are used in order to gain a first-order approximation of possible impact on biota. Thus, in the context of the current project, descriptions of 'threat' or 'risk' to the site from individual contaminants are scaled against the relevant EQS, assuming this to be an appropriate threshold for the protection of aquatic life.

For a number of reasons this is an uncertain supposition. The compliance limits for contaminants and other water quality parameters are themselves based on reviews of general toxicity data for aquatic life, coupled with a safety margin below the lowest reliable adverse effects concentration. The assumption is that below the EQS, adverse biological and ecological effects *are unlikely*. Above the EQS, effects *might be expected to occur* though this will depend on the magnitude and duration of the exposure. The application of EQS values involves uncertainties arising from limited toxicity data, differential responses between chronic and acute toxicity, inter-species variation in sensitivity, and modifying factors within each individual ecosystem (notably, the issue of synergy and additivity discussed below). Sensitivity may also vary between different levels of biological organisation; lower-order effects (molecules and cells) are likely to occur at lower levels of contamination, and in advance of, community and ecosystem-level response. Often this involves a high degree of precaution in setting standards and could give rise to an apparent mis-match between chemical data and measured biological responses, particularly at the level of biological diversity. Conversely, it is also possible that subtle effects may occur at concentrations below the EQS, giving rise to a failure to protect the system. Compliance/non-compliance patterns are therefore not necessarily synonymous with ecological implications: at present the latter can only be gauged by considering a wider array of ecosystem characteristics. EQS values are used here merely help to prioritize sites and contaminants which merit closer investigation. They do not necessarily assure Favourable Condition.

Another drawback to the EQS approach is that it considers the toxicology of contaminants individually, assuming that each is acting independently of others. In reality, some of the more significant discharges contain a range of contaminants which, though they may individually pass the 'EQS test', may pose a greater threat to nature as a result of additive toxicity. The question of synergistic/ antagonistic interactions from outfalls should be a priority for future research.

6.1 Toxic Contaminants

6.1.1 Metals

Water

Results are discussed here on a metal by metal basis, based on EA statistics for freshwater, estuarine water and outfall data, collected over the last ten years.

Arsenic

The EQS for As in fresh waters is 50µg l^{-1}. Dissolved As concentrations in the Exe at Thorverton Weir are shown in figure 5. The majority of values here are close to the detection limit of 1µg l^{-1} and can be considered as background values for As in rivers. No obvious temporal trends can be discerned from the data. Apparent higher concentrations in the River Exe in 1995 reflect higher detection limits rather than real change. A similar pattern for As is also observed lower down the Exe at Trews Weir.

Arsenic concentrations in the River Clyst at Clyst St. Mary were determined in 1994, and median, min and max values (1.35, 1 and 2.2 µg l^{-1}, respectively) confirm there is little anthropogenic influence from riverine sources to the Exe Estuary.

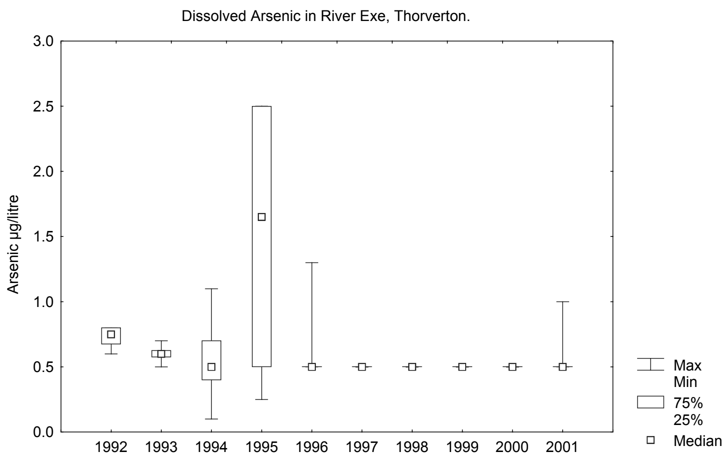


Figure 5. Concentrations of dissolved As (µg l^{-1}) in the River Exe at Thorverton Weir. Data source EA.

The pattern of dissolved As in estuarine water in the Exe estuary is plotted in figure 6. This includes sites near the Exmouth and Countess Wear STWs. Annual averages are invariably below the EQS for tidal waters (25 µg l^{-1}), by an order of magnitude. Even highest concentrations, adjacent to Bull Hill, are only marginally above background. Although there are no data for dissolved As in discharges, there is no indication that As concentrations in the marine site pose a threat for biota.

There are no obvious temporal trends for As in tidal waters.

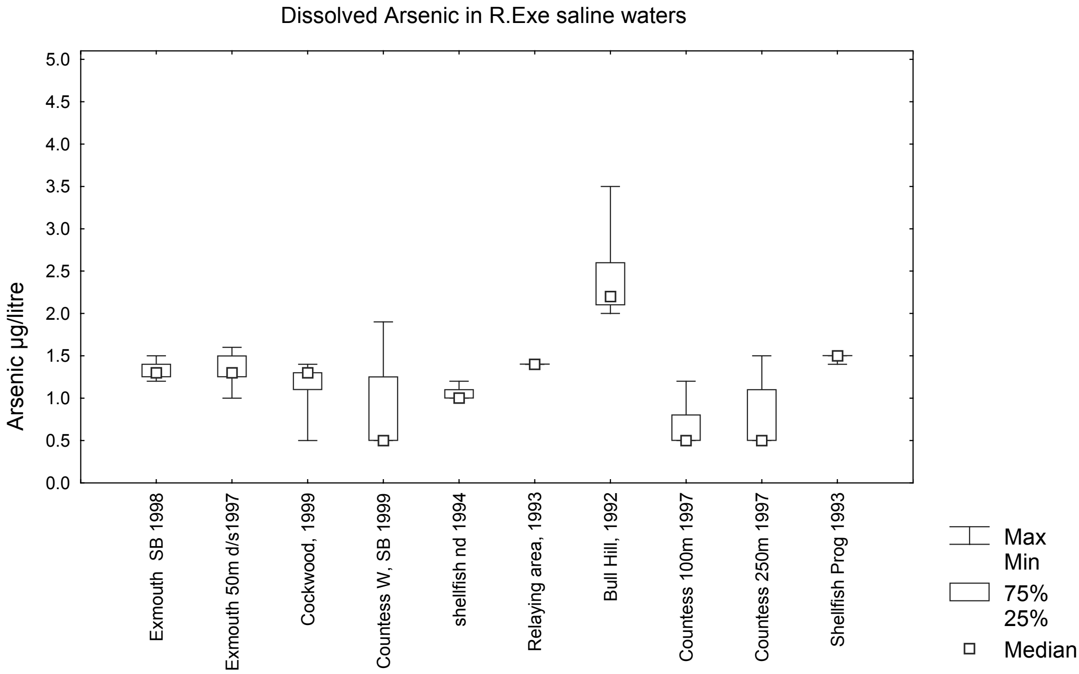


Figure 6. Concentrations of dissolved As µg l^{-1} in estuarine waters, Exe Estuary. Data source EA.

Cadmium

The EQS for Cd in fresh waters is 5µg l^{-1} and relates to 'total' rather than dissolved metal. The only available values for total Cd in freshwater are for the Exe at Thorverton (Figure 7.). Apparent concentrations appear to have decreased since 1990 though this reflects lowered detection limits (almost two-thirds of all data are below DL). Annual averages have been at 0.1µg l^{-1} or lower for almost a decade, indicating compliance with the EQS and that there are no untoward inputs upstream of Thorverton.

The majority of values for freshwater are for dissolved Cd. Comparative monitoring of the River Exe (Thorverton and Trews Weir), Exeter canal (Countess Wear), River Kenn (Powderham) and River Clyst (Clyst St Mary), in 1994, confirmed the absence of any significant Cd inputs to the Exe Estuary. Most records were close to detection limits, such that median dissolved Cd levels at all sites were 0.1 µg l^{-1}. Since then, gradual reduction in DL has reduced the apparent annual average by almost five fold at the River Exe sites. Other than the observation that detection limits have decreased during the recording period, no obvious temporal trends can be discerned from the data.

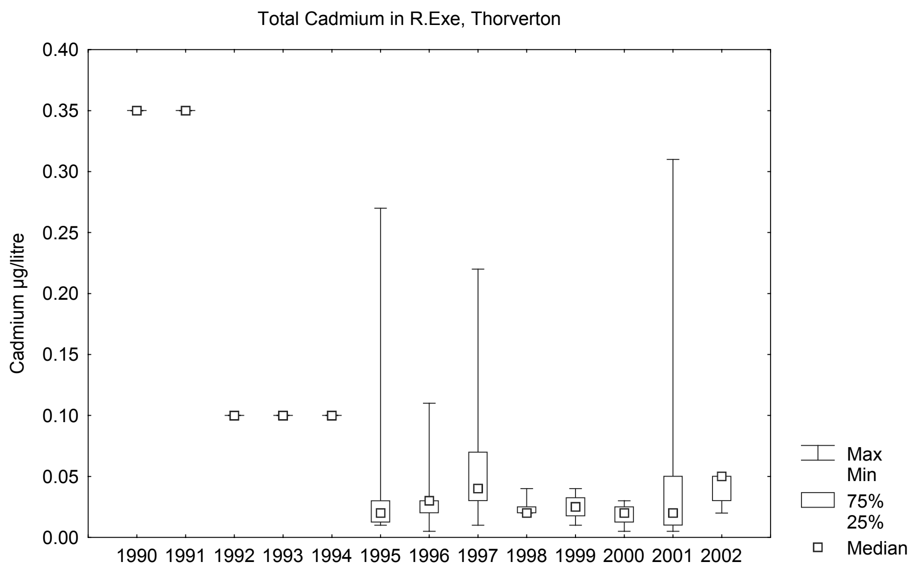


Figure 7. Concentrations of total Cd (µg l^{-1}) in the River Exe, Thorverton. Data source EA.

The distribution of dissolved Cd in tidal waters is largely determined by the influence of detection limits (more than 90% of tidal water values were below DL). Nevertheless, annual averages are invariably below the EQS for saline waters (2.5 µg l^{-1}) by at least one order of magnitude as indicated in figure 8. This also applies to more recent samples (2001) from near sewage works at Countess Wear and Exmouth.

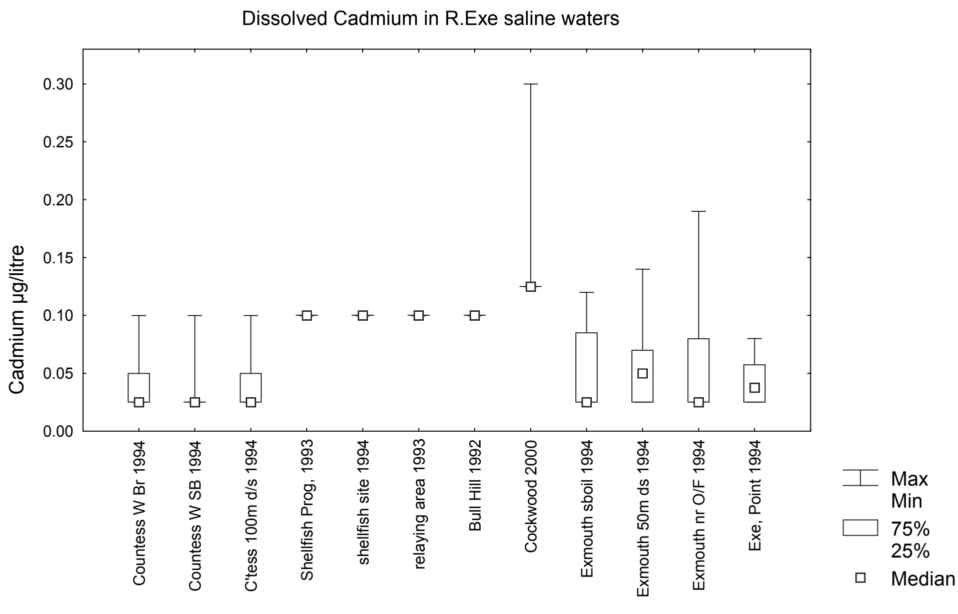


Figure 8. Concentrations of dissolved Cd µg l^{-1} in estuarine waters, Exe Estuary. Annual summary statistics. Data source EA.

Cadmium concentrations in Countess Wear and Exmouth STW effluent samples are also largely below detection limits (<0.1µg l^{-1} in 2001) and therefore appear to constitute relatively small loadings to the estuary.

Consequently there is little evidence to suggest Cd concentrations would have deleterious effects on biota.

No temporal trends are discernible in the data.

Chromium.

Most of the concentrations of Cr in freshwater are at or below the detection limit (98%). Riverine concentrations of Cr in the River Exe at Trews Weir (annual averages) have varied from 0.5 to 0.25µg l^{-1} since 1990, largely as a function of (decreasing) detection limits. Comparisons between the River Exe (Thorverton and Trews Weir), Exeter Canal (Countess Wear), River Kenn (Powderham) and River Clyst (Clyst St Mary), suggests equivalent low levels of Cr concentrations in all parts of the catchment (0.5 to 0.25µg l^{-1} based on annual average). There appear to be no significant Cr inputs from rivers to the Exe Estuary.

The EQS for Cr in fresh waters (suitable for salmonids) ranges between 5 and 50 µg l^{-1} depending on hardness. Annual averages at all monitored sites comply with even the lowest standard by an order of magnitude.

Dissolved chromium concentrations in Countess Wear STW effluent samples have decreased from around 10 to 1µg l^{-1} (annual averages) between 1990 and 1997 (figure 9) and therefore appear to contribute relatively small loadings to the estuary. Analyses of Dawlish and Exmouth STW final effluent also indicate very low dissolved Cr concentrations (<0.5 µg l^{-1}). In 2001, total Cr concentrations in Countess Wear and Exmouth STW final effluent were 0.7 and 0.34 µg l^{-1}, respectively.

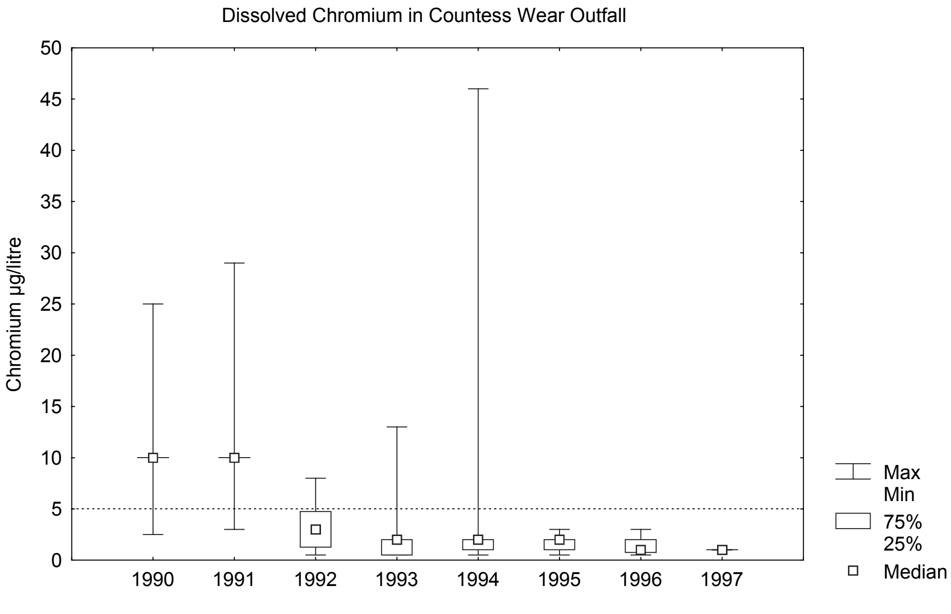


Figure 9. Cr concentrations in Countess Wear STW final effluent. (Data source: EA)

Summary statistics for dissolved Cr in estuarine waters of the Exe are shown in figure 10. Median values for all sites are essentially equivalent to (half) detection limits, throughout the SPA (more than three-quarters of all values were <DL). These are lower than the EQS (15 µg l^{-1}) by more than an order of magnitude.

Consequently there is little evidence to suggest Cr concentrations would have deleterious effects on biota.

No temporal trends are discernible in the data.

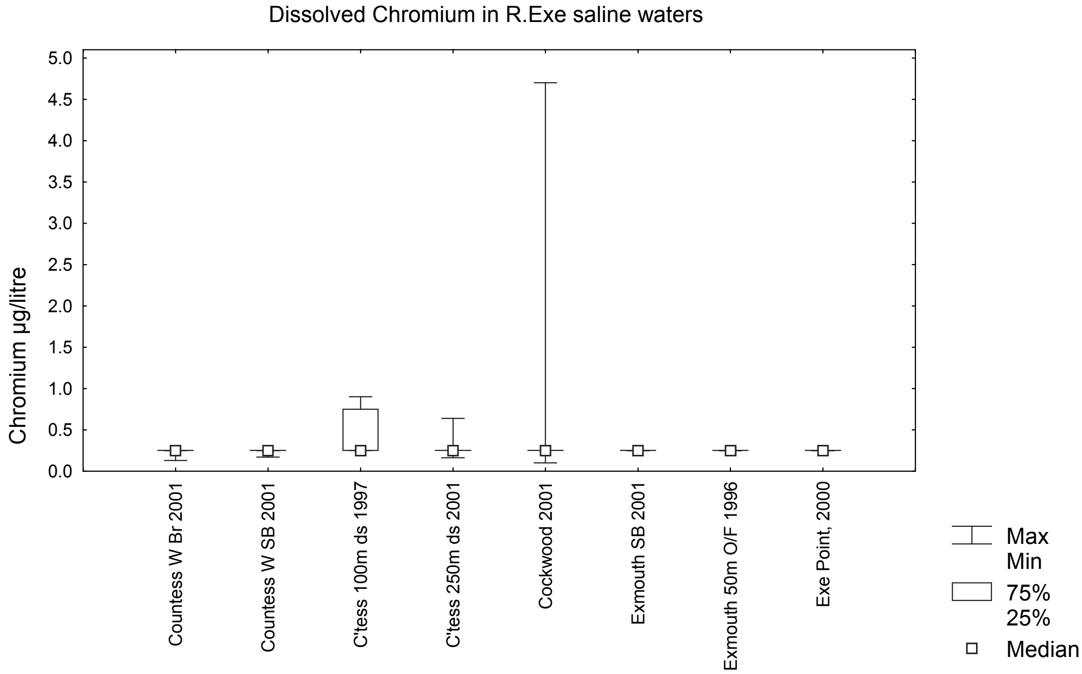


Figure 10. Concentrations of dissolved Cr (µg l^{-1}) in estuarine waters, Exe Estuary. Annual summary statistics. Data source EA.

Copper

Comparisons between the River Exe (Thorverton and Trews Weir), Exeter Canal (Countess Wear Road Bridge), Alphin Brook, Polly Brook, North Brook, River Kenn (Powderham) and River Clyst (Clyst St Mary), shown in figure 11, suggest comparable levels of Cu in all parts of the catchment (1 to 2 µg l^{-1} based on annual averages). There appear to be no outstanding Cu inputs from rivers to the Exe Estuary.

The EQS for Cu in freshwater is in the range 1 - 28 µg l^{-1} depending on hardness. Annual averages at all monitored sites appear to exceed the lowest standard by a small margin. However, as almost half of the measurements of Cu in freshwater are at or below the detection limit (1-2.5 µg l^{-1}) the toxicological significance cannot be interpreted meaningfully, though it is unlikely that any acute effects would be manifested.

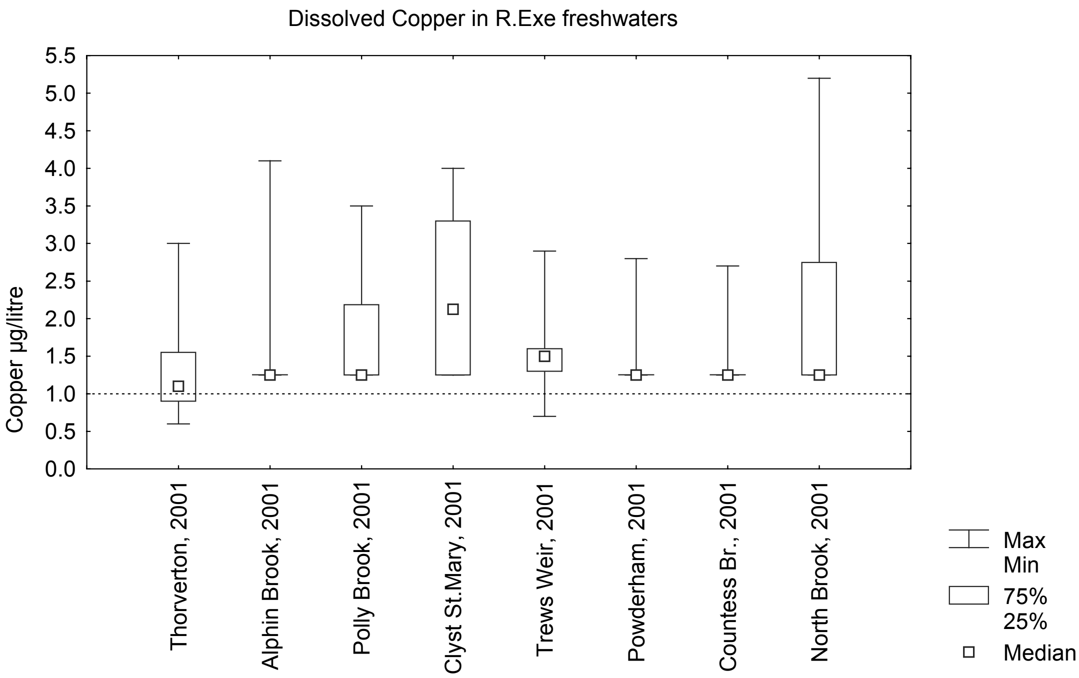


Figure 11. Concentrations of dissolved Cu (µg l^{-1}) in freshwater sources to the Exe Estuary. Summary statistics 2001 (Data source EA). Dashed line = lower EQS value for Cu in freshwater.

Summary statistics for dissolved Cu in estuarine waters of the Exe in 2000 are shown in figure 12. Nearly all samples were above detection limits. Annual median values for the sites shown range between 0.7 and 2.1µg l^{-1} and are lower than the EQS (5 µg l^{-1}) by at least a factor of 2. It is therefore unlikely that Cu concentrations in the estuary would have deleterious effects on biota.

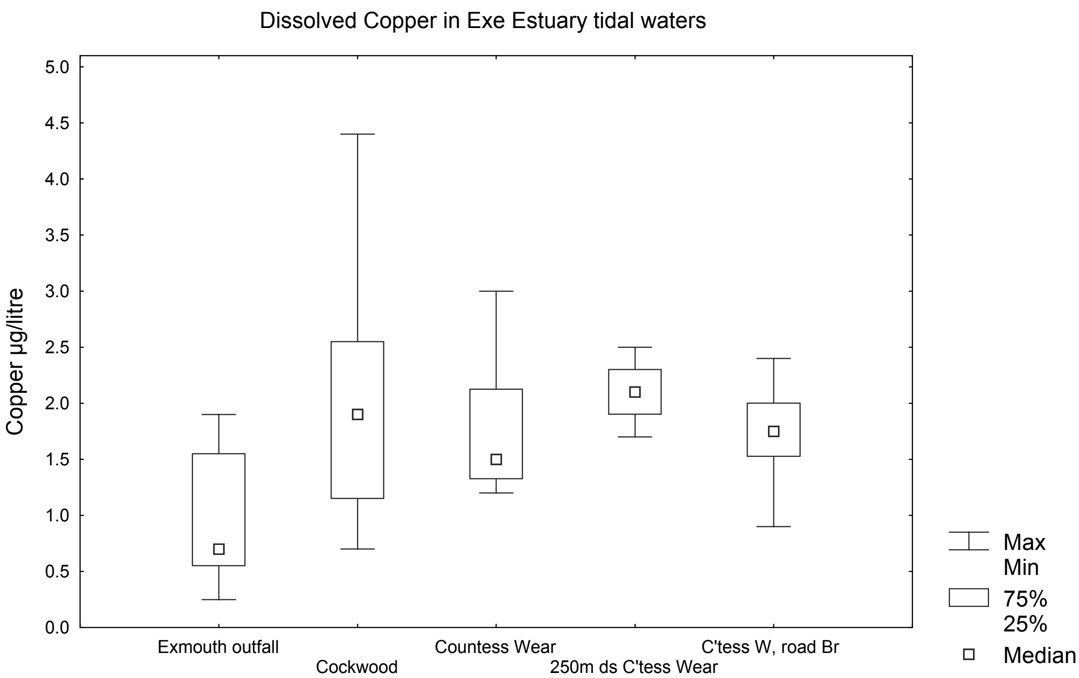


Figure 12. Concentrations of dissolved Cu (µg l^{-1}) in Exe estuarine waters, annual summary statistics for 2000. Data source EA.

No temporal trends are discernible in the data other than an indication of decreasing Cu levels in the Exmouth STW outfall surface boil between 1995 and 2002 (figure 13).

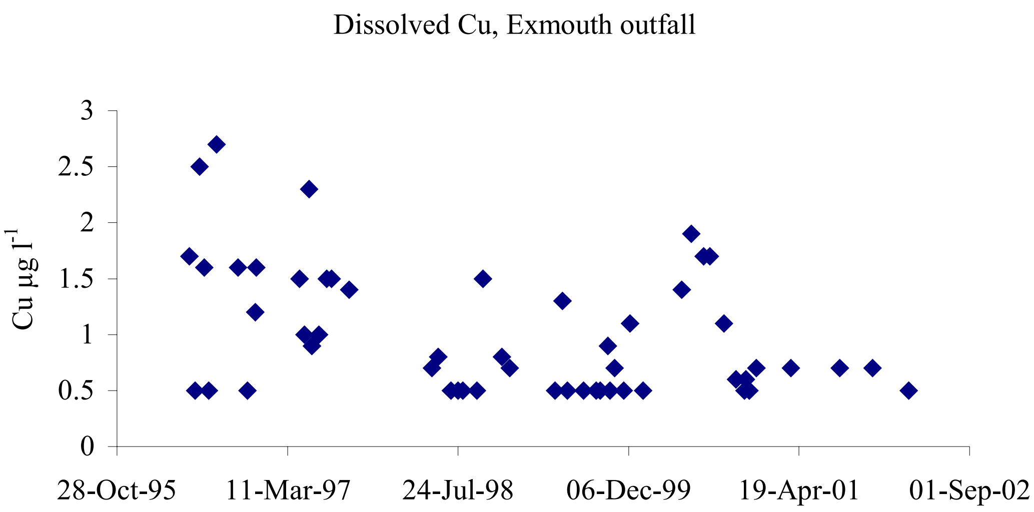


Figure 13. Dissolved Cu concentrations in samples from the Exmouth STW outfall surface boil. Data source EA.

Copper concentrations in Countess Wear STW effluent samples appear to have decreased slightly from 7 to 4.5µg l^{-1} (annual averages) between 1992 and 1997 and therefore contribute small loadings to the estuary. Single analyses of Dawlish and Exmouth STW final effluent indicate very low dissolved Cu concentrations (<1 µg l^{-1}). In 2001, average *total* Cu concentrations in Countess Wear and Exmouth STW final effluent were 3.65 and 22.8 µg l^{-1}, respectively and it appears the latter may represent a small source of predominantly particulate Cu.

Iron

Comparisons between the River Exe (Thorverton and Trews Weir, 2001) and River Clyst (Clyst St Mary, 1994) suggest that levels of Fe could be slightly elevated in the latter (figure 14). Nevertheless the annual average of 160 µg l^{-1}, though almost double than in the Exe, is substantially below the EQS for dissolved Fe (1000µg l^{-1}). Riverine sources of Fe therefore do not appear to represent a threat to the Exe Estuary. There are indications in temporal data for Trews Weir (figure 15) and Thorverton (not shown) that both annual averages and the incidence of extreme values for dissolved Fe have decreased in recent years.

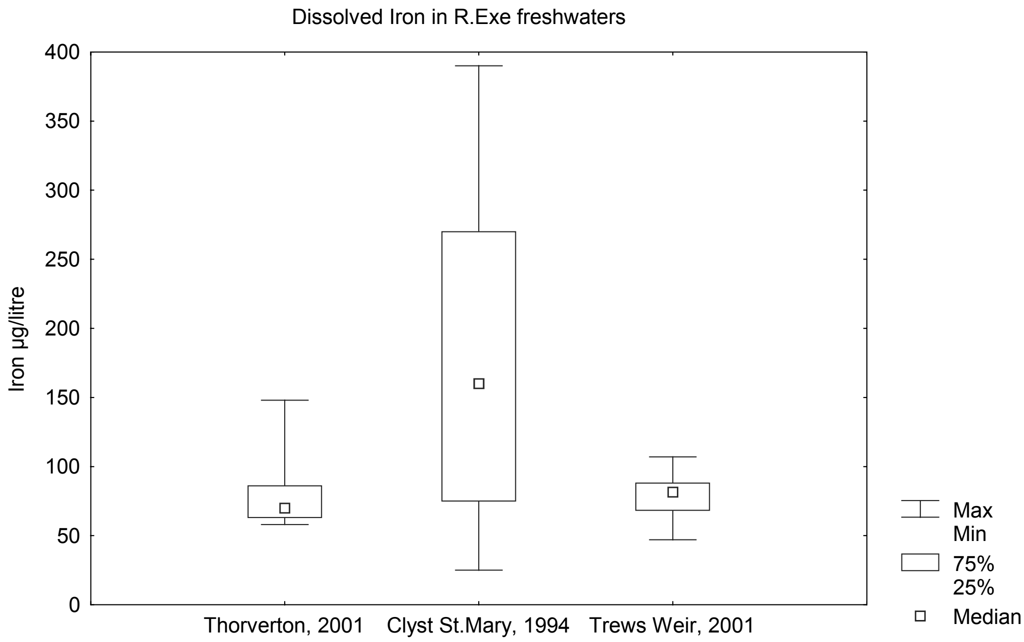


Figure 14. Concentrations of dissolved Fe (µg l^{-1}) in freshwaters feeding the Exe estuary. (Data source EA).

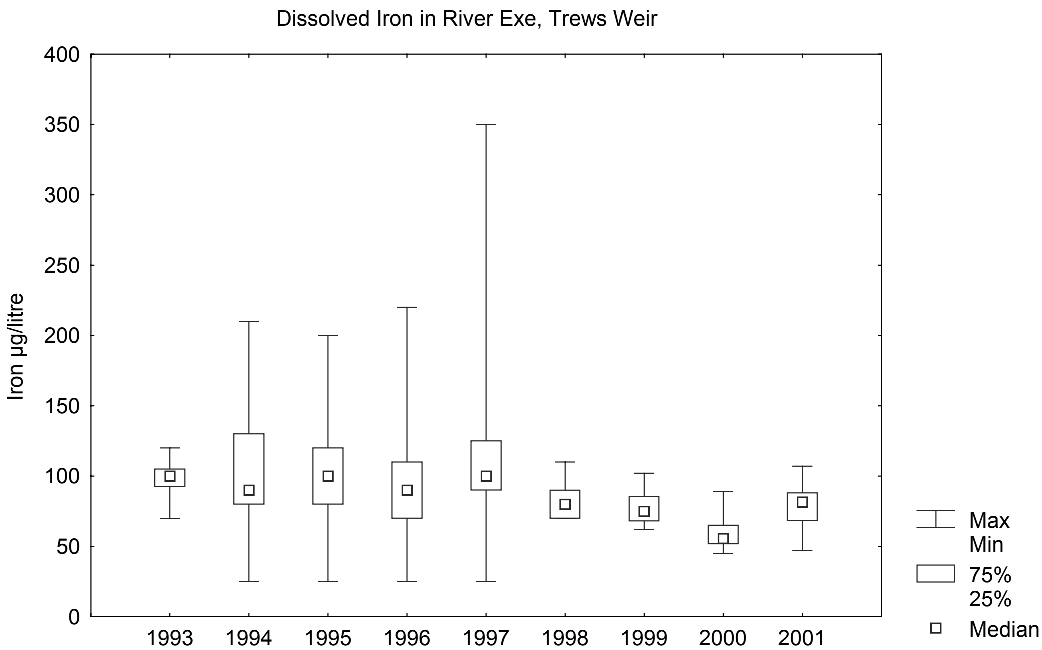


Figure 15. Trends in dissolved Fe concentrations at Trews Weir. (Data source, EA).

Dissolved Fe concentrations in estuarine waters of the Exe (1994-5) are shown in figure 16. Median values for all sites are well below the EQS (1000 µg l^{-1}). It is therefore unlikely that Fe would represent a threat to marine biota at the site. Highest levels are recorded at Countess Weir, though these are not substantially different from the riverine samples described above. The source of this Fe is therefore probably riverine and not necessarily related to STW inputs. This appears to be confirmed in analyses of Countess Wear STW effluent samples, which average 70µg l^{-1} for dissolved Fe – comparable to levels in river water.

Fe is relatively insoluble in seawater and dissolved Fe concentrations would therefore be expected to decline seawards. Hence lower annual average values are encountered at Exmouth despite occasional elevated values associated with surface boil samples (figure 16).

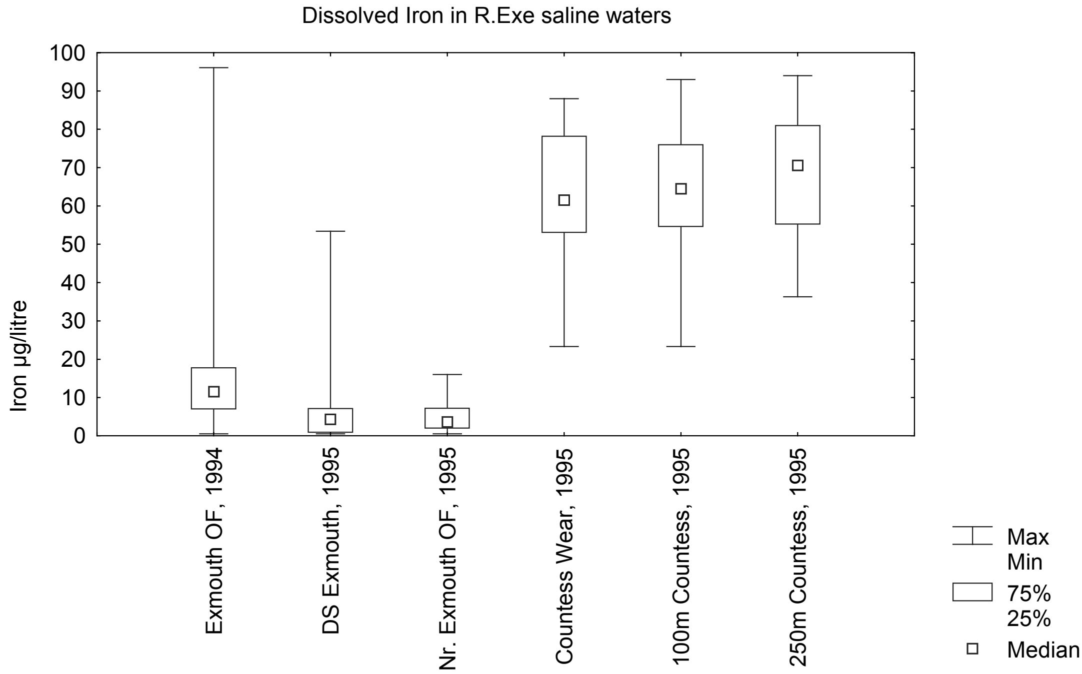


Figure 16. Concentrations of dissolved Fe (µg l^{-1}) in Exe estuarine waters. Annual Summary statistics for most recent year. (Data source EA).

Nickel

Comparisons of dissolved Ni concentrations in the River Exe (Thorverton and Trews Weir), Exeter Canal (Countess Wear Road Bridge), River Kenn (Powderham) and River Clyst (Clyst St Mary) are shown in figure 17. Although there appear to be some differences between water bodies this is largely artifactual due to changing detection limits over time. Seventy percent of freshwater Ni values in the database are below detection limits which vary between 1 and 5µg l^{-1}. Thus, there appear to be no outstanding Ni inputs from rivers to the Exe Estuary and no perceived threat to biota: all concentrations are more than an order of magnitude below the fresh water EQS for dissolved Ni, which ranges between 50 and 200 µg l^{-1} depending on hardness.

Dissolved nickel concentrations in Countess Wear STW effluent samples (expressed as annual averages) have ranged between 5 and 11.5µg l^{-1} over the last decade and therefore contribute small loadings to the estuary. Single analyses of Dawlish and Exmouth STW final effluent indicate low Ni concentrations (<3 µg l^{-1}). In 2001, average total Ni concentrations in Countess Wear and Exmouth STW final effluent were also comparatively low at 6.5 and < 5µg l^{-1}, respectively.

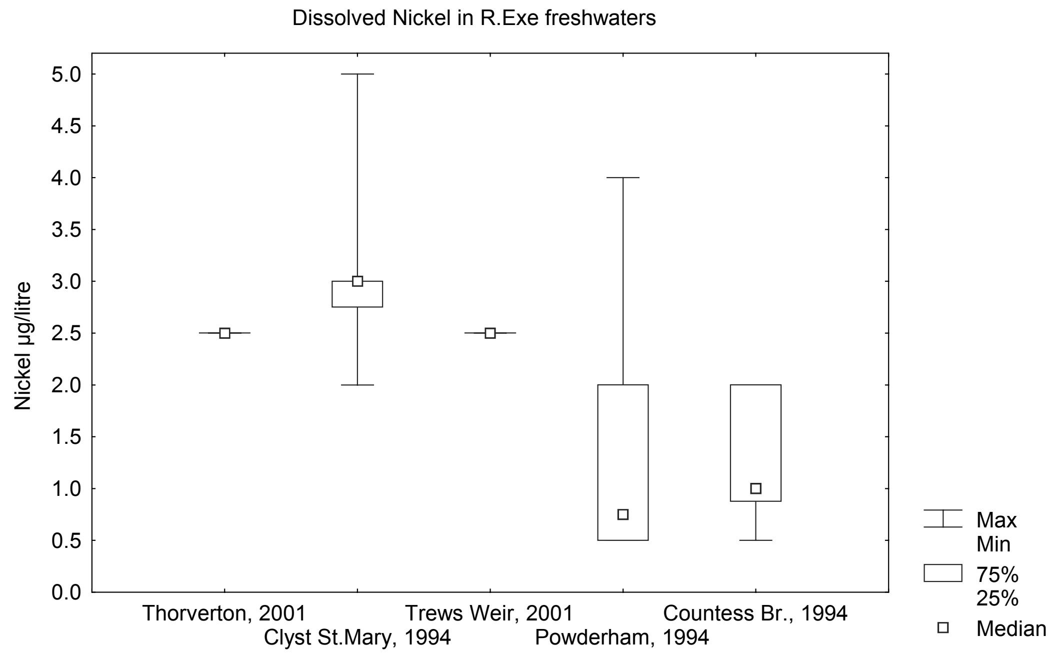


Figure 17. Concentrations of dissolved Ni (µg l^{-1}) in freshwaters feeding the Exe Estuary. Data source EA.

The majority (>90%) of dissolved Ni determinations in estuarine waters are below detection limits which vary between 0.5 and 3 µg l^{-1}. Annual averages therefore display little variation between sites in the estuary (figure 18) and are well below the EQS for tidal waters (30 µg l^{-1}). It is therefore unlikely that Ni would represent a threat to marine biota at the site.

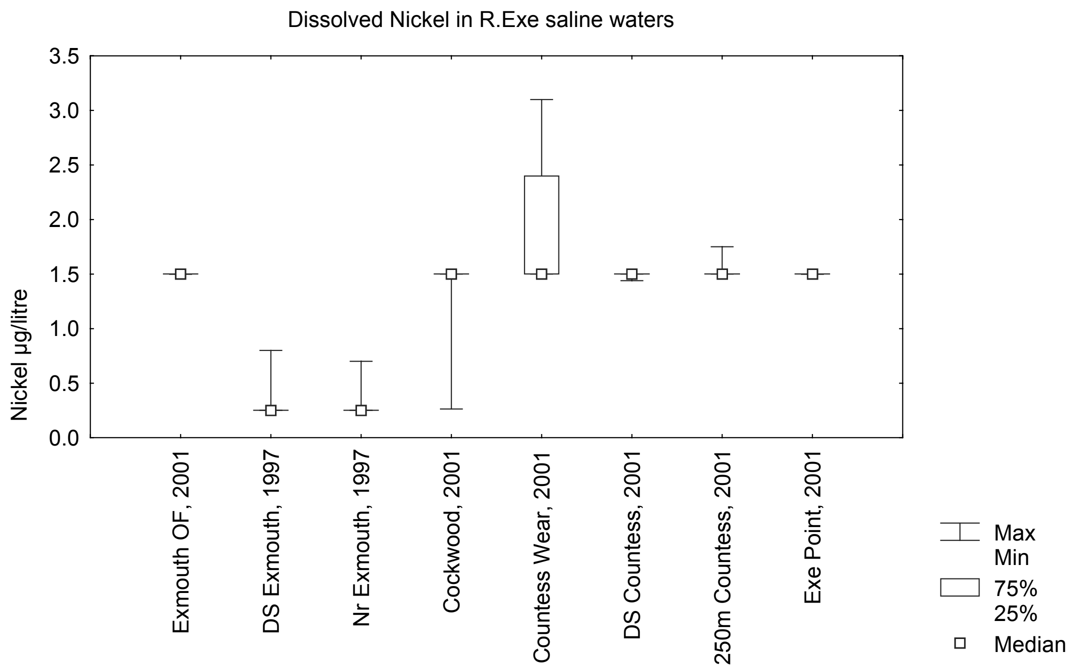


Figure 18. Concentrations of dissolved Ni (µg l^{-1}) in Exe estuary waters. (Data source EA).

Lead

Dissolved Pb concentrations in the River Exe (Thorverton and Trews Weir), Exeter Canal (Countess Wear Road Bridge), River Kenn (Powderham) and River Clyst (Clyst St Mary) are shown in figure 19. There are no major differences between water bodies; three quarters of freshwater Pb values in the database are below detection limits which vary between 0.1 µg l^{-1} (post 1998) and 2µg l^{-1}. Thus, there appear to be no outstanding Pb inputs from rivers to the Exe Estuary and no perceived threats to biota: annual average concentrations are an order of magnitude below the fresh water EQS for dissolved Pb which ranges between 4 and 20 µg l^{-1}, depending on hardness. Only occasionally do samples approach this concentration.

Dissolved lead concentrations in Countess Wear STW effluent samples (expressed as annual averages) ranged between 1 and 4 µg l^{-1} between 1992 and 1997 and therefore contribute small loadings to the estuary. The trend appears to be downward but is probably influenced by changing detection limits. A single analyses of Dawlish and Exmouth STW final effluent indicates low dissolved Pb concentrations (<2.5 µg l^{-1}). In 2001, average *total* Pb concentrations in Countess Wear and Exmouth STW final effluent were also comparatively low at 2.4 and 1.4 µg l^{-1}, respectively, implying little in the way of particulate Pb input from these sources.

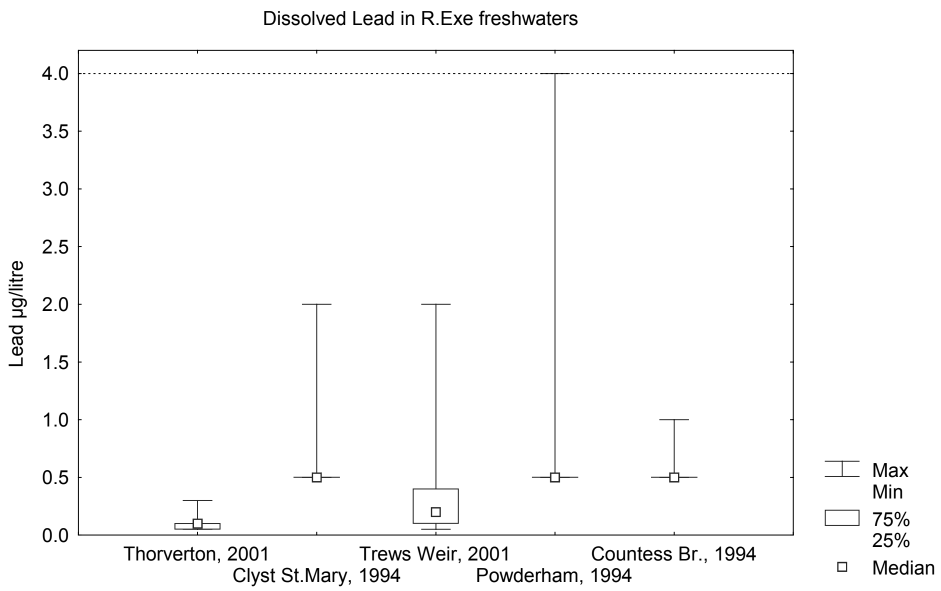


Figure 19. Concentrations of dissolved Pb (µg l^{-1}) in freshwaters feeding the Exe. (Data source EA).

The distribution of dissolved Pb at estuarine water sites in the Exe Estuary is shown in figure 20. Little can be gleaned from this data regarding sources or temporal trends because the majority (60%) of values are reported as below detection (0.2-2.5µg l^{-1}). Nevertheless, by incorporating ½DL values, the plots indicate that average Pb concentrations throughout the Exe Estuary are invariably more than an order of magnitude below the EQS (25 µg l^{-1}) and therefore probably of little concern for biota.

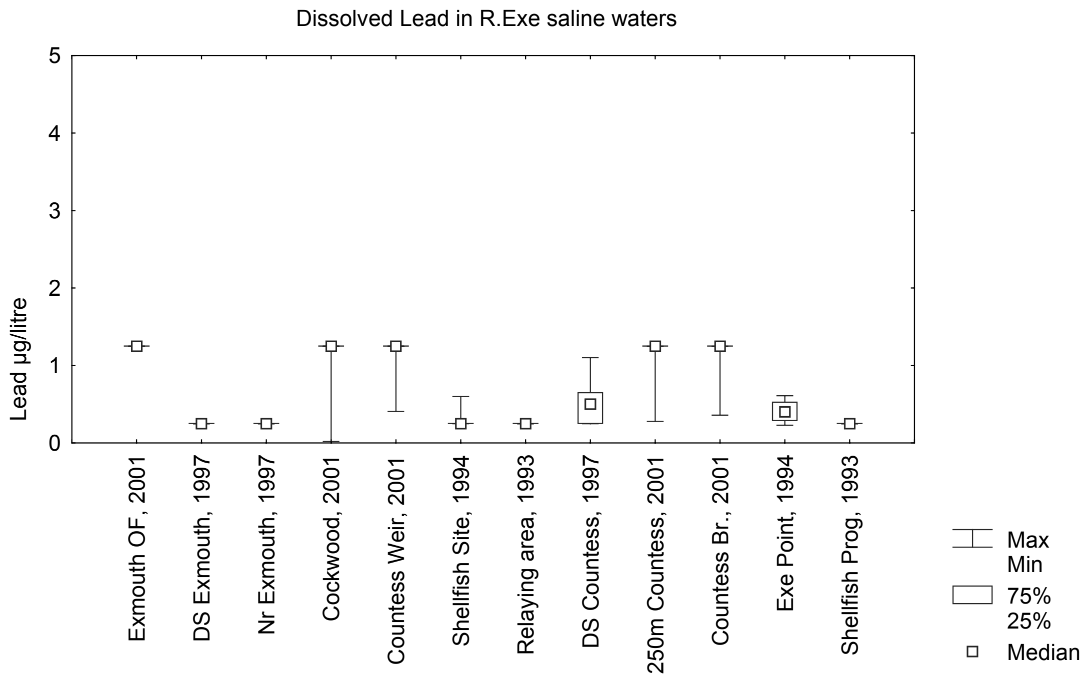


Figure 20. Dissolved Pb (µg l^{-1}) in Exe estuarine waters. (Data source EA).

Zinc

The EQS for Zn in fresh waters (suitable for salmonids) is thought to relate to 'total' rather than dissolved metal and ranges from 8 to 120 µg l^{-1} depending on hardness. The only available values for total Zn in freshwater are for the Exe at Thorverton (Figure 21). Annual average concentrations appear to have remained relatively consistent since 1990 (µg l^{-1}) and indicate compliance with the EQS. Extreme values sometimes approach 40µg l^{-1} though the incidence of high values has decreased in recent years. Nevertheless, the river Exe is a steady, low-level source of Zn to the estuary.

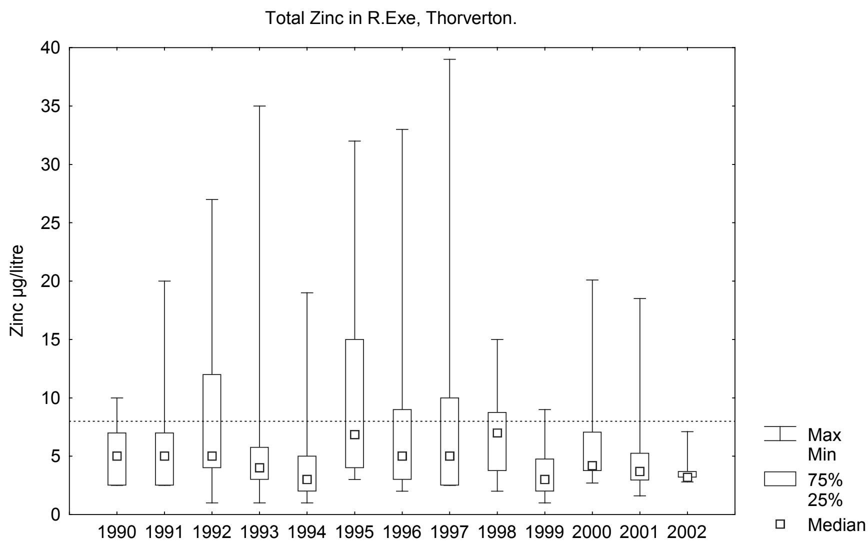


Figure 21. Total Zn concentrations (µg l^{-1}) at the Thorverton Gauging station, River Exe. (Data source EA).

The majority of values for freshwater are for dissolved Zn. Concentrations in the River Exe (Thorverton and Trews Weir), Exeter canal (Countess Wear), River Kenn (Powderham) and River Clyst (Clyst St Mary) are shown in figure 22. Median values are for different years (recent data for the latter three sites are not available), however dissolved Zn levels in each of these catchments falls below the standard for total Zn.

The temporal pattern for dissolved Zn at Trews Weir (figure 23) and also Thorverton (not shown) is similar to the trend for total Zn in that there appears to have been a decrease in annual averages (and also in the incidence of extreme values) since 1998.

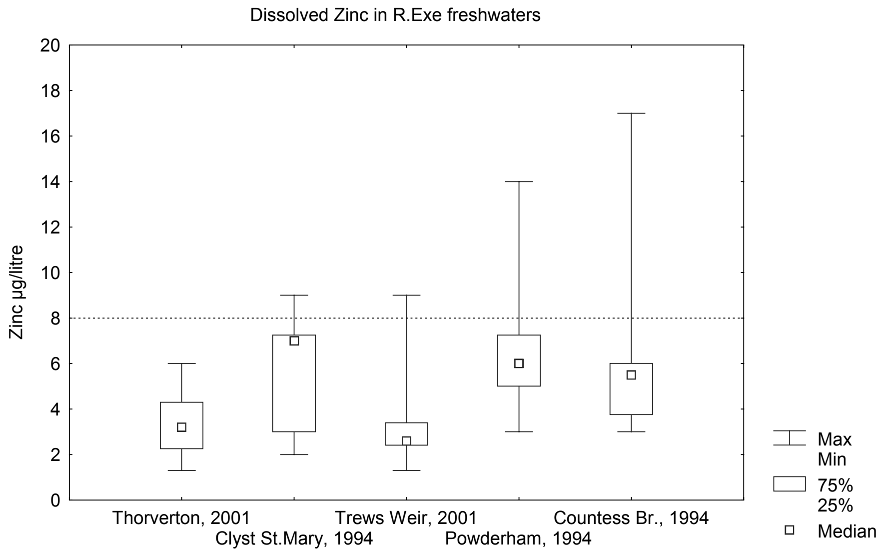


Figure 22. Concentrations of dissolved Zn (µg l^{-1}) in freshwaters feeding the Exe. (Data source EA). Note 'EQS' line is for total Zn.

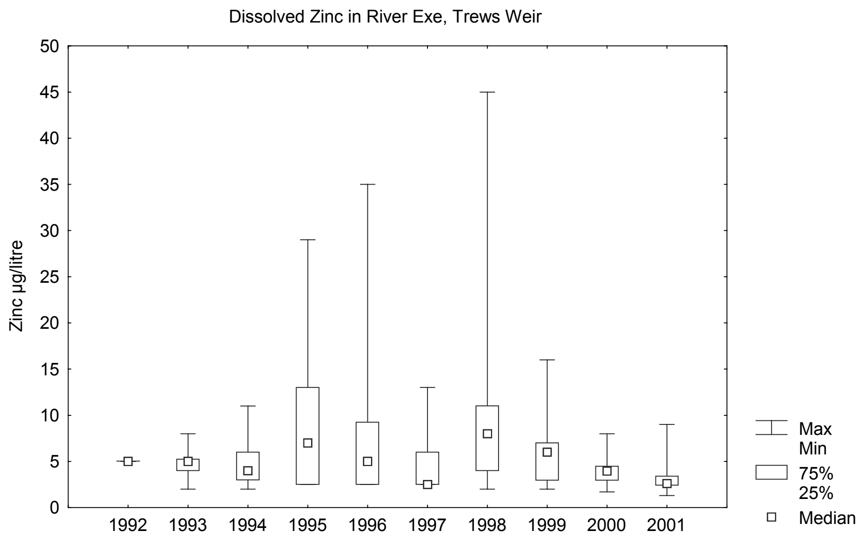


Figure 23. Dissolved Zn concentrations (µg l^{-1}) at Trews Weir, River Exe. (Data source EA).

Dissolved Zn concentrations in the Exe Estuary are shown in figure 24. Median values for all sites fall below the current Zn standard (though the EQS of 40µg l^{-1} is thought to be for *total* Zn). Even if the Zn standard were revised downwards to 10µg

l^{-1} as has been proposed by Hunt and Hedgecott (1992), all sites would probably comply. There is an indication of slight Zn enhancement in surface boil samples near the Countess Wear and Exmouth STW but it is unlikely these concentrations would affect the majority of estuarine biota, most of which are able to regulate this essential element at low levels of contamination.

Zinc concentrations in Countess Wear STW effluent samples (expressed as annual averages) have ranged between 46 and 95µg l^{-1} between 1990 and 1997 and therefore contribute sizeable loadings to the estuary. The trend appears to be downward since 1992 (figure 25). Single analyses of Dawlish and Exmouth STW final effluent indicate much lower Zn concentrations (<4 µg l^{-1}). In 2001, average *total* Zn concentrations in Countess Wear and Exmouth STW final effluent were 42.8 and 16.8µg l^{-1}, respectively. It seems likely that much of this input is likely to be in dissolved form.

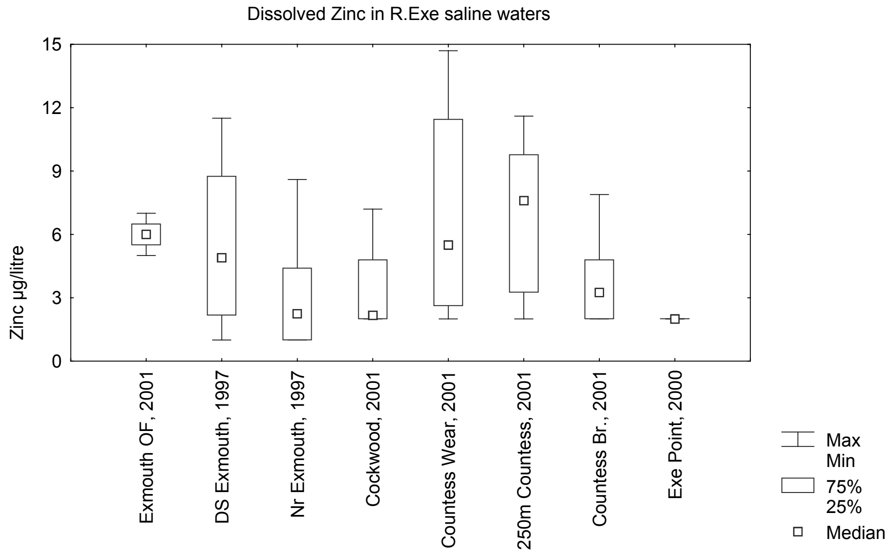


Figure 24. Concentrations of dissolved Zn (µg l^{-1}) in Exe estuarine waters. (Data source EA).

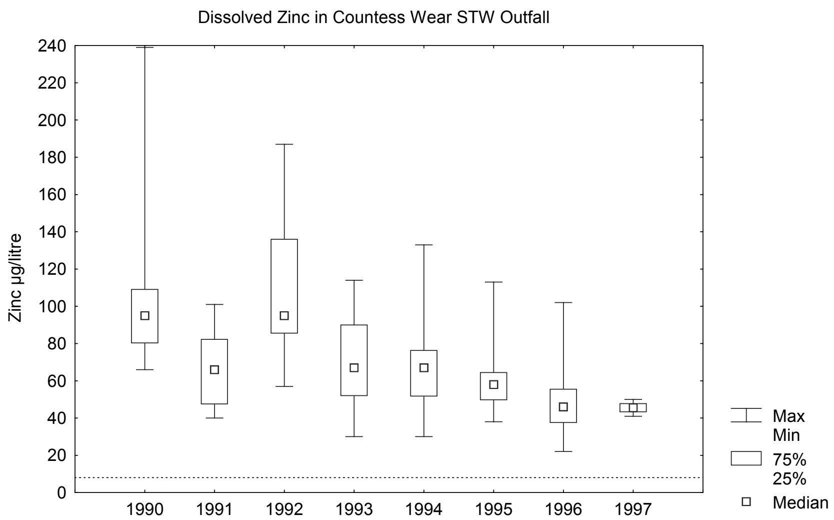


Figure 25. Concentrations of dissolved Zn (µg l^{-1}) in final effluent from Countess Wear STW, annual averages 1990-1997. (Data source EA).

Mercury

The EQS for Hg in all fresh waters, based on total metal, is 1µg l^{-1}. Determinations for Hg in the River Exe are for dissolved Hg. At Thorverton and Trews Weir values were all below detection limits (10 ng l^{-1} in 2001) and therefore riverine sources may not be significant.

Hg contributions from STW discharges also appear to be small (though data is very limited). The concentration in Countess Wear STW effluent samples (expressed as annual averages) was 0.1µg l^{-1} (total) in 1996 and in Exmouth STW final effluent 0.01 µg l^{-1}(dissolved) in 1999.

The EQS for Hg in estuarine water is 0.3 µg l^{-1} (dissolved Hg) and there is no evidence to indicate harmful inputs of Hg to the SPA from the above sources. This is borne out by tidal waters data, where 98% of values were below detection limits (0.01-0.02 µg l^{-1}).

In general therefore water quality is not compromised to any great extent by metals.

Sediments

The catchment of the Exe is not generally considered to be heavily mineralised and deposition of particulates of terrestrial origin would not be expected to result in particularly high metal concentrations in estuarine sediments. Table 4 compares average sediment-metal data for the Exe Estuary with other estuaries in the south - west, including the highly contaminated Restronguet Creek (Fal), Poole Harbour, the Severn, and the Avon in Devon (little anthropogenic input). Clearly, for metals such as As, Cu, Pb, and Zn, concentrations in Exe sediments pale in comparison with those derived from mining sources in Restronguet Creek. Hg is also low though there may be slight enrichment with Cd and Ag, relative to the Devon Avon which receives very little anthropogenic input. There is also potential for enrichment towards the head of the estuary as indicated below.

Table 4. Metals in intertidal sediments (µg g^{-1} dry wt): typical values for Exe Estuary and other sites in south west England.

site	Ag	Cu	Zn	Pb	Cd	Mn	Fe	As	Hg	Se	Ref
Exe (mid)	0.4	38	192	73	0.9	735	34400	12	0.18		1
Poole	0.82	50	165	96	1.85	185	29290	14.1	0.81	1.51	2
Tamar		145-545	221-605	19-239	0.5	105-1500	21000-49000	25-236	0.2-1.5		3
Severn	0.42	35	242	84	0.63	672	26805	8.4	0.44	0.23	1
Restronguet	1.37	1690	1540	684	3	1030	54000	1080			4
Avon (Devon)	0.06	19	98	39	0.3	417	19400	13	0.12	<0.1	1

[1] own unpublished data [2] Bryan and Langston, 1992; [3] Ackroyd *et al* 1986 ; [4] Aston *et al* 1975

Surveys of metals in fine sediment fractions in 1987, by W.S. Atkins, demonstrate uniformity of metals concentrations throughout most of the Exe estuary which, they suggest, is a function of their common source – the input of Exe River water and associated sewage discharges (Atkins, 1988).

Further discussion of the distribution of metals in intertidal sediments of the Exe Estuary is presented in section 7.1 in relation to ecotoxicological guideline values. These generally indicate there is likely to be little impact from metals except perhaps close to the head of the estuary near Countess Wear.

Biota

Although measurements of metals in sediments and water are a useful guide to environmental contamination, ultimately it is the impact on biota which is of most concern. Unfortunately, studies specifically designed to evaluate the issue of bioavailability in the Exe Estuary, using appropriate bioindicators, are few.

The distribution of key indicator species (e.g. *Nereis diversicolor*, *Scrobicularia plana*, *Mytilus edulis*, *Cerastoderma edule*, *Littorina* spp. *Fucus* spp,) and the bioavailability and impact of metals in UK estuaries, have been the subject of research at the MBA over a period spanning three decades (see Bryan *et al.,* 1980, 1985; Langston *et al*., 1994b). These include a small number of data for the Exe from the 1970s and 1980s. Though comparatively old, they nevertheless provide a useful background to assess characteristics of the site. They also act as a valuable baseline for future changes.

Comparative data for metals in *Nereis diversicolor* and *Scrobicularia plana*, from the Exe Estuary (Powderham and Topsham) and other UK sites, give an indication of the relative scale of metal bioavailability (tables 5 and 6).

Polychaetes are among the most widespread inhabitants of contaminated and uncontaminated sediments. Nereids such as *Nereis diversicolor* accumulate a number of metals in amounts which reflect bioavailability in their sedimentary environment (Bryan *et al.,* 1980; 1985; Langston, 1980, 1982). Tolerance to a wide range of salinity also makes *Nereis* extremely useful for monitoring in estuaries and *N. diversicolor* is relatively abundant throughout most of the SPA. It should be noted, however, that Zn and Fe are partially regulated by *Nereis* and therefore body burdens can underestimate contamination with these metals. It is important to recognise also that sediment conditions can modify availability somewhat (e.g. high sediment Fe and organics can reduce uptake of As, and Hg, respectively: Langston, 1980; 1982).

Table 5 shows metal concentrations in *Nereis diversicolor* from Powderham and Topsham in the Exe (mean values spanning ~25 years, therefore incorporating the recent history of contamination rather than current status). For comparison, also shown are equivalent data from Holes Bay (Poole), the Severn, and the Avon (Devon), the latter estuary being relatively free from anthropogenic input.

The degree of enrichment for Powderham worms, relative to Avon baselines, is also included in table 5. There is very little obvious enrichment except perhaps for the pollutant metals Hg, Cd, Ag and Sn (the latter probably reflects a small degree of TBT contamination). At Topsham, further upstream, slightly higher levels were encountered for these metals.

Table 5. ***Nereis diversicolor*****. Metal concentrations (µg g^{-1} dry weight) in the Exe Estuary (Topsham and Powderham) and other sites in the south-west, including the Avon (uncontaminated).** (Langston, Burt and Chesman, unpublished data)

	Ag	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg	As	Sn
Exe												
Powderham	0.16	0.39	0.38	15.3	577	15.6	4.4	2.42	168	0.21	9.7	0.34
Topsham	0.44	0.51	0.14	21.9	532	14.6	4.4	4.0	197	0.32	7.0	1.44
Poole	0.49	0.64	0.6	12	337	11.5	8.9	3.6	165	0.24	7	1.1
Severn	8.01	3.79	0.52	54.4	396	14.3	4.94	3.56	264	1.42	12.8	0.31
Avon (Devon)	0.1	0.14	0.5	19	564	11.8	3.3	5.4	163	0.07	8	0.09
Powderham ÷ Avon	1.6	2.7	0.76	0.8	1.0	1.3	1.3	0.44	1.0	3.0	1.2	3.8

The deposit-feeding clam *Scrobicularia plana* is also a valuable indicator species, particularly in terms of understanding trends in sediment metal bioavailability. It is in many respects a better accumulator and indicator of metals than *Nereis* (with the exception of Cu), and has the advantage of not regulating Zn. Its range in the Exe extends over most of the estuary. Its ability to survive in upper estuaries is presumed due to the buffering influence of its burial behaviour in sediments (upto 25cm) and an ability to isolate itself, through shell closure, from extreme low salinities.

Table 6 shows summary statistics for metals in *Scrobicularia plana* from Powderham and Topsham in the Exe, in comparison to Poole Harbour, the Severn, and Devon Avon (the latter relatively free from anthropogenic input).

The degree of enrichment for Powderham clams, relative to Avon baselines, is also included in table 6. Again there is very little obvious enrichment except perhaps for the pollutant metals Ag and Sn. At Topsham, further upstream, slightly higher levels were encountered for some, but not all, metals.

Both species indicate that there may be slight increases in bioavailable pollutant metals, which are presumed to be of anthropogenic origin. These are generally, relatively small compared with increases seen at impacted sites in the Severn, Fal and Poole Harbour. It is stressed that these represent a historical perspective of contamination. The current status of the SPA needs to be defined more extensively in similar fashion, and at intervals in the future, to ensure bioavailability does not increase.

Table 6. *Scrobicularia plana*. Metal concentrations (µg g^{-1} dry weight) in the Exe Estuary (Topsham and Powderham), and other sites in the south-west, including the Avon (uncontaminated). (Langston, Burt and Chesman, unpublished data)

	Ag	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg	As	Sn
Exe												
Powderham	1.79	1.24	4.65	26	1378	47.4	6.75	36.9	1015	0.75	34.7	0.74
Topsham	2.49	1.32	3.75	25	2350	46.2	4.9	32.6	1447	0.46	11.6	1.32
Poole	22.5	12	5.8	46	1490	6	10.7	18	878	1.08	13	1.44
Severn	8.37	7.18	3.68	47.4	1271	69	6.44	43.5	775	0.64	20	0.39
Avon (Devon)	0.24	0.93	2.7	61	796	41	8.2	23	1078	0.9	23	0.26
Exe (P'ham)												
÷	7.5	1.3	1.72	0.42	1.74	1.15	0.82	1.6	0.94	0.83	1.5	2.84
Avon												

Published data on metal levels in other Exe biota are extremely scarce. Metal levels in native mussels from the Bull Hill beds are shown in table 7 and compared with levels in samples transplanted to Restronguet Creek in the Fal (Perryman, 1996). Clearly, body burdens imply low levels of bioavailable Cu, Zn and Fe in the Exe, relative to Restronguet Creek (Fal Estuary), as would be expected. Concentrations in Exe mussels are in fact among the lowest we have encountered in UK estuaries, as indicated by comparisons with minimum values from our own data set of more than 250 samples. Copper and zinc concentrations in Exe mussels are well below any of the upper category guidelines proposed by ADRIS (Association of Directors and River Inspectors in Scotland) or NOAA (National Oceanic and Atmospheric Administration).

An anomaly was found for metals in mussels (and sediments) from Exmouth in a survey conducted in 1987. For example, the level of Cd in these bivalves was an order of magnitude higher than at other sites in the Estuary. The sources of metals in this localised 'hotspot' were attributed to dockside scrap metal operations and antifouling (Atkins, 1988).

Table 7. Metal concentrations (µg g^{-1} dw) in *Mytilus edulis* from the Exe Estuary (Bull Hill), and in mussels transplanted to Restronguet Creek, compared with UK baselines.

Site	Cu	Zn	Mn	Fe
Exe, Bull Hill[1]	2.4	52	2.4	78
Restronguet[1] (transplanted)	27	350	3.8	240
UK Min[2]	2.33	45.5	2.4	56.1

Data source [1] Perryman, 1996; [2]own unpublished data

The EA database for the Exe contains entries for unspecified shellfish collected at the shellfish beds in the lower Exe (west bank) from the period 1992-1994 (table 8).

Table 8. Metal concentrations in 'shellfish' (EA data) in relation to guideline values.

	mg kg^{-1} (dry wt.)					
	Countess Wear Road Bridge	non-designated shellfish programme site	EC	JMP upper	ADRIS guide	NOAA 'high'
Arsenic		11.0				17
Cadmium	1.00	0.23	5*	5	15	6.2
Chromium		16.4				
Copper	8.11	5.89				12
Lead	6.61	19.1	7.5*		50	4.8
Mercury		0.04		1	3	0.23
Zinc	87.7	52.6			500	200

*limits adopted from recently amended EC regulations (446/2001), converted to dw by assuming a wet:dry weight ratio of 5, an approximation based on our own data for wet to dry ratios in shellfish

Again these concentrations are mostly well below any of the upper category guidelines proposed by EC, JMP(OSPAR), ADRIS or NOAA (table 8). The only exception appears to be Pb from shellfish at the non-designated shellfish programme site, which would not meet today's guidelines (EC and NOAA). It is not known however whether these data (now a decade old) are an accurate reflection of the current shellfish status.

6.1.2 TBT and other organotins

Use of tributyltin (TBT) antifouling paint on boats less than 25m in length was prohibited in 1987, though larger vessels (essentially the commercial fleet and Navy) are still entitled to use them, at least until 2003 when recommendations from IMO for a total ban should be implemented. Since there is little use of the estuary by commercial shipping the impact of TBT would be anticipated to be relatively small.

Presumed analytical difficulties make interpretation of TBT results in the EA data set problematic. There are data for two freshwater sites on the Exe. At Thorverton samples were analysed in 1993 and 1994. Out of 32 samples twenty eight were below detection limits which varied from 10-100ng l^{-1}; the freshwater EQS is 20 ng l^{-1}, thus detection limits were sometimes above the EQS. TBT concentrations in the four 'positives' ranged from 10-113 ng l^{-1} (tributyltin). Since the standard is a maximum allowable concentration the results indicate exceedence. Applying half detection limits to remaining samples, median values for the two years in which TBT was monitored were 5ng l^{-1}. The same approximation has been used to plot summary statistics for Trews Weir samples (figure 26). Prior to 1999, high detection limits (up to 388 ng l^{-1}) produce anomalous box whiskers (note however, the maximum of 492 ng l^{-1} is indicated as a real value). In subsequent years analytical techniques have presumably improved and detection limits were in the range 2-4 ng l^{-1} (expressed as the tributyltin cation): most samples were close to, or below, these limits between 1999 and 2002 and comply with the EQS.

Only one estuarine site has been sampled for TBT, at Exmouth STW (surface boil) from 1993-1994. All four samples were below the detection limit (<28 ng l^{-1} –above the EQS for coastal waters of 2 ng l^{-1}). STW effluent at Exmouth and Countess Wear STW were sampled on several occasions during 1996; most were below detection limits which ranged from 10-68 ng l^{-1}. One sample from Exmouth however had a positive value of 43 ng l^{-1}.

It is even more difficult to interpret data for triphenyltin (TPT) in rivers, estuarine waters or effluent streams since all values are reported as below detection limits. These varied between 12 and 124 ng l^{-1} in the same range of samples described above, though mostly the lower value applies. Since the EQS for TPT is 20 ng l^{-1} in freshwater and 8 ng l^{-1} in coastal waters it is likely, but not certain, that compliance would be achieved.

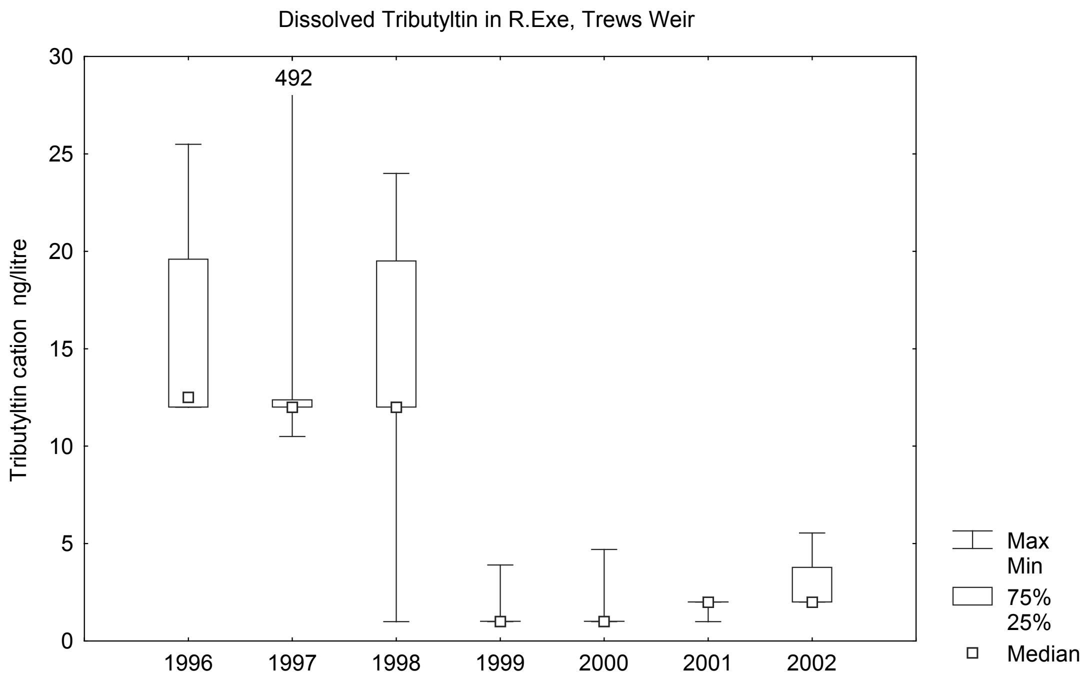


Figure 26. TBT in the River Exe at Trews Weir. Data souce:EA

The only information on TBT in the literature are summarised in table 9. These limited observations tend to support the assertion that concentrations are relatively low, though more data are needed to resolve the current status and provide an accurate assessment of risk from organotins.

Table 9. Published information on TBT and other organotins in the Exe Estuary

sample type	site	TBT	DBT	MBT	source
water	Starcross, 1994	<40ng l^{-1}			1
water	Lympstone, 1987	2.8-5.2 ng l^{-1}			2
sediment	Lympstone, 1987	<0.01µg g^{-1} dw	0.01 µg g^{-1} dw		2
Scrobicularia plana	Lympstone, 1987	0.61 µg g^{-1} dw	0.41 µg g^{-1} dw		2
Mytilus edulis	Exmouth, 1989	0.02 µg g^{-1} ww	0 µg g^{-1} ww	0 µg g^{-1} ww	3
Mytilus edulis	Exmouth, 1991	0.02 µg g^{-1} ww	0.02 µg g^{-1} ww	0.007µg g^{-1} ww	3

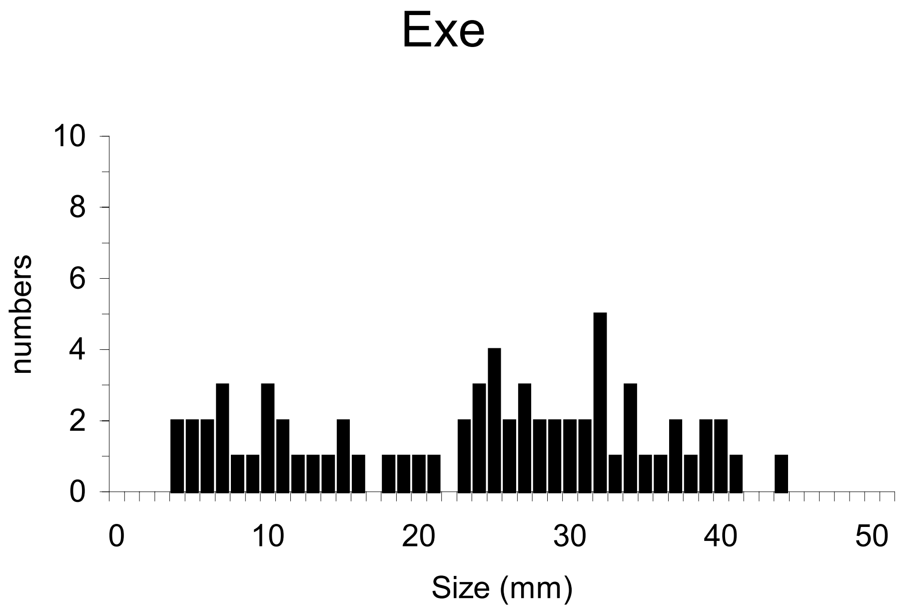
[1]Cleary and Stebbing, 1985; [2]Langston and Burt, 1991; [3]MAFF, 1993

The classic TBT indicator *Nucella lapillus* is not a native species within the Exe Estuary (unsuitable substrates and other physical and chemical constraints). Imposex-related phenomena in dog-whelks have been observed on adjacent shorelines in the past, and the species appears to have disappeared, as a result, at Maer Rock and Orcombe Point (Dixon, 1986). TBT levels measured at Lympstone in 1987 would have been high enough to induce the phenomenon. As far as we are aware there are no indications that these populations have recovered.

No reports could be found concerning TBT-related effects on shell growth in the pacific oyster in the Exe, though elsewhere this species was badly effected during the 1980s.

Other mollusc species in the Exe Estuary show little evidence of TBT impact. Experiments and field observations have shown that concentrations of sediment-bound TBT in the range 0.1-0.3µg g^{-1} would almost certainly contribute to the decline of infaunal bivalves such as *Scrobicularia plana*. Low numbers of post-juvenile stages, and resulting abnormal size-frequency distributions have been a feature of clam populations at a number of TBT-contaminated locations in the UK (Langston and Burt, 1991). On this basis TBT in sediments at Lympstone, on the Exe Estuary (table 9), would be unlikely to affect clam populations.

Thus, the age-frequency structure for *S.plana* from the Exe (Lympstone) signifies successful recruitment and is considered typical of "normal" populations (Langston *et al*., 1990). In contrast, samples from contaminated sites such as Parkstone in Poole Harbour suggest that although spatfall occurs, juveniles may not survive long enough to establish the type of age-frequency distribution found in the Exe and other relatively TBT-free sites (figure 27).



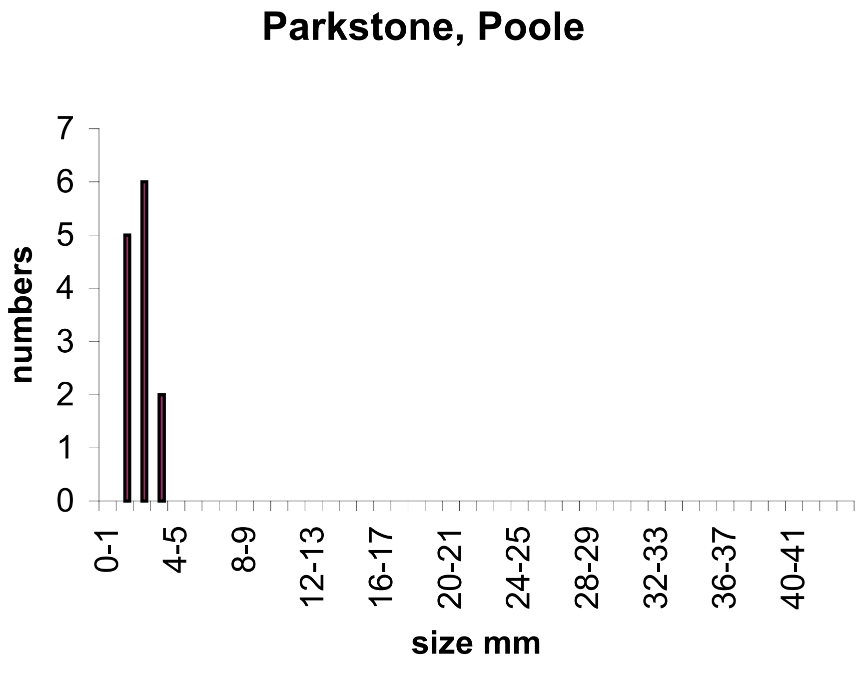


Figure. 27. *Scrobicularia plana*. Size frequency histogram of populations from Lympstone, Exe Estuary (sediment TBT<0.01 µg g^{-1}) and from Parkstone, Poole Harbour (sediment TBT 0.27 µg g^{-1}). From Langston *et al.,* 1990.

There are no statutory sediment guidelines for TBT, though OSPARCOM (2000) has set a provisional ecotoxicological guideline value of 0.00005µg g^{-1}. It is felt however that this guideline (which has no legal significance and is intended as a guide for further work) may be set too low. Mollusc populations do not appear to have been affected by sediment TBT in the Lympstone area (TBT < 0.01µg g^{-1} in sediment) though a wider survey is needed to establish current status and trends.

6.1.3 Hydrocarbons (Oil, Petrochemicals, PAHs)

Oil

Oil pollution is a continual threat to all inshore marine habitats, and is particularly pronounced in estuaries due to their enclosed nature (restricted flushing). Risks in the marine site probably include small leaks, spills and discharges, although there is always the possibility of a major accident.

There are a number of ways in which oil could potentially impact on the interest features of the Exe SPA. Inter-tidal habitats are under greatest threat from the physical effects of oil pollution: the most vulnerable of these are inter-tidal sand and mudflats and salt-marshes (see reviews of vulnerability of shores to oil damage by Gundlach and Hayes, 1978; Elliott and Griffiths, 1987). In extreme events lethal effects would induce community changes.

The direct effects of oil on shellfish beds are potentially serious. In the event of moderate spillages, significant mortalities of bivalves would be expected.

Birds would be affected by consumption of contaminated food and damage to plumage.

Oil pollution may result in hydrocarbons becoming incorporated into sediments and subsequently, buried. Heavily contaminated sediments are likely to have acute effects on populations of bottom-dwelling fish such as plaice and sole (in extreme cases, such as the Amoco Cadiz spill, whole year classes were wiped out over large areas of northern Brittany). Sub-lethal changes could be manifested as increased bioaccumulation and tainting, induction of components of the MFO enzyme system (e.g. ethoxyresorufin-O-deethylase – EROD - activity), and higher order changes in productivity, fecundity and behaviour. Olfactory responses in crustacea can affect their searching, feeding and grooming responses. Fish behaviour, including migration, is also known to be affected by oil spills with most fish avoiding areas of heavy contamination.

Sensitivity of *Zostera* beds to chronic exposure to oil (refinery effluent) may not be very high (Hiscock, 1987). The likely impact of acute exposure (oil spillage) will be influenced by the type of oil, the degree of weathering and the nature of the habitat affected. In general, it is the associated faunal communities that are more sensitive to oil pollution than the *Zostera* plants themselves (Jacobs, 1980, Zieman 1984, Fonseca, 1992). As is often the case, dispersants are likely to be more harmful to *Zostera* than oil, and coated plants should be left untreated.

Eggs and planktonic larval stages of fish, molluscs and crustacea are also vulnerable to contact with oil in surface waters. Because of the physically contained nature of the Exe marine site, recruitment could be threatened over relatively long time scales.

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. Processed products include petrol and diesel and a range of petrochemicals, e.g. propylene, acetylene, benzene, toluene and naphthalene. In addition to shipping, sources also include river-borne discharges, (including road runoff and licensed and unlicensed discharge to sewers) diffuse discharges from industrialised municipal areas, oil production sites and the atmosphere (PAH's).

There are no EQS values for hydrocarbon oils in estuarine waters *per se*. Two directives list criteria which can be used as general guidance; the Bathing Waters Directive (*see* annex 4), under the heading organic substances - 300µg l^{-1} as the 90^{th} percentile (non-routine sampling prompted by visual or olfactory evidence of hydrocarbon presence); and the Shellfish Waters Directive (*see* annex 3), listed under organic substances, which states that 'hydrocarbons must not be present 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'. Also under the Shellfish Waters directive, hydrocarbon contamination is (presumably) included in 'general physico-chemical parameters' – tainting substances – where 'the concentration of substances affecting the taste of shellfish must be lower than that liable to impair the taste of the shellfish'.

These EQS guidelines for Shellfish waters are obviously difficult to quantify, however tainting (an odour or flavour foreign to the product) can occur in commercial species contaminated with crude and refined oils. Species with a high body fat content such as salmon or herring are more easily tainted and retain the taint for longer than lean-muscle species. GESAMP (1993) report studies detecting taints in fish and macro-crustaceans resulting from exposure during acute incidents, chronic discharges and in experimental studies. There are no accepted permissible standards for organisms. In some instances, hydrocarbons may be present at well above background levels, even though no taint can be detected. Conversely fish can be tainted where analysis indicates that contamination is only at background levels. Experimental studies indicate that taints can be detected when fish are exposed to concentrations of oil in water in the range 0.01 to 1mg l^{-1}. Tainting can occur very rapidly on exposure (within a few hours at concentrations of oil above 1 mg l^{-1}), and fish have been shown to lose their taint within 1 to 4 days (experimental study on cod). However, field studies have indicated that fish may still be tainted days or weeks after a spill of fuel oil (GESAMP 1993). Because fine sediments absorb and retain oil, infaunal species such as clams and burrowing shrimps, and some demersal fish may be at risk of tainting on a more prolonged basis.

The EA database provided no information on 'hydrocarbon oils' for rivers or discharges and only limited data for estuarine shellfish waters in the SPA (figure 28). Their significance is difficult to assess with respect to the above guidelines. Although the majority (68%) of samples were <DL, there were occasional high values, and median concentrations in the Bull Hill samples were elevated, perhaps to levels where tainting could occur in fish. These data are now almost 10 years old however, and in need of updating in order to comment, realistically, on sources and current water quality status with regard to hydrocarbons, together with their potential impact on estuarine biota and shellfish beds.

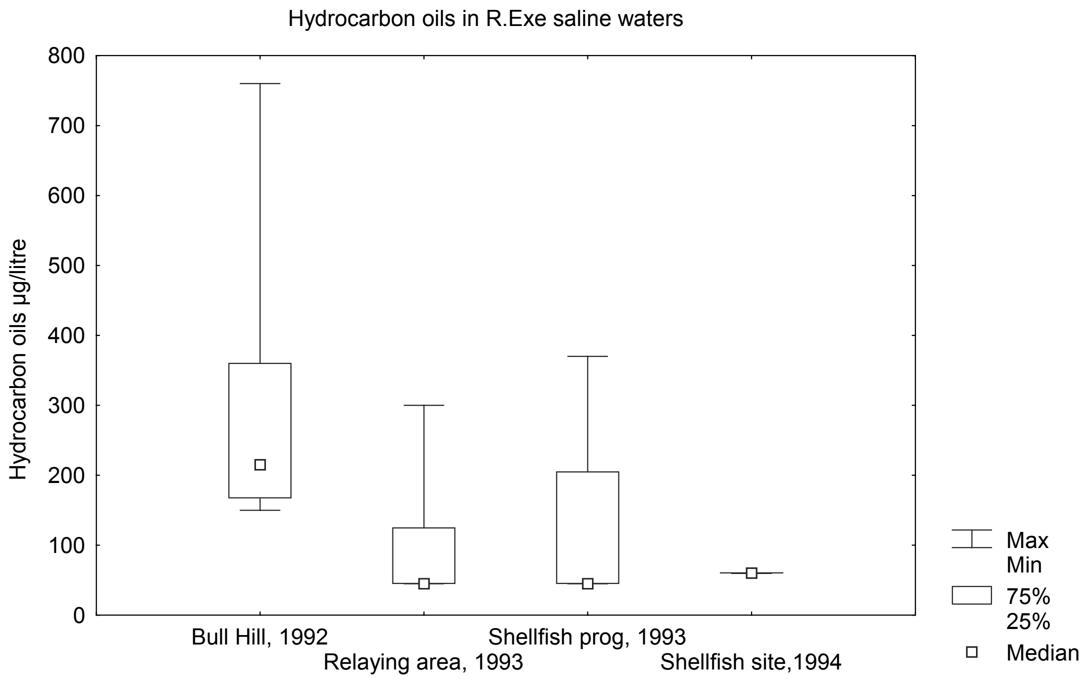


Figure 28. Hydrocarbon oils in waters of the shellfish area, Exe Estuary. (Data source EA).

PAH's

PAH's are ubiquitous environmental contaminants, estimated to constitute some 8% by weight of the total hydrocarbon composition (Kirby *et al*., 1998). Although they can be formed naturally (e.g. oil seeps, forest fires) the predominant source of PAHs is often anthropogenic emissions, and the highest concentrations are generally found around urban centres (Cole *et al*., 1999). Most of this pollutant load enters waterways from storm water overflows by means of adsorption to particulates. Thus, in the aquatic environment, PAHs are generally highest in sediments, intermediate in biota and lowest in the water column. They are of particular concern in the marine environment as the lower molecular weight PAHs are toxic to marine organisms (Law *et al*., 1997). PAH concentrations in sediments may be persistent (particularly where tidal action is restricted, and degradation limited by anoxia). In addition, some PAHs have been identified as endocrine disruptors (Anderson *et al*., 1996a,b; Kocan *et al.,* 1996).

One general concern over a number of PAHs, particularly those of high molecular weight (benzo[a]anthracene, dibenz[a,h]anthracene, benzo[b]fluoranthrene, benzo[k]fluoranthene, chrysene, benzo[a]pyrene) is that the mixed function oxidase (cytochrome P450) system can be triggered, producing carcinogenic and mutagenic metabolites in fish. Elevated levels have been linked to liver neoplasms and other abnormalities in demersal fish (Malins *et al.,* 1988). However, the risk of carcinomas is probably low at environmental concentrations of 1μg l^{-1} or less (Payne *et al*., 1988; Law, *et al.,* 1997; Cole *et al*., 1999). This is probably the situation for waters throughout the Exe system, though data is scarce.
In the absence of information on total PAHs in waters of the Exe, data on individual PAHs were extracted from the EA database to try to establish distributions, sources

and trends. However, the only data available concerns freshwater samples from the River Exe. Concentrations are summarised in table 10. These are considered to be of relatively low biological significance when placed in context with various guidelines such as those proposed by OSPARCOM (1994).

Since there are no recent data for PAHs in tidal waters, it is not possible to fully characterise the impact of PAHs in the estuarine water column, though in view of the riverine concentrations shown in table 10 (at Thorverton and Trews Weir) values in the Exe Estuary would be expected to be low in comparison with concentrations in industrialised estuaries (e.g River Tees, up to 10724ng l^{-1}; Law *et al*. 1997). Estimated ΣPAH concentrations in the River Exe upstream of the tidal limits (Trews Weir, table 10) fall below the threshold of 1 µg l^{-1} considered by Cole *et al.,* (1999) to be environmentally important.

Table 10. Individual PAHs in the River Exe (fresh water); annual averages† 1995 and percentage of samples below detection limits. (Data source EA).

	PAHs in water, River Exe ng/litre (% below detection limit)				**Guideline values** ng/litre
	Thorverton Weir		Trews Weir		
Benzo[a]pyrene	0.95	50%	3.43	43%	10-100[1]
Benzo[b]fluoranthene	0.88	100%	8.0	13%	
Benzo[e]pyrene	1.03	86%	1.33	71%	
Benzo[g,h,i]perylene	2.76	71%	2.46	29%	20[3]
Benzo[k]fluoranthene	0.88	100%	8.0	12%	100[3]
indeno-[1,2,3-cd]-pyrene	12.0	100%	12.0	100%	
Chrysene	0.5	100%	1.65	50%	
Fluoranthene	3.0	100%	5.68	57%	10-100[1]
Naphthalene*			328	80%	500 aa; 80,000max[2]
Σ above PAHs	22		371		

† Mean calculated using ½ DL values, where below detection
*annual average for naphthalene is for 1999.
Guideline values:
[1]JMP provisional ecotoxicological assessment criteria (Oslo and Paris Commissions (1994) Ecotoxicological Assessment Criteria for trace metals and organic microcontaminants in the North-East Atlantic);
[2] EQS for naphthalene is 500ng l^{-1} annual average; 80µg l^{-1} maximum;
[3]Maximum permissible concentrations in Dutch waters are 100 ng l^{-1} and 20 ng l^{-1} for benzo(k)fluoranthrene and benzo(ghi)perylene, respectively.

A study conducted in 1981 by Herrmann and Hubner also tends to confirm that PAH concentrations in estuarine waters of the Exe generally would be expected to fall below ecotoxicological guidelines (though fluoranthene in the upper estuary, near Topsham - table 11 - would have exceeded the lower OSPAR threshold). Concentrations of PAHs in the main channel in upper estuary were highest due to the high levels of suspended solids, and decreased, in the main channel, towards the mouth of the estuary. Concentrations of PAHs in samples over tidal flats

(Powderham Sands), away from the main channel, are considerably lower confirming that the PAHs are largely transported along the tidal channel and are dominated by particulate fluxes (Herrmann and Hubner, 1982).

Table 11. PAH concentrations in Exe river and estuarine water. (From Herrmann and Hubner, 1982).

	PAH concentration ng l^{-1}			
	benzo(a)pyrene	**fluoranthene**	**benzo(ghi)perylene**	**indenopyrene**
		freshwater		
Trews Weir	2.2	22	1.2	2.3
		estuary –tidal channel		
channel upper (nr Topsham)	4	53	8.6	11.0
channel mid (off Lympstone)	2.3	34	4.1	4.8
channel lower (Bull Hill)	1.3	9	1.0	1.3
		estuary - over tidal flats		
Powderham sands	0.48	12	1.3	3.6

Based on observed environmental behaviour, physical and chemical properties, microbial degradation rates and statistical analyses, PAHs are divisible into two groups: *Group 1* or low molecular weight (≤200) PAHs (including naphthalene, phenanthrene and anthracene) have a low affinity for particulates and are subject to microbial degradation. Their solubility and vapour pressure is higher than group 2 PAHs, and photo-oxidation and air-water exchange are important in estuaries. Consequently group 1 PAHs tend to have comparatively shorter residence times and often exhibit a complex distribution pattern. In contrast, *group 2* or high molecular weight (≥200) homologues (including benzo(a)pyrene, fluoranthrene, pyrene and chrysene), are readily adsorbed onto particulates. They are often correlated with suspended solids along estuaries and, due to the high particulate affinity and microbial refractivity, the principal fate of group 2 PAHs may be sediment burial.

Since many PAHs (especially group 2) have such an affinity for particulates, concentrations in estuarine sediments tend to be much higher than in water. Data from a pilot study of PAHs in sediments around the UK are reported as part of the National Monitoring Programme (MPMMG, 1998; Woodhead *et al*. 1999). Concentrations range from undetectable at offshore sites (such as the central English Channel) to 43,470µg kg^{-1} dry weight on the River Tyne at Hebburn. Total PAH concentration in sediments from Exe sites are highly variable and are low in sandier substrates but moderately high upstream, notably in mud samples at Turf (table 12). Lindley *et al*., (1998) also found elevated levels of PAHs in fine sediment samples taken from the Exe above Turf Locks in 1995: concentrations were greater in anaerobic (3-6cm) layers than in the surface sediments.

Table 12. Concentrations of PAHs in sediment, Exe Estuary (adapted from Woodhead *et al.*, 1997)

	Concentrations of PAHs in surface sediment (µg kg^{-1} dry wt)				
	Exe Turf Buoy	Exe No 21 Buoy	Exe No 13 Buoy	Threshold effect level* TEL	Probable effect level* PEL
Naphthalene	197	<13	<13	34.6	391
Acenaphthene	283	<4	<4	6.7	89
Fluorene	232	<15	<15	21.2	144
Phenanthrene	416	<11	42	86.7	544
Anthracene	94	<1	<1	46.9	245
Fluoranthene	935	<4	<4	113	1494
Pyrene	689	<2	<2	153	1398
Benzo[a]anthracene	380	<2	<2	74.8	693
Chrysene	240	<2	<2	108	846
Benzo[e]pyrene	876	<3	<3		
Benzo[b]fluoranthene	479	<3	<3		
Benzo[k]fluoranthene	230	<1	<1		
Benzo[a]pyrene	479	<2	<2	88.8	763
Dibenzo[a,h]anthracene	11	<3	<3	6.2	135
Benzo[g,h,i]perylene	346	<5	<5		
Total PAH	5889	nd	42	1684	16770

ND: no PAH compounds detected
* Thresholds from Macdonald *et al*., 1996

Although PAH concentrations at Turf, near the entrance to the Exeter Canal, are not as high as those recorded in highly industrialised estuaries, the reported levels represent a potential contribution to the threat of harmful effects to benthic organisms. As indicated above, carcinogenic and mutagenic intermediates, and the formation of PAH-DNA, adducts may arise in fish through the actions of cytochrome P450. Parts of this enzyme system (e.g ethoxyresorufin-O-deethylase – EROD – activity) can be induced in fish exposed to sediments containing ΣPAH concentrations between 1000-3000 µg kg^{-1} dry weight, and possibly lower (Payne *et al*., 1988; Woodhead *et al*., 1999) – i.e. within the range encountered at Turf. Similar levels have also been shown to reduce growth of larval fish, presumably weakening their resistance to disease and other stressors (Misitano *et al.,* 1994). Less is known of the toxicity to invertebrates, though sub-lethal effects on crustacea, perhaps exacerbated by UV, have been observed at 1000-6000 µg kg^{-1}dry weight (Alden and Butt, 1987; Ankley *et al.,* 1994).

PAH concentrations at Turf are above the Threshold Effect Level (ΣPAH) of 1684 µg kg^{-1} dry weight, proposed by Macdonald *et al*., (1996) but below the Probable Effects Level of 16770 µg kg^{-1}dry weight (table 12). The same applies also for most individual PAHs, though concentrations of acenaphthene and fluorene are above their PELs by a small margin (table 12). Any effects, if they occur, are likely to be chronic rather than acute and restricted to muds towards the head of the estuary, rather than in sandier sediments further downstream.

The study of PAH behaviour in the Exe Estuary in 1981 by Herrmann and Hubner also demonstrated that PAHs have an affinity for fines, and that hydrodynamic transport processes largely govern distributions in sediments. Natural settling processes at the turbidity maximum create a region of high PAH concentration in the upper estuary and much lower concentrations in the lower, marine-dominated estuary (Herrmann and Hubner, 1982). Mean values were 125 $\mu g\ kg^{-1}$ (dw) for indenopyrene, 218 $\mu g\ kg^{-1}$ for benzo(a)pyrene, 161$\mu g\ kg^{-1}$ for fluoranthene and 115$\mu g\ kg^{-1}$ for benzo(ghi)perylene.

In view of the uncertainties over the proposed ecotoxicological guidelines for sediments, further work will be needed to assess the extent of contamination in sediments and the actual biological consequences of PAHs for the Exe marine site.

Unfortunately, no body burden data for PAHs could be found for Exe biota and it is only possible to speculate on the impact on organisms. Exposure pathways to most aquatic organisms probably consist of both water and dietary sources, including sediments. Feeding habit and lifestyle will be significant factors in modifying the bioavailability of PAHs, as with most contaminants. Because of their stronger affinity for sediments, high molecular weight PAHs are likely to be accumulated more strongly by deposit-feeders, rather than by those types which process overlying waters.

Irrespective of assimilation pathway, PAHs, because of their affinity for organic matter, have a tendency to be accumulated by organisms. Set against this, the MFO system of certain taxonomic groups is capable of metabolism and elimination of some of the smaller molecules (though as indicated above this does not make the hosts immune to effects). Fish and polychaetes are among the most efficient PAH metabolisers (tissue concentration factors generally less than 500) whilst in crustacea and bivalves metabolism is slow, particularly for larger PAHs (concentration factors 3000-6000).

Bivalves are therefore probably better indicators of PAH distributions (though not necessarily biological effects) compared with fish, and are of particular relevance in the Exe Estuary in view of its designation as a shellfish water. Measurement of PAHs in molluscs (both commercial and native bioindicator species) should be seen as a priority for future monitoring.

There are no UK standards for PAHs in shellfish, though the German Federal Health Department has a cautious guideline of 25 $\mu g\ kg^{-1}$ in fish oil. A Canadian guideline value of 1-4 $\mu g\ kg^{-1}$ (depending on the level of fish/shellfish consumption) has been established for benzo (a) pyrene, again based on human health concerns, rather than in an ecotoxicological context.

According to NOAA's mussel-watch programme in the United States, a ΣPAH concentration of 1100$\mu g\ kg^{-1}$ dry weight in molluscs would classify as being high - equivalent to 220$\mu g\ kg^{-1}$ wet weight (assuming a wet:dry weight ratio of 5, an approximation based on our own data for wet to dry ratios in shellfish).

6.1.4 Pesticides, Herbicides, PCBs, volatile organic compounds.

This section deals with pesticides, herbicides, PCBs and volatile organic compounds (VOCs), including any evidence of their involvement in endocrine disruption.

CEFAS monitors levels of selected pesticides and other potential endocrine disrupting chemicals in bivalves from UK designated shellfish waters. Analyses of cockles, mussels and oysters made between 1995 and 1996 imply that pesticide body burdens in most shellfish waters in England - including, presumably, the Exe Estuary - were close to or below detection limits. Typically, concentrations on a wet weight basis were; α,γ HCH - 0.003 mg kg^{-1}; dieldrin 0,001 - 0.007 mg kg^{-1}; DDT - 0.001-0.003 mg kg^{-1}. The maximum concentration of PCBs (Σ25 congeners) was 0.07 mg kg^{-1} wet wt. Thus, concentrations of pesticides and PCBs in these bivalves were generally considered of little toxicological importance (CEFAS, 2001).

Unfortunately, the data on this group of compounds, specifically relating to the Exe Estuary, is only fragmentary. Analyses of unspecified shellfish species have been extracted from WIMS and summarised in table 13. Concentrations of most compounds are below detection limits, therefore estimates of means are largely based on ½DL values. Because the data are extremely sparse, both numerically and geographically (two adjacent sites in the lower estuary, Bull Hill and the non-designated shellfish programme site), a comprehensive risk assessment is not possible, though the predominance of <DL values supports the notion that pesticides, herbicides and PCBs pose little threat to the Exe SPA.

Table 13. Organic contaminants (µg kg^{-1} wet wt) in unspecified shellfish from the shellfish beds in the lower Exe, 1992-1994. (Data source EA).

Compound	Mean µg kg^{-1} (wet wt.)*	Values <detection (%)	No. of values
ALDRIN	2.33	100%	4
DDT (PP)	7.57	67%	3
DDT (OP)	1.58	100%	3
DDE (OP)	2.23	100%	2
DDE (PP)	3.42	67%	3
DIELDRIN	1.46	100%	4
ENDOSULPHAN ALPHA	1.36	100%	4
ENDOSULPHAN BETA	2.50	100%	1
ENDRIN	1.40	100%	4
HCH GAMMA	1.66	75%	4
HEXACHLOROBENZENE	0.93	100%	4
HEXACHLOROBUTADIENE	1.36	100%	4
ISODRIN	1.21	100%	4
TRIFLURALIN	2.38	100%	3
PCB NO.28	0.0000050	100%	4
PCB NO.101	0.0000050	100%	3
PCB NO.118	0.0000063	75%	4
PCB NO.138	0.0000050	100%	4
PCB NO.153	0.0000050	100%	4
PCB NO.180	0.0000050	100%	3
PCB Total (Σabove isomers)	0.0000313		

*Mean calculated using ½ DL values, where below detection

More extensive, targeted sampling will be needed confirm the absence of any significant accumulation of these synthetic organic contaminants, and should incorporate sediments and sediment-dwelling species such as clams and worms. The most likely anticipated threat would be from sediments in the upper estuary where there is very little current data. The discussion below describes some of the EA observations on organic contaminants in water, and potential threats, which may help to target future sampling.

Organochlorine pesticides (OCs)

OCs of relevance include agricultural pesticides dichlorodiphenyltrichloroethane (DDT) and its metabolites DDE and TDE; chlorinated cyclodiene insecticides such as aldrin, dieldrin and heptachlor (most widely used as seed dressings and soil insecticides); and hexachlorocyclohexanes (HCHs), such as lindane (used against pests and parasites of farm animals and also in insecticidal seed dressings). Although most of these compounds have been banned in the UK, they may persist in environmental samples. Several organochlorine pesticides have been identified as endocrine disrupting substances (e.g dieldrin, aldrin, endrin, lindane, endosulfan, DDT and its metabolites). Many OCs are toxic List I contaminants.

Once in the environment OCs are persistent contaminants. They are stable and degrade very slowly, some taking 100 years to break down completely into harmless chlorides, whilst others do not degrade to any appreciable extent. Moreover when OCs do break down, the products are often more toxic and hazardous than the original substance. In general, these compounds have low water solubility and are therefore likely to sorb strongly to suspended solids and sediments. The majority of OCs are lipophilic, dissolving readily in fats, and tend to accumulate in the fatty tissues of living organisms. Invertebrate and fish species accumulate OCs in their tissues which can be transferred and magnified along the food chain, resulting in very high concentrations of OCs in upper trophic levels such as birds and marine mammals.

With the exception of isolated cases of exposure to concentrated compounds, the effects of OCs on marine life tend to be chronic rather than acute, with different OC compounds having similar effects and possibly acting synergistically (Leah *et al.,* 1997).

DDT

DDT and its residues interfere with calcium metabolism and were responsible for the well-documented phenomenon of eggshell thinning in sea- and land-birds during the 1960's when many eggs did not survive incubation, and a number of species were threatened with extinction. In general, environmental concentrations of the parent compound DDT are now lower than its metabolites and, like other organic substances, preferentially absorb onto sediments, particularly where these are fine-grained and/or contain a high proportion of organic carbon (Cole *et al.*, 1999).

No published papers on levels of DDT in sediments or water of the Exe could be found. It is likely that the majority of pesticides present in the environment nowadays are predominantly at low levels in the water column, and that sediments, together with biota, form the major reservoirs for these compounds.

Over the last decade, concentrations of p,p-DDT in freshwaters entering the SPA via the rivers Exe and Clyst have, for the majority of samples (99%), been below detection limits. These have varied between 5 and (most recently) 1ng l^{-1} – compared with an EQS of 10ng l^{-1}. Likewise all values for o,p-DDT during the 1990s (measured at Thorverton only) were below the limits of detection (3-12 ng l^{-1}). On this evidence, riverine sources of DDT are probably not a significant issue. This is evidently also the case for sewage discharges. Concentrations in Countess Wear STW final effluent in 2001 were consistently below DL (5 ng l^{-1}). The last samples analysed from Exmouth STW (1996) and Dawlish STW (1992) were also below limits of detection (0.4 and 4 ng l^{-1} respectively). As a result, the impact on the marine site from DDT is considered to be minimal: only 2% of the tidal waters sampled during the last decade had concentrations above detection limits (currently 0.4ng/l). Variations in the summary statistics for different estuarine sites shown in figure 29 are therefore largely a reflection of changing detection limits but demonstrate compliance with the estuarine EQS (10 ng/l ppDDT, 25 ng/l for total DDT) by a substantial margin.

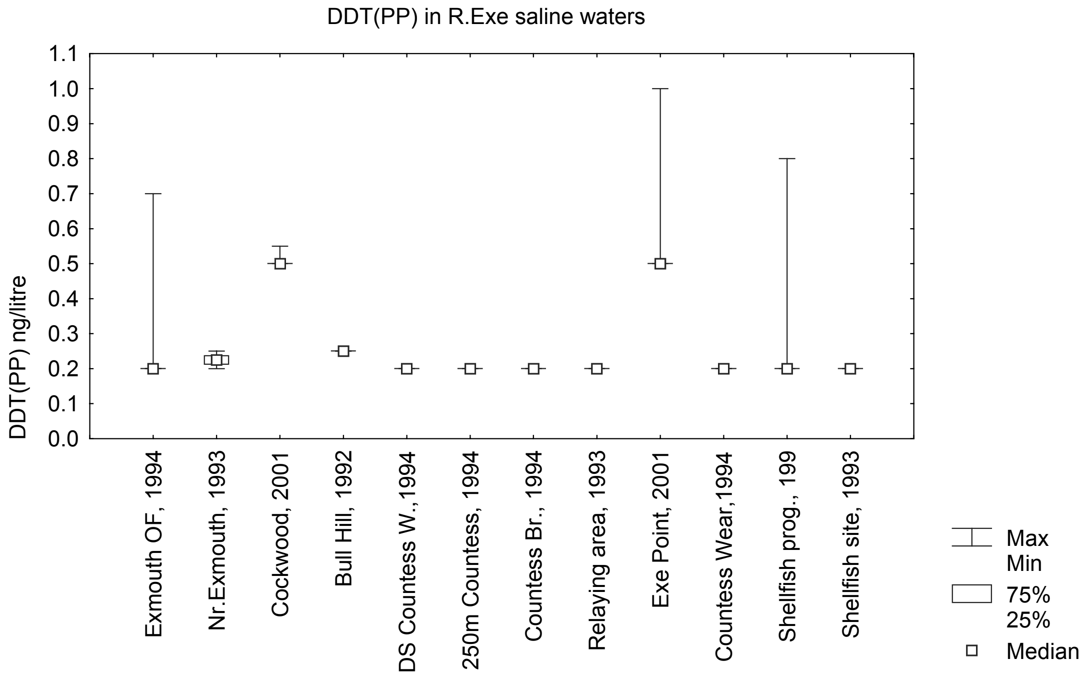


Figure 29. ppDDT in Exe estuarine waters. Data source EA.

The scarce data on DDT in sediments (from EA sources) are discussed in section 7 (see tables 31 and 32). Even though the sum of DDT and DDE isomers in sediments from the head of the estuary appears to be above the PEL, this is probably artifactual, due to the fact that the majority of values are below detection limits which are themselves often above the guideline value.

EA shellfish samples contain low levels of DDT (table 13). Even when different isomers are combined, concentrations are an order of magnitude below the recommended 'no-effects' guideline of 100 μg kg^{-1} (dw) set by ADRIS (Association of Directors and river Inspectors in Scotland) under the EU Shellfish Growing waters directive, to protect shellfish and their larvae (ADRIS, 1982). They are also below the 'high value' of 140 µg kg^{-1} which categorises the top 15% of values seen in NOAA's Mussel Watch programme in the USA. This suggests that the sampled Exe 'shellfish' are not at risk from DDT.

Dieldrin and Endrin

Dieldrin, along with other 'drins' (aldrin, endrin, isodrin), is another endocrine-disrupting OC pesticide of potential concern in the SPA (Allen *et al.,* 2000). Dieldrin is highly toxic to fish and other aquatic animals and is said to be largely responsible for the dramatic decline of the otter population in the UK during the '50s and '60s. Dieldrin, used in sheep dips and seed dressings, leached into water systems and became concentrated in the fatty tissues of fish such as eels, which are a major component of the otter diet. The result was a dramatic decline, which reached its nadir, nationally, in the early 1970s, when otters were restricted to a handful of upland tributaries on the cleanest rivers[1].

Of the 'drins' group of pesticides, dieldrin tends to be the most common in biological samples, as other 'drins' tend to revert to dieldrin in the natural environment and are unlikely to be detected unless the organism has been recently exposed (MPMMG, 1998).

Over the last decade, concentrations of dieldrin in freshwaters entering the SPA via the Exe and Clyst have been below detection limits (most recently ~1 ng l^{-1} for the Exe at Thorverton and Trews Weir; 4 ng l^{-1} for the Clyst in 1994 when last monitored) – i.e. below the EQS of 10 ng l^{-1} (fresh- and salt-water). On this evidence, riverine sources of dieldrin are probably not a significant issue. This is also the case for monitored sewage (STW) discharges, where three quarters of samples were below limits of detection. Latest available summary statistics for dieldrin concentrations in final effluent from Countess Wear STW, Exmouth STW and Dawlish STW are shown in table 14 (based on ½ DL).

Table 14. Dieldrin concentrations in final effluent samples from STW (based on summary statistics for last year in which data are available)

STW effluent	Year	N	Min	ng l^{-1} Max	Median
DAWLISH (SEA LAWN) CRUDE SEWAGE OUTFALL	1992	8	1.9	17.3	7.55
EXETER (COUNTESS WEAR) STW FE	2001	14	0.5	5	2.5
EXMOUTH FE (EXMOUTH/BUDLEIGH SCHEME)	1996	4	1	6.5	3.05

As a result of these negligible inputs, impact on the marine site is likely to be minimal; only 20% of the tidal waters sampled during the last decade had concentrations above detection limits (0.5 - 5ng/l, most recently 1 ng l^{-1}). Latest available summary statistics for dieldrin concentrations in tidal waters are shown in

[1] http://www.nfucountryside.org.uk/wildlife/home.htm 2002

table 15 (again based on ½ DL). Median values are below the dieldrin standard by more than an order of magnitude throughout the Exe Estuary.

Table 15. Dieldrin concentrations in tidal waters, Exe Estuary (based on summary statistics for last year in which data are available)

site	year	n	Min	ng l^{-1} Max	Median
EXMOUTH OUTFALL AT SURFACE BOIL	1994	6	0.30	1.10	0.33
SEA IN VICINITY OF EXMOUTH OUTFALL	1993	2	0.30	0.35	0.33
RIVER EXE AT COCKWOOD	2001	8	0.50	0.55	0.50
RIVER EXE ADJACENT TO BULL HILL	1992	8	0.30	2.50	0.30
RIVER EXE 100M D/S COUNTESS WEAR STW	1994	8	0.30	2.50	0.80
RIVER EXE 250M D/S COUNTESS WEAR STW	1994	10	0.30	1.50	0.65
RIVER EXE AT COUNTESS WEAR ROAD BRIDGE	1994	6	0.30	1.00	0.35
RIVER EXE AT RELAYING AREA	1993	8	0.35	0.35	0.35
RIVER EXE AT THE POINT	2001	5	0.50	2.50	0.50
RIVER EXE COUNTESS WEAR STW SURFACE BOIL	1994	6	0.30	3.40	0.35
RIVER EXE NONDESIGNATED SHELLFISH SITE	1993	8	0.35	0.35	0.35

Dieldrin concentrations in estuarine sediments may appear to exceed the ISQG guideline (but not the PEL) though again this appears to be largely a function of detection limits (section 7).

EA shellfish samples from the Exe contain undetectable levels of dieldrin (table 13). Using half detection limits for these samples the average value is almost two orders of magnitude below the recommended 'no-effects' guideline of 100 µg kg^{-1} (dw) set by ADRIS. They are also below the 'high value' of 9.1 µg kg^{-1} which categorises the top 15% of values seen in NOAA's Mussel Watch programme. This suggests that the sampled 'shellfish' are not at risk from dieldrin.

The pattern of distributions and concentrations of other 'drins' such as endrin is virtually the same as for dieldrin. Concentrations in freshwaters of the Exe and Clyst have, without exception been below detection limits (most recently ~1 ng l^{-1} for the Exe at Thorverton and Trews Weir; 4 ng l^{-1} for the Clyst in 1994 when last monitored) – i.e. below the EQS of 5 ng l^{-1} (fresh- and salt-water). On this evidence, riverine sources of endrin are probably not a significant issue. This is also the case for monitored sewage (STW) discharges, where all samples were below limits of detection. Latest available summary statistics for endrin suggest concentrations were <5 ng l^{-1} in final effluent from Countess Wear STW (2001), Exmouth STW (1999) and Dawlish STW (1992).

Thus impact on the marine site is likely to be minimal; none of the tidal waters sampled during the last decade had concentrations above detection limits (most recently <1 ng l^{-1}. Endrin (and isodrin) concentrations in estuarine sediments and shellfish were all below detection limits (and, for sediments, below the ISQG and PEL guidelines).

Hexachlorocyclohexanes: γ-HCH (lindane) and other isomers.

Due to its toxicity and endocrine-disrupting effects, the use of lindane is currently being phased out in Europe following an EU decision in 2000 to ban it. However, its use on food crops (especially cocoa) imported from other counties results in lindane residues in sewage effluent. Lindane and dieldrin were amongst five pesticides listed as most frequently exceeding 0.1µg l^{-1} in estuaries and coastal waters of the south west during 1993 (NRA 1995), but the current analysis of EA data suggests this is no longer the case in the Exe.

The EA database contains entries for total hexachlorocyclohexanes (HCH), and individual isomers. The majority however are at or below the limit of detection. In freshwater (River Exe at Thorverton), for example, all values for α,β,δ HCH since 1990 are <DL of 0.3-2.5 ng l^{-1} (α-HCH), 2-14.5 ng l^{-1} (β-HCH) and 0.9-4 ng l^{-1} (δ-HCH). Monitoring of γ-HCH (lindane) has been more extensive, therefore γ-HCH is principally discussed here as representative of the distribution of this group of pesticides. However, since many of these recorded values are also below detection limits (60% in freshwater and 21% in seawater) data interpretation should be viewed with caution.

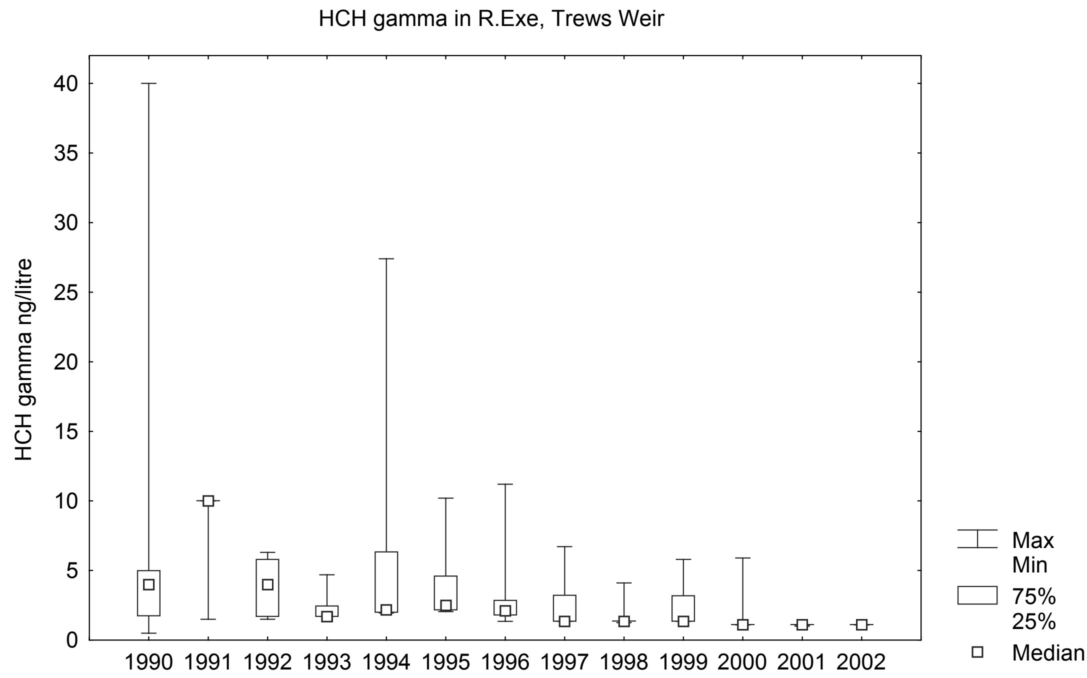
Summary statistics for concentrations of γ-HCH in the River Exe at Thorverton and Trews Weir are shown in figure 30. Annual median values have been consistently less than 5ng l^{-1} over the last decade and are currently around 1 ng l^{-1} – two orders of magnitude below the EQS of 100 ng l^{-1} for fresh-water. Individual samples have in the past contained elevated concentrations of γ-HCH, though incidences of these are rare and appear to be declining, presumably as the use of lindane in Europe is phased out. However its use on imported food crops from outside the EU could result in some γ-HCH residues being discharged in sewage effluent.

In 1994 γ-HCH was monitored in the river Clyst (Clyst St. Mary). Annual medians were similar to the Exe (1.95-7 ng l^{-1}) with the occasional higher value (up to 19.3 ng l^{-1}).

γ-HCH concentrations in estuarine waters of the Exe estuary are shown in figure 31. Median values for all sites fall below the standard for coastal waters (20ng l^{-1}).

There is an indication of slight enhancement of γ-HCH near the Countess Wear STW, suggesting a low level input from this source. However, the annual average concentration in surface boil samples for the most recent complete year (2001) was relatively low, with only occasional high values.

Undoubtedly STW have contributed measurable loadings of γ-HCH to the estuary in the recent past. For example in 1992, median concentrations of lindane in effluent samples from Countess Wear, Exmouth and Dawlish STW were 51, 29 and 32 ng l^{-1}, respectively. These inputs now appear to be declining substantially, as indicated for Countess Wear and Exmouth samples (expressed as annual averages) in figure 32. We can speculate that risks to biota from γ-HCH are now likely to be low.



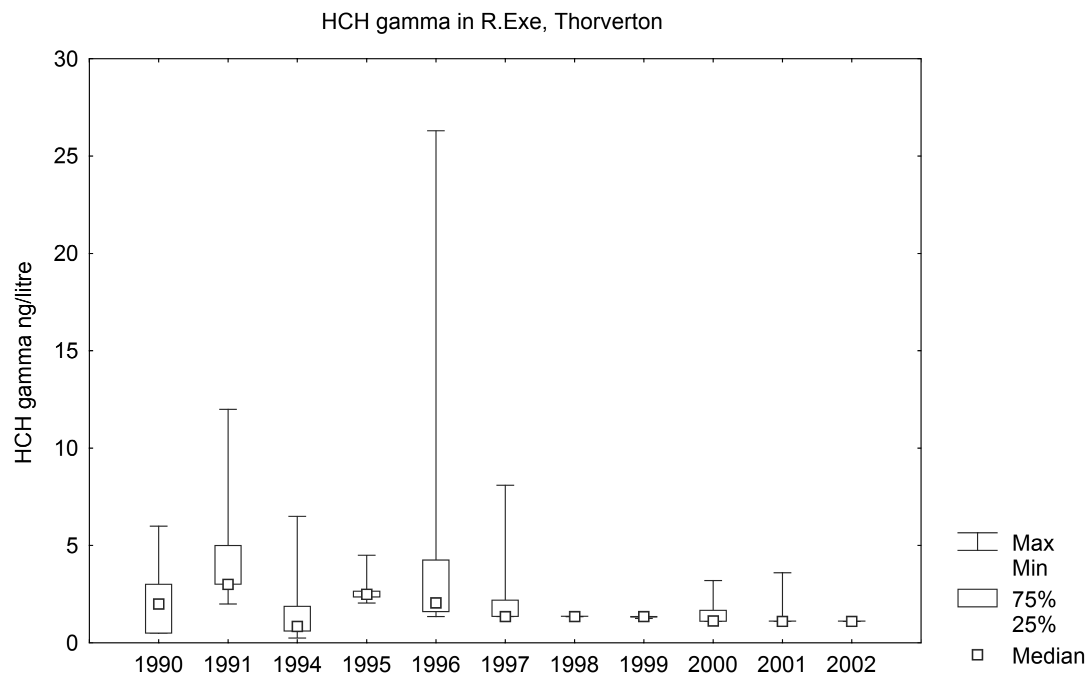


Figure 30. Concentrations of γ-HCH in the River Exe at Thorverton and Trews Weir; summary statistics. Data source EA.

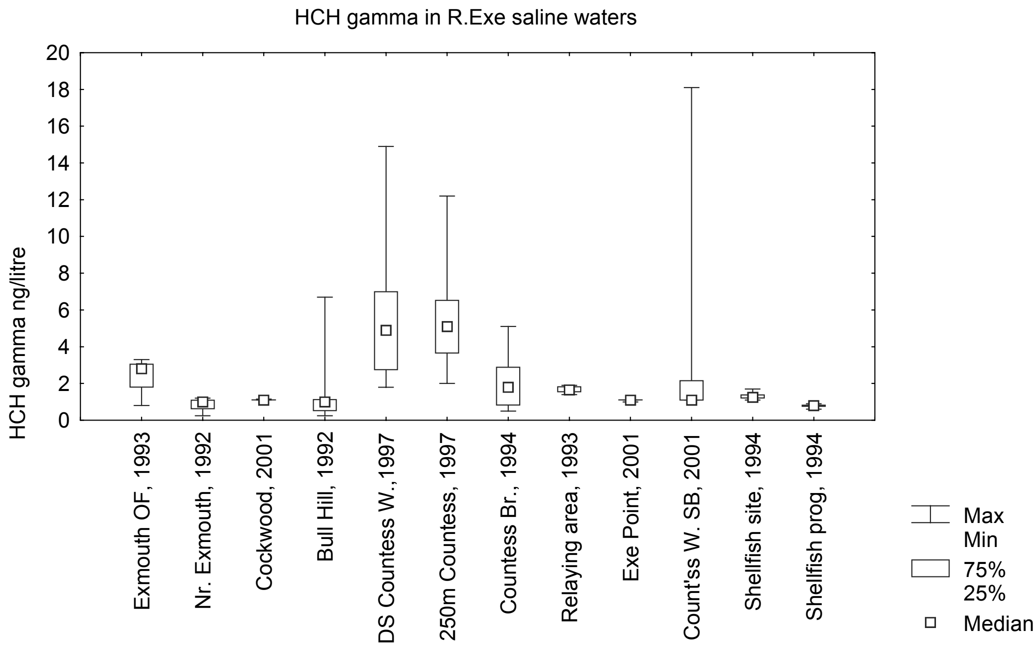


Figure 31. Lindane (γ-HCH) in Exe estuarine waters. Data source EA.

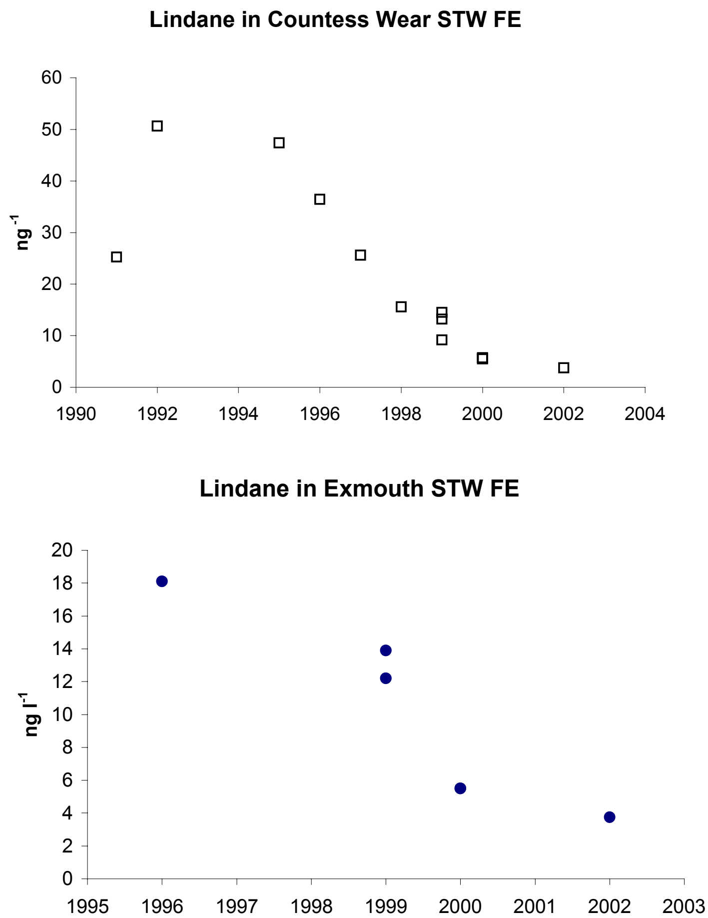


Figure 32. Annual median concentrations of lindane (γ-HCH) in final effluent from Countess Wear (upper figure) and Exmouth (lower figure) STW. (Data source EA).

Calculated mean values for γ-HCH in estuarine sediments measured in the early 1990s were above the probable effects level (see EA summary statistics in tables 31 and 32, section 7). Concentrations may have been slightly higher in the previous decade (Herrmann and Thomas, 1984) and were above the PEL throughout the estuary, without exception (table 16). It is possible, therefore, that the temporal trend in γ-HCH concentrations in Exe sediments may be downwards, in line with waters, though further monitoring is advisable to ensure standstill requirements of the Dangerous Substances Directive and Favourable Condition under the Habitats Directive.

The distribution of γ-HCH in Exe sediments described by Herrmann and Thomas (1984) was unusual, compared to that for other organic micropollutants such as PAHs and PCBs (see section 6.1.3 and later in this section). Rather than the expected decrease seaward, the pattern of γ-HCH (and also α-HCH, and another OC pesticide hexachlorobenzene-HCB) was characterised by diffuse agricultural inputs from the numerous small streams along the estuary. Concentrations were, in fact, highest at sites just inside the estuary mouth near Dawlish Warren (table 16).

Table 16. α- and γ-HCH, and HCB concentrations in Exe sediments (<63 μm fraction). (Data from Herrmann and Thomas, 1984).

	γ-HCH, α-HCH and HCB concentration ng g^{-1} (dw)		
	γ-HCH	**α-HCH**	**HCB**
upper estuary-tidal channel	9.8	4	8.8
upper estuary – flats	7.1	2.1	6.7
mid-estuary-tidal channel	8.3	7.8	4.4
mid/low estuary-flats	8.1	4.7	2.4
Cockle Sand-Exmouth	6	1.2	2.2
Dawlish Warren	13.1	8.9	31

EA shellfish samples from this part of the Lower Exe contain γ-HCH (table 13) though concentrations are well below the recommended 'no-effects' guideline of 30 μg kg^{-1} (dw) set by ADRIS. This suggests that the sampled 'shellfish' are not at risk from γ-HCH, though more detailed information is needed.

Endosulphan

Endosulfan is a mixture of two isomers, endosulphan A, and B, and is one of the few organochlorine pesticides which is still in use in the UK. It is a 'red list', and list II compound linked to fatal poisoning incidents in West Africa (Ton *et al.,* 2000). The high toxicity of endosulfan has led to its ban in many countries. Endosulphan has been identified as an endocrine disruptor, and is toxic to algae and invertebrates (particularly crustaceans) at concentrations above the EQS of 0.003μg l^{-1} (Cole *et al.*, 1999).

Over the last decade, concentrations of endosulphan (A and B) in freshwaters entering the SPA via the Exe and Clyst have, without exception, been below detection limits (0.6-40 ng l^{-1} for endosulphan A; 1-15 ng l^{-1} for endosulphan B - compared with an EQS of 3 ng l^{-1}). Using ½ detection limits, the most recent data for endosulphan A indicates annual median values of 0.3ng l^{-1} at Thorverton (1994), 3 ng l^{-1} at Clyst St Mary (1994) and 0.5 ng l^{-1} at Trews Weir (2001). On a similar basis the most recent data for endosulphan B indicates annual median values of 1ng l^{-1} at Thorverton (1994) and Trews Weir (2001) on the Exe, and 7 ng l^{-1} at Clyst St Mary (1994). On this evidence, riverine sources of endosulphan are probably not a significant issue, though an accurate assessment is clearly not possible since detection limits are sometimes above the EQS.

This is also the case for sewage discharges, for which all endosulphan determinations are <DL. In Countess Wear STW effluent (1999) the annual average concentration for endosulphan A and B in 1999 was 2ng l^{-1} (based on ½ DL; all values below DL). At Exmouth (1996) the corresponding values were 0.3 and 1 ng l^{-1}. On this basis inputs from STW sources appear to be negligible.

Up to the mid 1990s when routine monitoring of endosulphan in tidal waters appears to have ceased, all values were below detection limits. Calculated median values for the most recent years, based on ½ DL, are shown in table 17. and indicate values were below an EQS of 3 ng l^{-1}.

Table 17. Endosulphan A and B in tidal waters. Annual averages, assuming ½ DL values (Data source EA)

Exe estuary site	year	endosulphan A median ng l^{-1}	endosulphan B median ng l^{-1}
EXMOUTH OUTFALL AT SURFACE BOIL	1994	0.3	1
RIVER EXE ADJACENT TO BULL HILL	1992	0.75	0.75
RIVER EXE 100M D/S COUNTESS WEAR STW	1994	0.3	1
RIVER EXE 250M D/S COUNTESS WEAR STW	1994	0.3	1
RIVER EXE AT COUNTESS WEAR ROAD BRIDGE	1994	0.3	1
RIVER EXE AT RELAYING AREA	1993	0.3	1
RIVER EXE AT THE POINT	1994	0.3	1
RIVER EXE COUNTESS WEAR STW SURFACE BOIL	1994	0.3	1
RIVER EXE NON DESIGNATED SHELLFISH SITE	1994	0.3	1

Greve and Wit (1971) found that 75% of the endosulfan in the River Rhine was associated with particulate matter (mud and silt), therefore sediment levels in the SPA may be more relevant, toxicologically. However, all values for Exe sediments were below detection limits (see tables 31 and 32, section 7). Similarly endosulphan levels in EA shellfish samples from the Exe were undetectable (table 13). It is likely therefore that impact on the marine site is minimal.

Organophosphate pesticides (OPs)

OPs were first introduced for use in insecticides and fungicides in the 1950s, but remained second choice pesticides behind organochlorines until concerns over the environmental persistence of these compounds (notably DDT) began to surface in the 1970s. As the use of organochlorines tailed off, OPs succeeded them, and use in the UK increased during the mid 1980s. Throughout this time OPs became widely used both in livestock and arable farming. However, changes in the regulations on sheep dipping have meant that use of OPs in the livestock sector have declined in recent years. Overall, OPs now account for some 38% of total pesticide use globally, although the figure for Western Europe is somewhat lower than this (~26%). Organophosphate (and carbamate) pesticides have the potential to exhibit neurotoxic activity at low concentrations. Zinkl *et al.* (1991) cite examples of median lethal concentrations of OPs (parathion and azinphos-methyl) to fish as low as 10µg l^{-1}. Sub-lethal effects on olfactory function in Atlantic salmon were observed after exposure to the OP diazinon at concentrations as low as 1 µg l^{-1}, and significantly reduced levels of reproductive steroids in mature male salmon parr resulted from exposure to 0.3µg l^{-1} diazinon (Moore and Waring, 1996).

Organophosphates enter the marine environment via spillage, industrial effluents, spray-drift and run-off from agricultural land. Several OPs are on list II water quality standards for the protection of marine life. Principal OP compounds which have been identified as of potential concern in the marine environment include; azinphos-methyl, malathion and fenitrothion (Cole *et al.,* 1999).

Samples from the River Exe and, occasionally the Clyst, have been analysed for several OPs including azinphos (-ethyl and-methyl) fenitrothion, malathion and parathion (-ethyl and-methyl). All samples were below detection limits (see table 18). In earlier years these DLs were sometimes above EQS values (expressed as annual averages). For the most recent samples however, detection limits have been well below the EQS indicating riverine inputs are unlikely to be of biological significance.

Table 18. Organophosphates (ng l^{-1}) in Rivers Exe and Clyst. Data source:EA

OP	River	% values <DL	DL range 1990-2002* (ng l^{-1})	annual median† (most recent year)	EQS ng l^{-1} mean	EQS ng l^{-1} maximum
parathion-ethyl	Exe (Thorverton)	100%	9 - 10	9 (1994)	ns	ns
parathion-methyl	Exe (Thorverton)	100%	15 -16	15 (1994)	ns	ns
azinphos-ethyl	Exe (Thorverton)	100%	25 - 87	25 (1994)	ns	ns
azinphos-methyl	Exe (Trews Weir)	100%	3* - 65	1.5 (2001)	10	40
	Exe (Thorverton)	100%	65-114	32.5 (1994)		
malathion	Exe (Trews Weir)	100%	2* - 20	1 (2001)	10	500
	Exe (Thorverton)	100%	15 – 16	7.5 (1994)		
	Clyst (Clyst St.M)	100%	5	2.5 (1991)		
fenitrothion	Exe (Trews Weir)	100%	1* - 20	0.5 (2001)	10	250
	Exe (Thorverton)	100%	8 - 9	4 (1994)		

*lower detection limits (DL) apply to the latest (2001/2002) data; †calculated by halving 'less-than' values. ns – no standard applicable

Measurements of OPs in STW effluent samples are also largely below the limits of detection, which have generally been decreasing with time. Annual averages (calculated by halving 'less-than' values), for the most recent year available, are shown in table 19. Since these are unlikely to result in concentrations above the EQS in receiving water it is unlikely that these sources represent a threat to the SPA.

The only data for OPs in sea water are for azinphos-methyl in the Countess Wear surface boil in 1993. At that time all values were below detection limits of 114 ng l^{-1} and are therefore not adequate to characterise distributions in the estuary.

Table 19. Organophosphates (ng l^{-1}) in STW effluent samples

OP	River	% values <DL	annual median† (most recent year)	EQS ng l^{-1} mean	EQS ng l^{-1} maximum
azinphos-methyl	Exmouth	100%	10 (1996)	10	40
	Countess Wear	100%	14 (2001)		
malathion	Exmouth	75%	8 (1996)	10	500
	Countess Wear	93%	8 (2001)		
fenitrothion	Exmouth	100%	10 (1996)	10	250
	Countess Wear	99%	5 (2001)		

† calculated by halving 'less-than' values. ns – no standard applicable

Simazine and Atrazine

The *s*-triazine family of herbicides to which atrazine and simazine belong have been used in large quantities (several hundred tons annually) in the UK to control weeds on croplands, roads and railways. Both atrazine and simazine are on the UK red list of toxic compounds with a combined EQS of 2µg l^{-1} (annual average) or 10µg l^{-1} (maximum allowable concentration). Though toxic, they are not accumulated significantly by organisms. They have also been identified as endocrine-disrupting substances (Allen *et al*., 2000).

Because of their major usage and high water solubility *s*-triazine herbicides are widespread in aquatic systems. In 1992 and 1993, elevated levels of atrazine and simazine were found in groundwater, freshwater and estuarine water of the southwest region. Since 1993, however, they have been banned from non-agricultural use: run-off from treated land should therefore be the main source to coastal waters.

Summary statistics for atrazine in the River Exe at Trews Weir are shown in figure 33, using ½ DL values where appropriate. The majority of values prior to 2001 are below detection limits (95%). In 2001 only 23% (3 out of 13) results were below detection. The annual medians (and maximum) for this compound are consistently below the EQS by a substantial margin. The only other freshwater site monitored for atrazine was Thorverton (in 1994): all values at this site were <DL (9 ng l^{-1}).

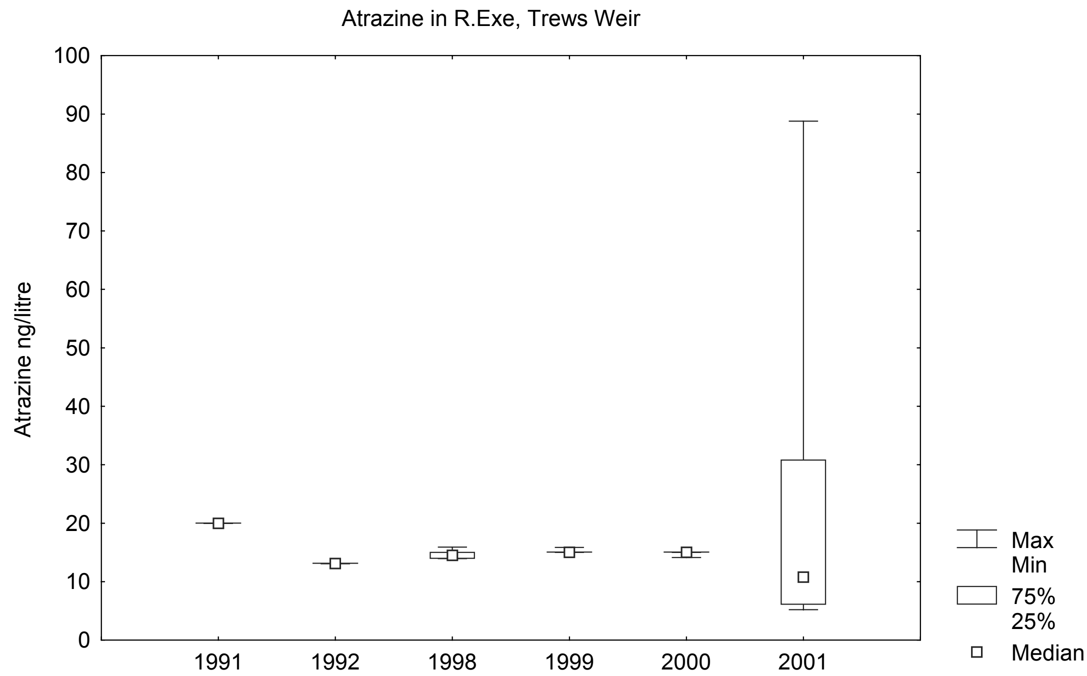


Figure 33. Atrazine in the river Exe at Trews Weir. Summary statistics. (EA data)

Summary statistics for simazine in the River Exe at Trews Weir are shown in figure 34, using ½ DL values where appropriate. The majority of values for prior to 2001 are below detection limits (92%). In 2001, 62% of results (8 out of 13) were below detection. The annual medians (and maximum) for this compound were consistently below the EQS by a substantial margin. The only other freshwater site monitored for atrazine was Thorverton (in 1994): all values at this site were <DL (5-7 ng l^{-1})

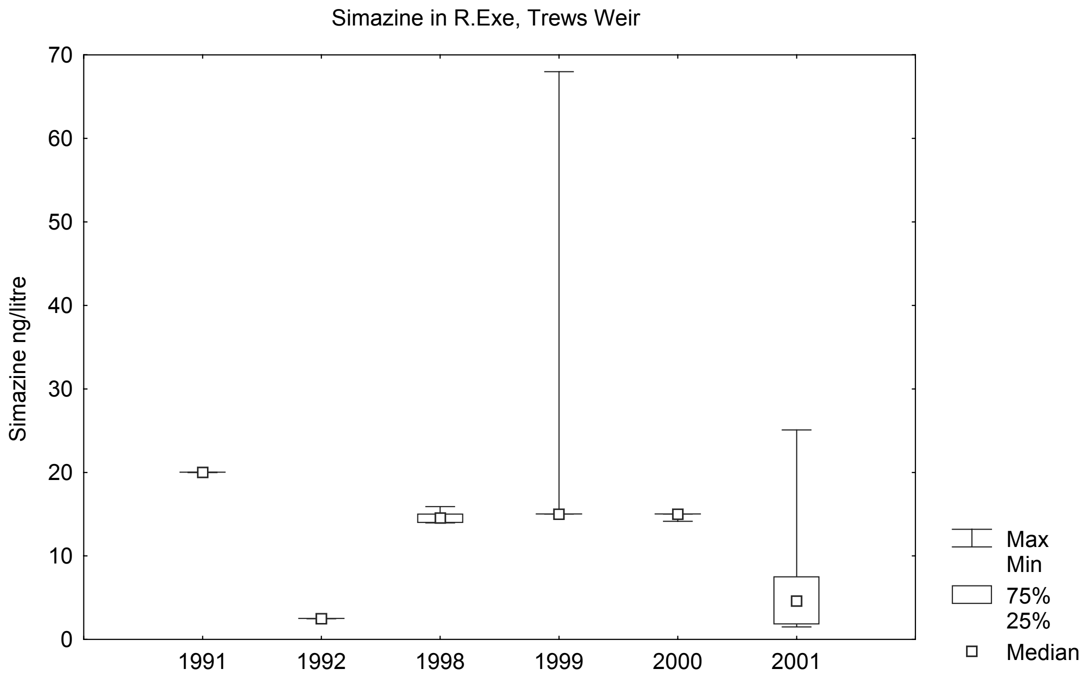


Figure 34. Simazine in the river Exe at Trews Weir. Summary statistics. (EA data)

Though atrazine and simazine appear, from the most recent data, to be present in the River Exe, sporadically at elevated levels, perhaps following agricultural application, exceedences of the EQS did not occur, even when the two are summed. Added together, the most recent annual averages (2001) for simazine and atrazine amount to 15 ng l^{-1}, and the maximum concentration 114ng l^{-1}.

Data for atrazine concentrations in Countess Wear STW samples indicate that high values (up to 1025 ng l^{-1}) have occurred, sporadically, in effluent samples in the past, though the magnitude of extreme values is decreasing generally with time (figure 35). Median values have been less variable over time and are probably influenced by the significant number of values below detection limits (44%). The median (min and max) concentration in Exmouth STW effluent (1996) was 83.8 (67-113) ng l^{-1} and appears to confirm that STW discharges are the source of at least some atrazine to the estuary.

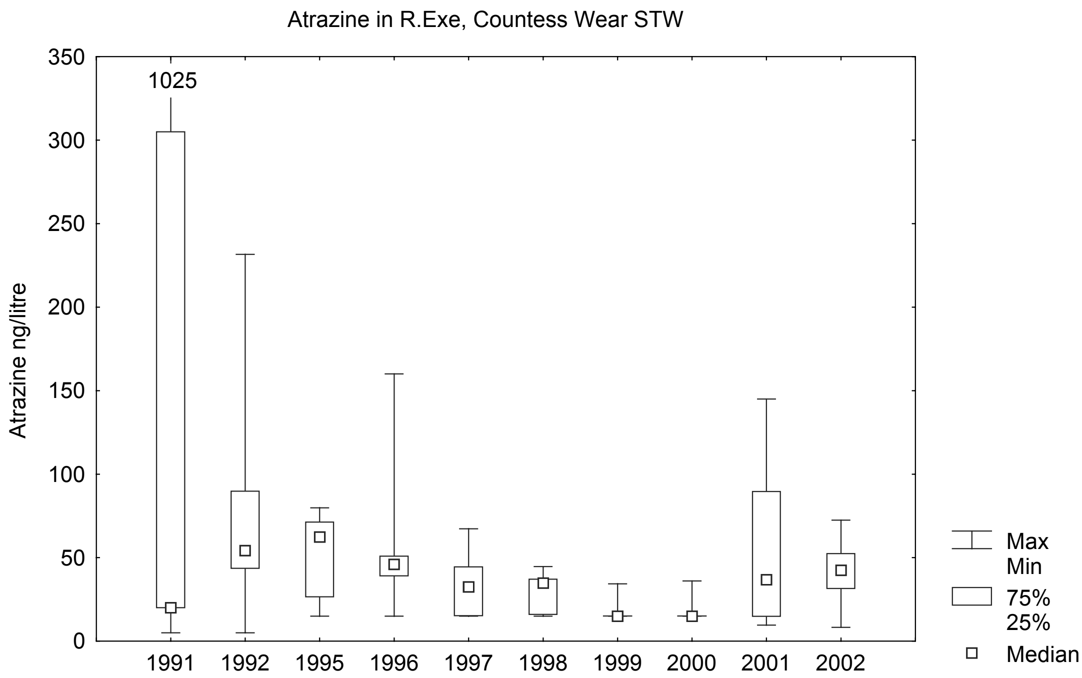


Figure 35. Atrazine in effluent samples from Countess Wear STW. (Data source EA).

Data for simazine concentrations in Countess Wear STW samples indicate similar trends to atrazine. Occasional high values (up to 935ng l^{-1}) have occurred in earlier years, though the magnitude of these extreme values is decreasing, generally, with time (figure 36). Median values have been less variable over time; a significant number of values (62%) are below detection limits. The median (min and max) concentration in Exmouth STW effluent (1996) was 40 (15-100) ng l^{-1}, illustrating that STW discharges are the source of some simazine to the estuary.

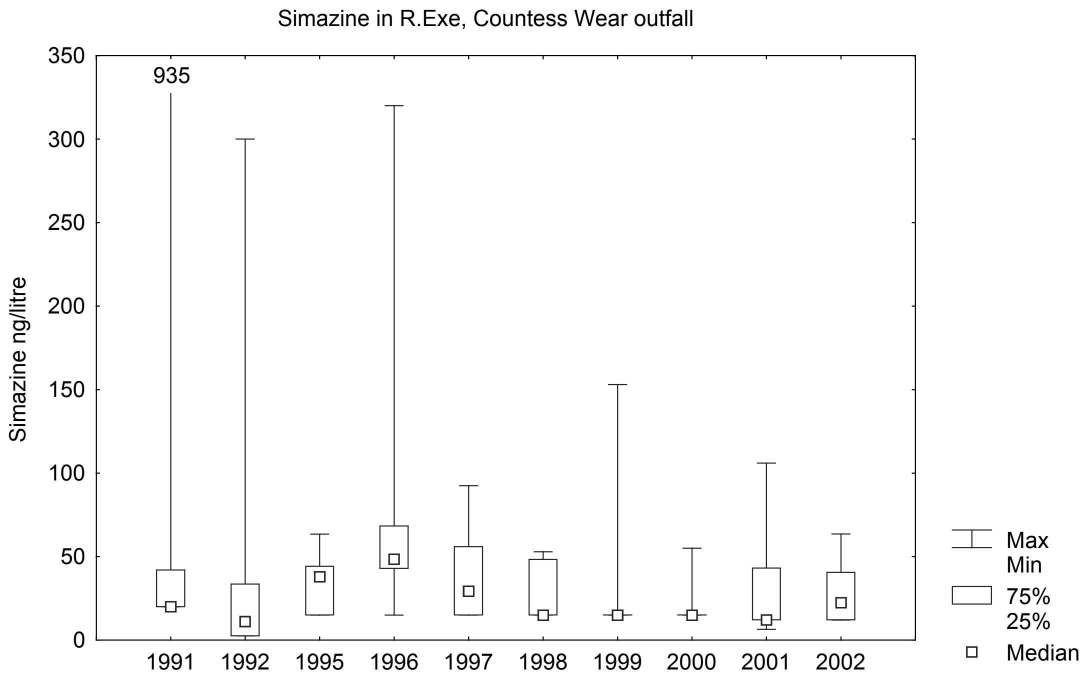


Figure 36. Simazine in effluent samples from Countess Wear STW. (Data source EA).

Despite some input of triazine herbicides from sewerage, it seems unlikely that these compounds represent a significant threat to the marine site. Unfortunately, data for tidal waters in the Exe Estuary is too limited to test this assertion rigorously. Samples are from one site only - the Countess Wear STW surface boil. In 1993, the median (min and max) concentration for atrazine was 37 (33-241) ng l^{-1} and the equivalent statistics for simazine 7.3 (2.5-48.5) ng l^{-1}. These values appear to fall comfortably within the EQS of 2µg l^{-1} (annual average) or 10µg l^{-1} (maximum allowable concentration). Nevertheless, more extensive confirmation throughout the site would seem appropriate in view of possible inputs from STW.

Polychlorinated Biphenyls - PCBs

With the exception of isolated cases of exposure to concentrated compounds, the effects of PCBs on marine life tend to be chronic rather than acute. PCBs are implicated in endocrine disruption and linked to eggshell thinning and deformities in seabirds (Allen and Thompson 1996). Biomagnification of PCBs may result in impaired reproductive success in fish and seals (von Westernhagen *et al.,* 1981, Reijnders 1986), and also immunosuppression in seals (Brouwer *et al.,* 1989) which in turn has been linked to the phocine distemper epizootic of 1988 (Hall *et al.,* 1992). PCBs are also carcinogenic and on the red list of dangerous substances.

Several PCB congeners have been monitored by the EA in fresh-water, estuarine water and STW final effluent. Virtually all samples (>96%) were below detection limits (<5ng l^{-1} from 1992 onwards) and estimated annual averages, shown in table 20, have been calculated by halving 'less-than' values.

Table 20. PCB concentrations (annual averages†) in fresh-water, estuarine water and STW final effluent (Data source EA).

	concentration in water ng l^{-1}			
PCB congener	Thorverton R.Exe 1994	Trews Weir R.Exe 1992	Cockwood Exe estuary 2001	Countess W & Exmouth STW 1996
28	0.77	1.35	0.5	0.68
52	2.41	1.6	0.5	2.65
101	0.75	1.6	0.5	0.73
118	0.65	1.1	0.5	0.63
138	0.72	1.6	0.5	0.58
153	0.85	1.35	0.5	0.85
180	1.07	1.1	0.5	0.8

† calculated by halving 'less-than' values. ns – no standard applicable

The low concentrations in aqueous samples implies little acute threat. In view of their affinity for, and persistence in, sediments, information on PCBs in the particulate phase would seem more appropriate for assessment of distributions. Unfortunately EA sediment PCB data is limited to two sites in the lower Exe Estuary both apparently with extremely low concentrations (well below guideline values as indicated in section 7). It seems unlikely, on this evidence, that there are currently any PCB sources of major significance in the estuary, but more extensive monitoring is needed for confirmation.

The distribution and transport of PCBs was characterised more extensively in the early 1980s by Herrmann and Thomas (1984), and superficially resembled the pattern for PAHs, described in section 6.1.3. PCB concentrations in water and sediment increased from the river into the estuarine mixing zone and, in the tidal channel, decreased from there towards the sea (table 21, and 22). Concentrations also tended to decrease from the channel, laterally, over tidal flats. Most of the PCB load appears to have originated from the river, carried into the estuary in particulate form which becomes focused by hydrodynamic processes at the turbidity maximum (the same is probably true of most organic micropollutants with a high adsorption coefficient). However, despite the preponderance of higher values in the upper estuarine silts (table 22), there were signs of occasional irregular localised sources of PCB superimposed on the main input(s) from the River Exe (nb Cockle Sand site, Exmouth, table 22).

Table 21. Concentrations of PCBs in Exe estuary waters. (Data from Herrmann and Thomas, 1984).

	PCB concentration ng l^{-1}		
	pentachlorobiphenyl	hexachlorobiphenyl	heptachlorobiphenyl
		estuary: tidal channel	
channel upper (nr Topsham)	17	7.9	5.4
channel mid (off Lympstone)	27	5.0	4.2
channel lower (Bull Hill)	9.5	14	2.7
		estuary: tidal flats	
Powderham sands	13	15	2.6

Table 22. PCB concentrations* in Exe sediments (<63 µm fraction). (Data from Herrmann and Thomas, 1984).

	PCB concentration ng g^{-1} (dw)		
	pentachlorobiphenyl	hexachlorobiphenyl	heptachlorobiphenyl
upper estuary-tidal channel	33	20	97
upper estuary – flats	20	10	78
mid-estuary-tidal channel	19	10	11
mid/low estuary-flats	8	4	28
cockle sand, Exmouth	157	66	198
Dawlish Warren	9	4	51

* PCB concentrations are given as equivalents of dominant peaks of penta-, hexa-, and hepta-chlorobiphenyl of Chlophen A60.

The concentrations in these water and sediment samples appear to be higher by an order of magnitude than the later EA data, though it is not clear whether this reflects a genuine temporal trend or methodological variation. Nevertheless, the fact that some of the sediment values in the study by Herrmann and Thomas approach or exceed the ISQG and PEL (21.5 and 189 ng g^{-1}, respectively, for total PCB), and are therefore of possible biological significance, supports the notion that more extensive monitoring is needed to clarify the present situation.

The same recommendation applies to bioaccumulation data. Like the majority of organochlorine substances, PCBs are lipophilic, dissolving more readily in fats than in water; therefore they tend to accumulate in the tissues of living organisms. In shellfish samples from the Lower Exe beds very few analyses undertaken by the EA in the 1990s were above detection limits (table 13). The reported values (mainly '<') are so low, in fact, that it may be worth checking concentration units in the EA data. Even if the values in table 13 are mg kg^{-1} rather than μg kg^{-1}, however, they would still fall comfortably below guideline values for biota.

According to NOAA's mussel-watch programme in the United States, a ΣPCB concentration of 430 μg kg^{-1} dry weight in molluscs would classify as being high - equivalent to 86 μg kg^{-1} wet weight (assuming a wet:dry weight ratio of 5, an approximation based on our own data for wet to dry ratios in shellfish). For a group of seven PCB isomers (ΣPCBs 28, 52, 101, 118, 138, 153, 180), OSPAR ecotoxicological guidelines (background levels) for mussels are in the range 5-58μg kg^{-1} dw (estimated 1-11.6 μg kg^{-1} ww). This compares with an estimated 0.00003 μg kg^{-1} wet wt in shellfish from the lower Exe, for a similar group of isomers (table 13). The implication is a remarkably low level of PCB contamination and bioaccumulation in the Exe, which would be useful to verify on a broader scale in light of the earlier observations on PCB distributions in sediments.

Volatile organics (solvents, freons).

A number of volatile organic compounds (VOCs) are, potentially, endocrine disruptors, as well as being toxic directly and may be discharged into the Exe in small quantities. These include:

Chloroform (trichloromethane)

Chloroform, a List I substance, is an industrial solvent used in the UK in the production of fumigants and anaesthetics. It is also a principal transformation product of chlorine-based biocide products used in cooling water systems: chloroform is the major organohalogen formed at sites using freshwater sources, whereas bromoform predominates where water is taken from estuarine and marine sources (Cole *et al.,* 1999). By-products formed during chlorination of power plant cooling water may have adverse effects on the growth of marine invertebrates during their larval stages (Stewart *et al.,* 1979). It has been known for some time that reproductive tissues, especially sperm, and the immature stages of organisms are sensitive to very low concentrations of organohalogens (Davis and Middaugh, 1978).

Chloroform has an EQS of 12μg l^{-1} (annual average) in all waters.

The majority of values for chloroform in the River Exe (Thorverton and Trews Weir) were below detection limits (97%). These DLs have ranged from 0.1-0.3μg l^{-1} over the last decade, and most recent values are at the lower end of this range. Annual average concentrations, based on ½DL, are invariably below the EQS (12 μg l^{-1}) by a considerable margin (e.g. 0.05 μg l^{-1} at both sites in 2000), implying that riverine sources are not a threat.

Some discharges of chloroform occur from STW, though concentrations in effluent from Countess Wear STW have decreased significantly over the last decade (figure 37). In 2001 the annual average concentration was 0.9 ± 0.7 μg l^{-1} and does not appear to be a direct toxicological concern. The same applies to effluent from Exmouth STW (average concentration in 1996, 0.8 ± 0.3 μg l^{-1}).

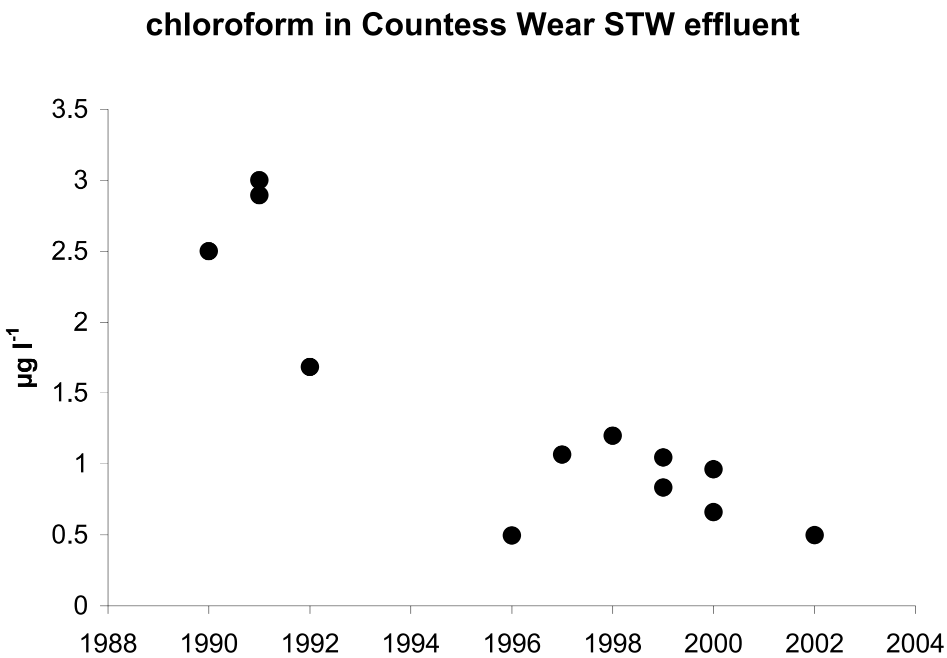


Figure 37. Chloroform (annual averages) in effluent samples from Countess Wear STW. (EA data).

The majority of values for chloroform in the Exe Estuary were below detection limits (93%). Annual average concentrations in tidal waters, based on ½DL, were invariably below the EQS of 12µg l^{-1}, as indicated in figure 38, and even extreme values (at sites near the STW at Countess Wear and Exmouth) do not appear to represent a significant toxicological threat.

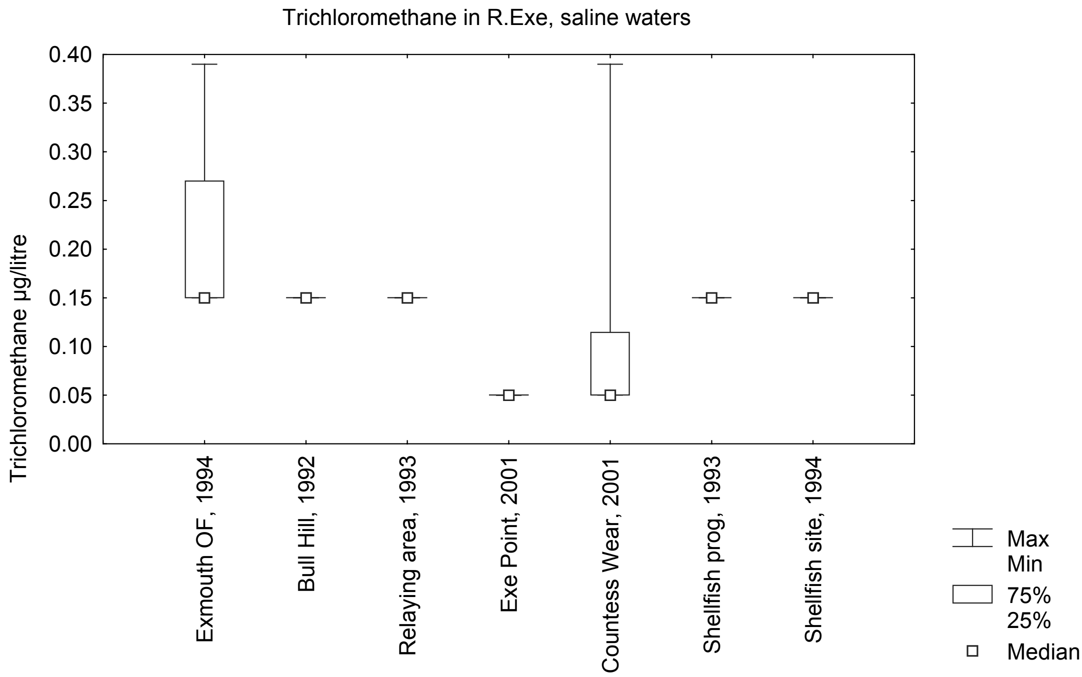


Figure 38. Chloroform (trichloromethane) in tidal waters of the Exe Estuary. Annual averages for years indicated. (EA data).

Carbon tetrachloride (Tetrachloromethane)

Carbon tetrachloride is mostly produced for use in the manufacture of chlorofluorocarbons (CFCs). Carbon tetrachloride is also used as a chemical intermediate in the manufacture of pharmaceutical and pesticide products. Carbon tetrachloride production in the United Kingdom has recently ceased and its major use (production of CFC-11 and CFC-12) is now in decline. For UK marine waters, Willis *et al* (1994) reported levels to be between <0.1 – 44µg l^{-1}, with higher levels in source-dominated areas. Concentrations measured in the open ocean were generally much lower, at around 0.5 ng l^{-1}.

Carbon tetrachloride is another List I compound, also with an EQS of 12µg l^{-1} (annual average) in all waters.

The majority of values for carbon tetrachloride in the River Exe (Thorverton and Trews Weir) were below detection limits (99%). These DLs have ranged from 0.05-0.2µg l^{-1} over the last decade. Annual average concentrations, based on ½DL, are invariably below the EQS of 12 µg l^{-1} by a considerable margin (e.g. 0.05 µg l^{-1} at both sites in 2000) implying riverine sources are not a threat.

Discharges of carbon tetrachloride via STW are relatively minor (83% of analyses are below detection limits). In 2001 the estimated annual average concentration in effluent from Countess Wear and Exmouth STWs was 0.05 µg l^{-1}.

All measurements of carbon tetrachloride in tidal waters of the Exe were below detection limits which range from 0.05 to 0.1 µg l^{-1}. Consequently annual average concentrations, based on ½DL, (0.025 to 0.05 µg l^{-1}) were invariably well below the EQS of 12µg l^{-1} and do not appear to represent a significant toxicological threat.

Chlorinated Ethylenes (trichloroethylene, tetrachloroethylene [perchloroethylene])

These are List I substances produced in large quantities and widely used in industry in the production of food packaging, synthetic fibres and industrial solvents. MPMMG (1998) indicate that concentrations of chloroethylenes in UK coastal and estuarine waters are unlikely to exceed relevant EQS (10µg l^{-1} annual average) derived for the protection of saltwater life.

Data for trichloroethene is examined here as being representative of this group of compounds. More than 99% of values for fresh- and tidal-waters at the sites described above, were below detection limits. These limits have ranged from 0.1- 0.2µg l^{-1} over the last decade. Concentrations were invariably below the EQS, usually by more than an order of magnitude, implying little threat. Discharges of trichloroethene via STW were relatively minor (60% of analyses were below detection limits). The estimated annual average concentrations in effluent from STWs at Countess Wear (2001) and Exmouth (1996) were 0.09 µg l^{-1} ± 0.08 µg l^{-1} and 0.47 ± 0.12 µg l^{-1}, respectively.

Trichloroethane

Trichloroethane, a list II substance, is used as an industrial solvent. Potential sources of contamination include direct discharge of wastewaters, accidental spillages and deposition from the atmosphere.

1,1,1 Trichloroethane has an EQS of 100µg l^{-1} (annual average) in all waters. More than 99% of values for fresh- and tidal-waters of the Exe were below detection limits. These limits have ranged from 0.1- 0.3µg l^{-1} over the last decade. Concentrations were invariably below the EQS, by at least two orders of magnitude (highest concentration 1µg l^{-1}).

Discharges of trichloroethane via STW were relatively minor (68% of analyses were below detection limits). In 1996 the estimated annual average concentrations in effluent from STWs at Countess Wear and Exmouth were 0.23 µg l^{-1} and 0.15 µg l^{-1}, respectively.

It seems unlikely, therefore, that volatile organics represent a significant threat to the marine site.

6.1.5 Alkylphenols And Other Endocrine Disruptors

Alkylphenolpolyethoxylates (APEs) are a major component in surfactants in detergents and their presence in sewage effluent and adjacent freshwaters has been associated with both ED and even acute toxicity in extreme cases. APEs have also been used in large amounts by the oil and gas industry as a component in rig washes (now being phased out), in paints and cosmetics, and as a spermicide (Blackburn *et al.,* 1999). There is now a voluntary ban on their use in the UK domestic market.

In fresh water, concentrations upto 180µg l^{-1} of the degradation product nonyl phenol (NP) have been measured near to STW on the River Aire, Yorkshire. In contrast, no detectable levels of APE residues were found at five sites examined on the River Exe, from Countess Wear (A38 Bridge) to Cove, some 50km upstream (table 23; from data in Blackburn and Waldock, 1995; Blackburn *et al.,* 1999).

Concentrations of alkylphenols in tidal waters are generally much lower than in fresh water, except in industrial estuaries such as the Mersey and Tees (5 µg l^{-1} nonyl phenol). There is a new proposed EQS for nonylphenol - 1µg l^{-1} (Annual Average) and 2.5µg l^{-1} (Maximum Allowable concentration) (EA R&D Technical Report P42). In tidal waters of the Exe Estuary alkylphenols (NP and other APE derivatives) were below detection limits at four sites (table 23 data from Blackburn *et al*., 1999).

APEs are considered to be relatively lipophilic and will tend to be sequestered by particulates. In freshwater sediments close to a known source in the river Aire for example, concentrations up to 15µg g^{-1} have been found, and concentrations in the sediments of the Mersey and Tees Estuaries may exceed 1µg g^{-1} (Blackburn et al., 1999). In contrast, concentrations in both fresh water and estuarine sediments of the Exe were, without exception, below limits of detection (table 23).

These results imply that there is little threat to the Exe SPA from alkylphenols and their derivatives, though this does not necessarily mean that the possibility of endocrine disruption is commensurately low. Other compounds in effluents, or in diffuse pollution, particularly steroid hormones, could be the principal cause of oestrogenicity but, to date, have not been investigated in this system.

Table 23. Alkylphenols in water and sediments of the Exe Estuary. (Adapted from Blackburn, Kirby and Waldock, 1999).

site	date	Total extractable nonylphenol (µg/l)	Dissolved nonylphenol (µg/l)	Total extractable [NPEO + NP2EO] (µg/l)	Dissolved [NPEO+NP2EO] (µg/l)
			fresh water		
Cove	1995	<0.2	<0.2	<0.6	<0.6
Tiverton	1995	<0.2	<0.2	<0.6	<0.6
Thorverton	1995	<0.2	<0.2	<0.6	<0.6
Exeter	1995	<0.2	<0.2	<0.6	<0.6
A38 Exeter	1995	<0.2	<0.2	<0.6	<0.6
			estuary water		
No 39 buoy	1995	ns	<0.2	ns	<0.6
No 21 buoy	1995	<0.2	<0.2	<0.6	<0.6
No 13 buoy	1995	<0.2	<0.2	<0.6	<0.6
East Exe buoy	1995	<0.2	<0.2	<0.6	<0.6

site	date	Total extractable nonylphenol (µg/g dw)	Dissolved nonylphenol (µg/g dw)	Total extractable [NPEO + NP2EO] (µg/g dw)	Dissolved [NPEO+NP2EO] (µg/g dw)
			riverine sediment		
Cove	1995	<0.1		<0.5	
Tiverton	1995	<0.1		<0.5	
Thorverton	1995	<0.1		<0.5	
A38 Exeter	1995	<0.1		<0.5	
			estuarine sediment		
No 39 buoy	1995	<0.1		<0.5	
No 21 buoy	1995	<0.1		<0.5	
No 13 buoy	1995	<0.1		<0.5	
East Exe buoy	1995	<0.1		<0.5	

NPEO nonylphenol monoethoxylate; NP2EO nonylphenol diethoxylate; ns- not sampled

There are indications that a number of metals, notably Cd, Pb and Hg, may cause endocrine disrupting effects. Experimentally, Cd (1 mg l^{-1}) has been shown to induce vitellogenin production in female fish, to increase the secretion of gonad-inhibiting hormones in fiddler crabs and, at 25µg l^{-1}, alter hormone titres in sea-stars (Thomas, 1989; Rodriguez *et al*., 2000, Besten *et al*., 1991). However, concentrations used to demonstrate these effects were substantially higher than those found in the Exe Estuary.

Likewise for Pb and Hg, although it is known from mammals that ED action can occur at the level of the hypothalmic pituitary unit, or on gonadal steroid biosynthesis, evidence of comparable activity on estuarine and marine biota, exposed chronically in the field, is not available (Allen *et al.,* 2000). Levels of metal bioaccumulation in biota of the Exe do not appear to give cause for concern. However, experimental studies on freshwater crayfish have indicated that Cd and Hg at the relatively low concentration of 0.5µg g^{-1} body weight can arrest ovarian maturation due to inhibition of gonad stimulating hormone and serotonin, respectively (Reddy *et al*., 1997). Therefore until a systematic survey of endocrine disruption is carried out for the Exe, similar reactions in marine crustaceans and other organisms from the SPA cannot be ruled out.

Chronic stress can lead to elevation of cortisol, following ACTH secretion in the pituitary. This is a normal adaptive response for mobilising the energy needed to deal with stress, and is not strictly-speaking, endocrine disruption. However, prolonged chronic stress can suppress the normal response, due to exhaustion of the pituitary-kidney feedback mechanism. In North America, metal-exposed sea trout (*Salmo trutta*) populations have been shown to exhibit symptoms of inhibition of the ACTH/cortisol response to acute stress (Norris *et al.,* 1999). Similar effects have been seen in catfish exposed experimentally to Hg (Kirubagaran and Joy, 1991). Possible knock-on effects on energy metabolism and salinity adaptation are likely. Although there are currently no grounds to suspect such problems in the Exe, it would be informative to test these general stress responses in organisms (along with others described in annex 6), particularly downstream of the Countess Wear discharge - to establish whether or not this produces similar chronic effects.

Food items of various sorts will be the most likely route of exposure to birds, many of which are extremely sensitive to endocrine disrupting substances such as pesticides, PCBs, PAHs and metals (reviewed by Fry, 1995). Consumption of prey species such as molluscs (which are excellent bioaccumulators of contaminants), or accidental ingestion of sediment by waders feeding on mud-flats, appear to represent relatively small risks within the Exe SPA based on the rather limited evidence available. However, more detailed study is needed to evaluate, thoroughly, current risks to both invertebrates and higher organisms.

6.2 Non-Toxic Contaminants

Concentrations of non-toxic substances are an important issue in marine sites although they do not appear on priority lists. Areas of concern, identified by the nature conservation agencies include: nutrients (nitrogen, phosphorus and silicon), organic carbon, oxygen depleting substances (BOD and COD), pH, salinity, temperature (thermal discharges) and turbidity (Cole *et al*., 1999).

6.2.1 Nutrient quality criteria

Water quality with regard to nutrients is primarily assessed in terms of the trophic status, or degree of nutrient enrichment in estuaries and near shore waters. 'Nutrient enrichment' generally refers to nitrogen and phosphorus species which are elevated beyond background levels, as these are the two leading causes of poor water quality.

Nitrogen and phosphorus enter the estuarine environment via point or diffuse sources. Point sources are generally consented discharges and a direct result of human activities including; sewage effluent from sewage treatment works (STW), discharges from some industrial processes (including detergents) and cage fish farm installations. Diffuse inputs originate from both natural and anthropogenic sources. These comprise run-off/leaching from the land catchment (either directly into estuaries and coastal waters or via rivers and groundwater), atmospheric deposition, imports from off-shore waters and nitrogen fixation by plant life.

In a tidal estuary, such as the Exe, point source inputs may be of importance. The potential for nutrient enrichment and localised effects will be determined by physico-chemical and biological characteristics of the estuary such as flow, seasonal variability, flushing, tidal regime, primary production and rates of remineralisation.

The principal effect of extreme nutrient enrichment is eutrophication, defined as 'the enrichment of natural waters by inorganic plant nutrients, which results in the stimulation of an array of symptomatic changes' (EA, 1998). These changes include an increase in phytoplankton growth that is reflected by an increase in chlorophyll α concentrations. Dissolved oxygen concentrations in the water column fluctuate during the growth phase of a phytoplankton bloom and there is a potential for depletion of dissolved oxygen concentrations in the water column and sediments as a result of microbial activity following the die-off of phytoplankton blooms. pH may be affected. The bloom may contribute to increased turbidity in the water column, reducing light availability.

Nutrient enrichment can also result in proliferation of the larger macroalgae. In comparison to effects caused by phytoplankton blooms, macroalgae are considered harmful due to dense overgrowth that can occur in localized areas, or coastal embayments receiving excessive nutrient loading (Valiella *et al.*, 1997). Accumulations can be so high as to cover the bottom of a region, excluding other biota as well as creating an environment in which high oxygen consumption and the associated anoxic conditions accompany decomposition of the accumulated or displaced biomass (Raffaelli *et al,* 1998). These problems can be compounded by ammonia release from sediment; Owens and Stewart (1983) showed that ammonia release from sediment is greatest when macroalgae biomass declines, due to increased ammonifying microbial activity.

Many of these changes are quantifiable and, in addition to nitrogen, phosphorus and ammonia, a range of other parameters are usually measured to determine water quality in relation to nutrients. These include dissolved oxygen (DO), biological oxygen demand (BOD), chlorophyll *a*, suspended solids and turbidity. Nitrogen levels can be monitored as nitrate, nitrite and ammonium concentrations in tidal waters which, when added together, produce total inorganic nitrogen (TIN), an approximation of bioavailable nitrogen. Phosphorus is present in the aquatic environment in both inorganic and organic forms, the principal inorganic form being orthophosphate which is measured as dissolved orthophosphate (soluble reactive phosphate SRP), or as unfiltered (total) reactive phosphate (TRP).

Parr *et al* (1999) report a wide range of nutrient levels in UK coastal waters and estuaries; concentrations of 0.07 – 1.85mg l^{-1} TIN and 0.007 – 0.165mg l^{-1} TRP are found in coastal waters, whilst the upper reaches of estuaries have nitrogen concentrations similar to those in river water, 0.1 - 15mg l^{-1} TIN. TRP in upper estuaries, as in rivers, can also be variable, 0 – 11.4mg l^{-1}.

There is surprisingly little information in the literature regarding nutrients in the Exe. Atkins (1988) reported on results of an environmental survey of the Exe carried out in July-August 1987, giving an overview of several chemical parameters including BOD, nutrients, and DO. The BOD of the estuary was found to increase with distance up the estuary from the mouth to Topsham. This was said to reflect the dominating influence of the major sewage input at Countess Wear. Above the STW, BOD fell somewhat, but did not drop to the level recorded at the mouth of the estuary.

Nutrients displayed the same trend as BOD, increasing in concentration with distance from the mouth of the estuary to Countess Wear. However, with the exception of ammonia, the increase in concentration continued beyond the STW. It was observed that, although river water might be expected to carry much higher concentrations of nutrients than the receiving sea waters, levels of nutrients above Countess Wear were such that the inflowing river also appeared to be affected by sewage discharge or contaminated run-off (Atkins, 1988).

In terms of loading, Murdoch (2001) examined mean annual, and winter and summer total inorganic nitrogen (TIN) loads (January 1996 to June 2000) from the Countess Wear discharge and tributaries of the Exe Estuary (figure 39). This study did not take other STW discharges into account.

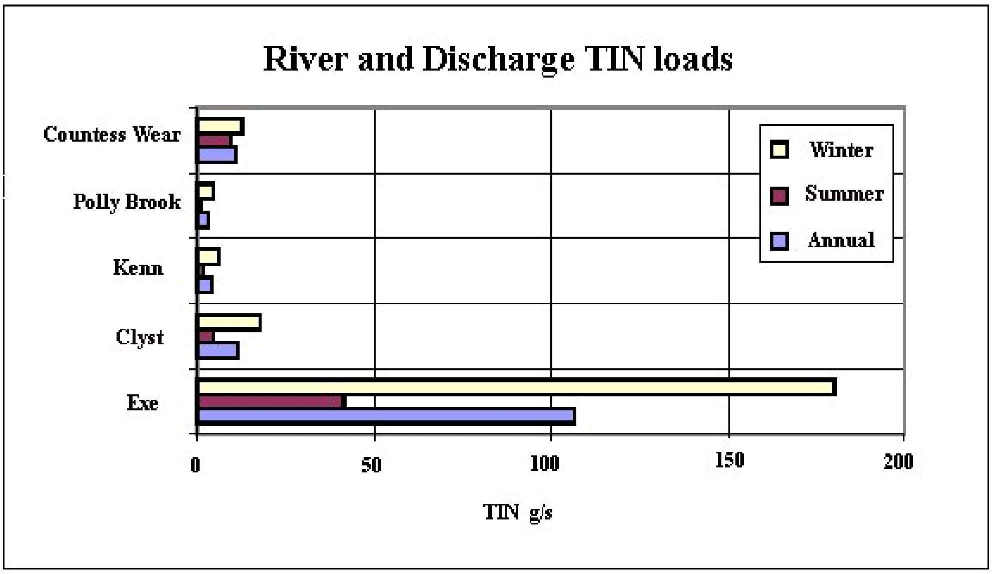


Figure 39. Discharge loads of TIN (g/s) for tributaries and Countess Wear STW discharge into Estuary, Jan 1996-June 2001 (from Murdoch, 2001).

The dominant TIN load was shown to be from the River Exe. On average, during this period, Countess Wear STW contributed approximately 10% of the annual River Exe load, however, during the summer months this contribution was ~25%, and was nearly 50% of the River Exe load in the driest summer (1996). The implication is that Countess Wear discharges may be anticipated to have the most significant impact on estuarine TIN concentrations during the summer months.
A recent Agency report has summarised the eutrophication problem in the Exe Estuary (EA, 2001b). Key findings are:

- Chemical and biological data collected over the period 1998-2000 indicate that the Exe Estuary is eutrophic, or at risk of becoming eutrophic.
- Winter TIN levels indicate that hypernutrification occurs, with overall highest levels recorded at Lower Wear, the site closest to Countess Wear STW (up to 6.85mg l^{-1} – figure 40a).
- Year round TIN values also tended to be highest at Lower Wear, at the head of the estuary, and decreased seaward.

- The results of nutrient (TIN) modelling (Murdoch, 2001, see above and section 8) are reiterated: Countess Wear STW contributes ~10% of the annual load (25% in summer) from the River Exe. Impact from Countess Wear STW is thus greatest in summer at Lower Wear. TIN modelling may have underestimated the relative contribution of N from Countess Wear STW.
- Orthophosphate concentration was also highest at Lower Wear, where up to 2410µg l^{-1} was recorded (figure 40b).
- There have been several complaints of foaming and potential algal blooms by members of the public (see section 6.2.5)
- Natural flushing of the estuary is thought to prevent obvious signs of eutrophication (sustained algal blooms) from developing.

Other findings of this report are discussed in the relevant sections, below.

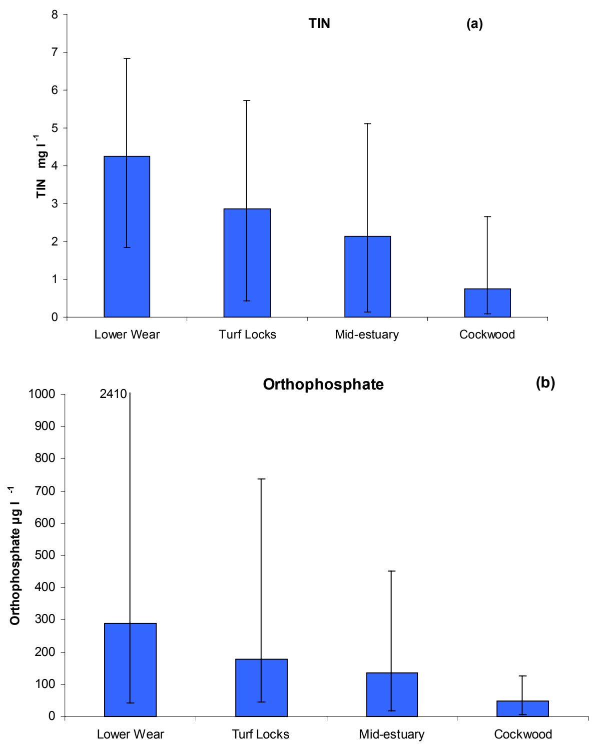


Figure 40. Mean values for (a) TIN and (b) Orthophosphate in tidal waters of the Exe Estuary (1998-2001). Error bars show min and max concentrations (from EA, 2001b).

Concerns that the Exe Estuary is exhibiting signs of eutrophication prompted investigations which recommended its designation as a Sensitive Area (Eutrophic) (EA, 2001b). The estuary was considered to be 'eutrophic now' (EA, 2001b). Designation could have facilitated significant reductions in nutrient loadings. However, it was not put forward to DEFRA due to the rapid flushing rate and lack of evidence, therefore it will not be designated in the foreseeable future.

Freshwaters of the Exe above the estuary are also high in nutrients: the River Exe, from the River Creedy at Crediton STW to the normal tidal limit of the Exe (St James

Weir) was designated as a Sensitive Area (Eutrophic) in 1994. In order to reduce the load, phosphate reduction commenced at Crediton (Lords Meadow) STW in 1998 (EA, 2001a), and the Agency are currently carrying out a study of the trophic status of the Exe from Tiverton to the Creedy confluence. Measures to address diffuse sources of nutrients will only be taken if the area is also designated as a nitrate vulnerable zone (NVZ)

In tidal waters, Dawlish Warren, Sandy Bay and Exmouth Beach (just outside the estuary mouth) were all designated sensitive areas, under the Bathing Waters Directive in 2002. Where such waters are identified, additional treatment in addition to secondary treatment is required to meet current standards (see appendix 4). This more stringent treatment involves disinfection to protect bathing waters identified under the Bathing Water Directive.

Nutrient concentrations vary with salinity, therefore measurements collected simultaneously from different regions within the estuary, or from the same region but at different states of the tidal cycle, may show considerable differences and not be truly representative of water quality. To compound this difficulty, nutrient concentrations also vary throughout the year with freshwater flow.

As yet there are no statutory water quality standards for nutrients in the UK and determination of the nutrient status of estuaries, and the ecological consequences, remain a notoriously contentious issue. To quote from the Agency's Technical Guidance for Water Quality: Review of Permissions to Discharge and New Applications (Habitats Directive) - 'Generally, it is impossible to calculate permit conditions in the absence of water quality standards…' and ' it is not easy to make a case or refuse or reject an application in the absence of such standards'. Therefore, judgement of nutrient status in the Exe Estuary, as elsewhere, consists largely of subjective assessment of monitoring information concerning the primary variables, coupled with contextual information on the site characteristics and condition. The primary variables are generally considered to be nitrogen and phosphorous (though there is still great scientific debate as to which forms to measure). It is usually considered essential to monitor these parameters alongside initial biological response indicators such as chlorophyll-a (a measure of primary production), dissolved oxygen and, for example, Secchi depth (a measure of turbidity). These data may then be fed into models to develop criteria for the selection of numerical water quality objectives.

Although no statutory standards exist for Nitrogen and Phosphorus in estuarine and marine sites, a number of 'guideline values' have been established which could be of relevance for assessment of the status of nutrients in the catchment of the Exe Estuary and for initiating management responses:

- EU nitrates directive 91/676/EEC, on the protection of all waters against pollution caused by nitrates from agricultural sources, calls for the identification of all waters that contain **50mg l^{-1} nitrate**.
- The USEPA is still in the process of arriving at their national nutrient strategy but has for many years proposed a limit of **10mg l^{-1} nitrate** nitrogen for the protection of domestic water supplies (against overenrichment and impacts on human and animal health). A phosphorus criterion was reported some years ago in the EPA 'Red Book' as **0.1µg l^{-1} (as P)** to protect estuarine and marine organisms against

the consequences of bioaccumulation (EPA, 1976). However, this was not established as a threshold for eutrophication and is currently under review.

- The North Sea Status report stated that hypernutrification in sea water exists when winter (maximum) **TIN (Total Inorganic Nitrogen) values exceed 0.144mg l^{-1}** (provided P>0.006mg l^{-1}), implying that nutrient concentrations need not be elevated by a large margin before algal proliferation commences (Parr *et al.,*1999). In estuaries however it seems likely that thresholds will be higher.

- Based on work in 2 eastern USA estuaries, Deegan *et al.,* (1997) have suggested that a DIN value of ~ **1mg l^{-1} DIN (Dissolved Inorganic Nitrogen)** or more might lead to poor habitat quality for fish populations, which may be due in part to cloaking effects of macroalgal mats on *Zostera* beds.

- There is a proposed EQS of **0.021mg l^{-1} un-ionised ammonia** (NH_3-N) for the protection of saltwater fish and shellfish, although due to the technical difficulties in measuring the unionised form, total ammonium is usually monitored and NH^3 calculated. However, even calculations can be difficult as the relative proportion of ionised and un-ionised ammonia depends on salinity, temperature and pH.

- The proposed EQS of **0.021mg l^{-1} un-ionised ammonia** (NH_3 N) also applies to EC designated salmonid and cyprinid freshwaters. In addition there is an EQS of **0.78mg l^{-1} total ammonia** for these waters (Seager *et al.,*1988).

GQA scheme: TIN and TRP
Recognising the dilemma in arriving at standards, there have been attempts in recent years to develop and test General Quality Assessment (GQA) schemes for nutrients in estuaries and coastal waters which may be adopted nationally and internationally. One such scheme was proposed for the EA by the WRc as part of their General Quality Assessment (GQA) scheme (Gunby *et al.,* 1995). For nitrogen, this method uses the combined concentrations of nitrate, nitrite and ammonium concentrations in tidal waters (total inorganic nitrogen, TIN), as an approximation of bioavailable nitrogen. Assuming conservative behaviour for TIN and a standard concentration in marine waters, allows the TIN concentration in the freshwater input to be calculated, provided salinity data are available. For phosphorus, Total Reactive Phosphate (TRP - phosphate in unfiltered samples) is measured and, as for nitrogen, the concentration in freshwater calculated. Estuaries are then grouped according to the class boundaries shown in table 24.

Table 24. TIN and TRP classification criteria for estuaries (based on Gunby *et al.*, 1995)

Class	Median projected TIN (mg l^{-1})	Class	Median projected TRP (mg l^{-1})
A/B	5.3	A/B	0.087
B/C	8.1	B/C	0.35
C/D	11.1	C/D	1.00

In view of the hydrodynamic differences between estuaries, together with seasonal and other site-specific factors, it is not known how valid they may be for the Exe Estuary. Nevertheless, in the absence of site-specific guidelines they at least represent benchmarks as to potential threats, against which to draw comparisons.

Table 25. Classification nutrient status of selected estuaries in England according to GQA TIN/TRP projection methodology (Cole *et al.*, 1999)

Estuary	**Projected median TIN concentration (mg l^{-1}) in freshwater**	**GQA TIN class**	**Projected median TRP concentration (mg l^{-1}) in freshwater**	**GQA TRP class**
Blackwater	14.3	D	6.8	D
Camel	5.9	B	0.4	C
Carrick	5.4	B	4.6	D
Colne	12.7	D	4.2	D
Crouch	11.3	D	5.3	D
Dart	4.3	A	0.2	B
Deben	11.5	D	6.2	D
Exe	**5.4**	**B**	**0.3**	**B**
Fal	9.4	C	5.1	D
Fowey	4	A	0.1	A
Hamford Water	10	C	6.8	D
Helford	7.3	B	3.2	D
Humber	8.8	C	0.1	B
Itchen	5.6	B	0.3	B
Lynher	5.5	B	0.1	A
Medway	5.1	A	0.4	C
Mersey	7.1	B	0.4	C
Nene	15.1	D	0.9	C
Ore/Alde	9.5	C	-1.0	A
Orwell	14	D	3.2	D
Ouse	12.2	D	0.8	C
Roach	11.9	D	11.4	D
Severn	7.6	B	0.5	C
Stour	13.3	D	2.5	D
Tamar	4.6	A	0.2	B
Test	6.3	B	0.3	B
Thames	12	D	2.4	D
Wash	13	D	1.5	D
Welland	13.1	D	0.4	C
Witham	21.9	D	0.5	C
Wyre	9	C	7.9	D
Yare	9.7	C	0.6	C
Yealm	5.9	B	4.2	D
MEAN	**9.5**	**C**	**2.5**	**D**

Indeed, Cole *et al*., (1999) made a comparison of the nutrient status of UK estuaries, based on the classification scheme summarised in table 24, having extrapolated freshwater values (from seawater values) on the basis of conservative mixing. Using these criteria, the projected classifications for TIN and TRP for the Exe are both grade B – i.e. better than the average for UK estuaries (table 25). However, these classifications result from modelled values as opposed to actual measurements and can therefore only be used as a rough guide.

There are other schemes which estimate the nutrient status from freshwater load inputs, thus encompassing point source discharges to rivers. For example, Dong *et al.,* (2000) calculate estuarine nutrient loads by multiplying annual averages of all nutrient concentration measurements for contributing rivers, by the annual freshwater flow. Some of the errors associated with load estimates were discussed at the beginning of section 6. In addition there is scope for error in that diffuse freshwater sources entering directly into the estuary will not be accounted for; likewise estuarine point sources may be not be accounted for and could make this type of estimate unreliable.

The issue of whether or not to focus on nutrient concentrations in the tidal waters or loading criteria has been a contentious one among both scientists and managers. Historically, sources of P are considered to be industrial effluents, rivers and streams and domestic sewage, and for N, rivers (predominantly) with a significant component from discharges (Owens, 1984).

As noted above, the characteristics of estuaries differ significantly, and therefore nutrient sources, their fate and effects in the estuarine environment are not easily predicted. Rather than relying on a classification scheme for the estuary as a whole it may be more beneficial to investigate the recent distribution of key determinands in finer detail. Based on the above criteria, and published data from other estuaries, it is possible to attempt a brief analysis of EA nutrient monitoring observations including;

- determination of background (reference) values and 'hotspots' for the area
- examination of historical data and trends in the Exe Estuary and comparisons with other areas
- validity of guideline values and classification schemes

We have used measurements of total inorganic nitrogen (TIN), nitrate[1], total reactive phosphate and ortho-phosphate as the principal markers in the following synthesis of nutrient status in the SPA.

6.2.2 Phosphate

Recent values for concentrations of orthophosphate in freshwaters entering the Exe Estuary are summarised in figure 41. Thorverton and Trews Weir are HMPs (Harmonised Monitoring Points). Occasional high values occurred in Alphin Brook

[1] Nitrate typically makes up the largest proportion of TIN inputs to estuaries, with nitrite and ammonia usually accounting for < 10%.

(up to 0.98mg l^{-1}) although this is not a principal source and will probably not represent a significant loading. Concentrations generally do not appear to be exceptional in comparison with other rivers in the south west (orthophosphate at HMPs on the Severn, for example, are in the range 0.05 – 0.7mg l^{-1} and in the Tamar, 0.02 – 0.08mg l^{-1}). Mean values for the Exe fall somewhere between these two. Annual average concentrations over the past 10-12 years indicate gradual reductions in orthophosphate concentrations for two of these sites (Alphin Brook, Polly Brook) whilst the remainder are generally unchanged.

Data for orthophosphate concentrations in sewage discharges to the Exe Estuary in 2001 are summarised in figure 42[2]. Highest values are for Countess Wear STW and Lympstone sewage discharge (10.9 and 10.5mg l^{-1} respectively). There have been gradual reductions in levels of orthophosphate in discharges from Exmouth STW over the past decade, whilst for Countess Wear, annual mean concentrations of orthophosphate have fluctuated between 3.9 and 7.8mg l^{-1} but there is no clear trend. Concentrations in discharges from Kenton and Starcross STW have gradually increased since 1998, although mean concentrations remain relatively low (2.9mg l^{-1} in 2001). *It is stressed that the data are for concentration only and do not take into the account volume discharged.*

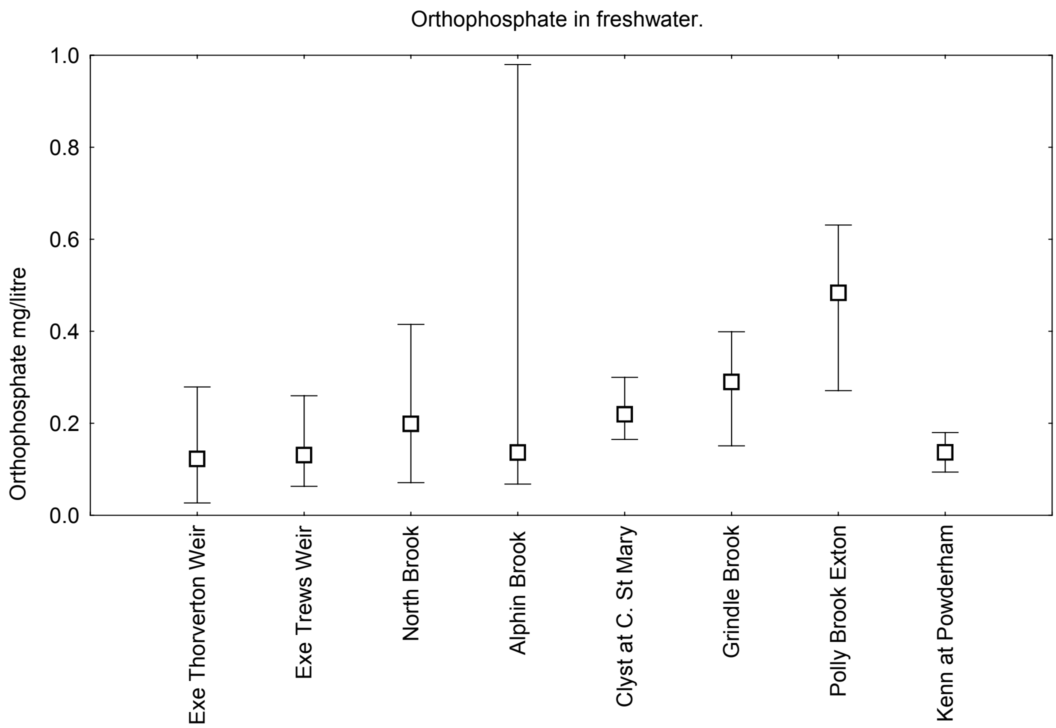
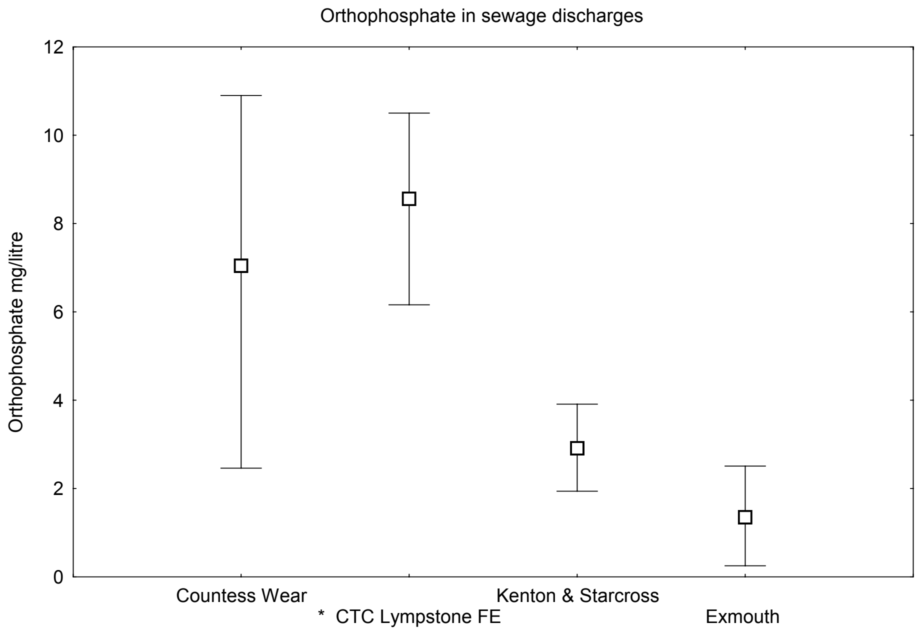


Figure 41. Mean levels of orthophosphate in freshwaters feeding the Exe Estuary 2001. Data source EA. Error bars show min and max concentrations.

[2] Four water company STWs discharge directly into the Estuary, Countess Wear, Kenton & Starcross and Exton N&S. There is no data available for Exton north and south. The Commando training camp at Lympstone (not water company) also discharges sewage effluent to the estuary. Exmouth and Dawlish STWs discharge outside estuary mouth to the east and west respectively.



* denotes non-water company discharge.

Figure 42. Mean levels of orthophosphate in discharges to the Exe Estuary and tributaries 2001 . Data source EA. Error bars show min and max concentrations.

Orthophosphate in tidal waters (in 2001) is shown in figure 43. Highest concentrations are recorded at Lower Wear, below Countess Wear STW (up to 1.23mg l^{-1}). Concentrations decrease with distance down the estuary.

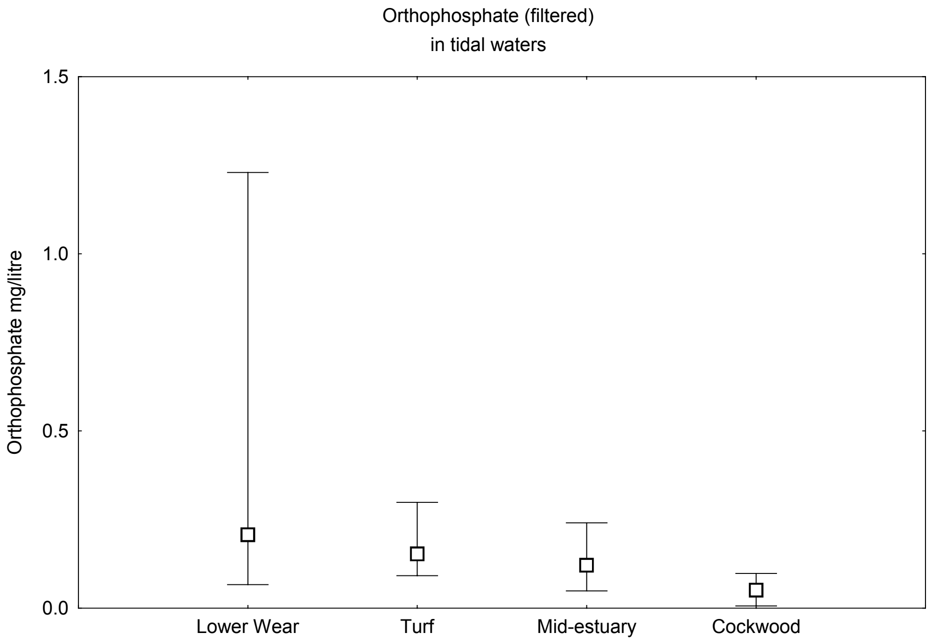


Figure 43. Mean levels (2001) of orthophosphate in tidal waters, Exe Estuary. (Data source EA).

Calculated as elemental P, the approximate background for the tidal waters (25th percentile) is in the range 7 to 38µg l-^{1} (table 26), invariably above the 0.1µg l^{-1} criteria set by the EPA(US) to protect estuarine and marine organisms, but in the lower range reported by Parr *et al* (1999) for coastal waters (7 – 165µg P l^{-1}). The more elevated background levels of orthophosphate in the estuary are at Turf Locks and Lower Wear, in the upper part of the estuary.

Table 26. Elemental P: 25th percentile for the Exe Estuary tidal water sites 2001. Data source:EA

	Elemental P - 25th percentile µg l^{-1}
Lower Wear	26.51
Turf	38.66
Mid-estuary	22.94
Cockwood	7.50

6.2.3 Nitrate

Recent values for nitrate in freshwaters entering the estuary are shown in figure 44. Concentrations appear to be elevated at several sites and individual values for nitrate levels in the Clyst, Grindle Brook and Polly Brook have exceeded 10mg l^{-1} during 2001. Since 1990 annual mean values for nitrate in most freshwater sources have remained relatively constant. The exception is Polly Brook where nitrate concentrations have been gradually increasing. Although the individual streams and brooks may not constitute a significant source of nitrate due to their relatively small freshwater input, the combined contribution to the estuary as a whole is likely to be measurable.

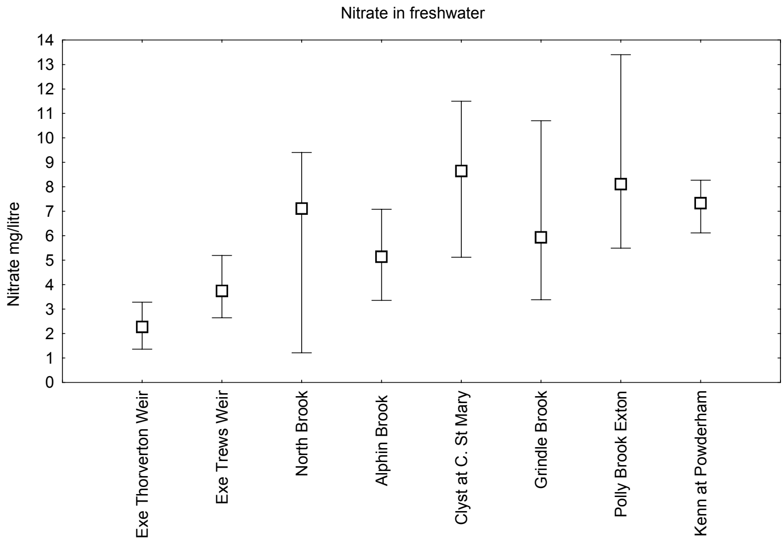
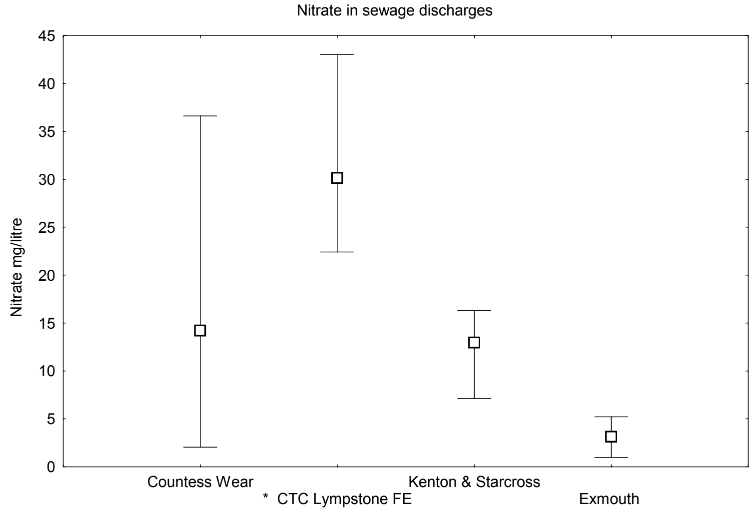


Figure 44. Mean levels of nitrate in freshwaters feeding the Exe Estuary 2001. Data source EA. Data source EA. Error bars show min and max concentrations.

Figure 45 summarises data for nitrate in sewage discharges to the estuary. Again, it is stressed that the data is for concentration only and does not take into the account volume discharged[1].



* denotes non-water company discharge**.**

Figure 45. Mean levels of nitrate in sewage discharges to the Exe Estuary 2001. Data source EA. Error bars show min and max concentrations.

Annual mean values for nitrate in the discharge from Kenton and Starcross STW decreased from 18.5 to 11.1mg l^{-1} between 1990 and 2001, and there has been a small reduction (4mg l^{-1}) in the effluent from CTC Lympstone since 1998. However, nitrate concentrations in discharges from Exmouth and Countess Wear STWs have begun to increase over recent years (figure 46). This may be in response to a reduction in levels of ammonia due to increased nitrification treatment (see next section).

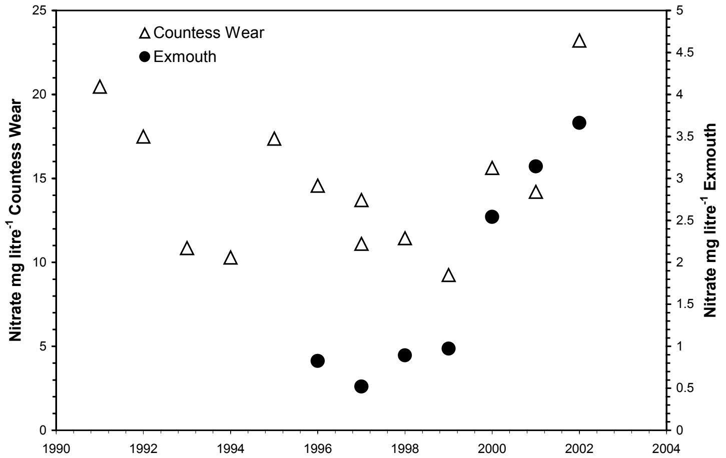


Figure 46. Mean annual nitrate in discharges from Exmouth and Countess Wear STW. (Data source EA).

[1] For rough comparisons, maximum daily flow rate for CTC Lympstone can be 373m^3 day^{-1}, and Kenton & Starcross discharged between 1000 and 10,000m^3 day^{-1} in 2001, whereas the maximum flows from Countess Wear and Exmouth STWs in 2001 were 92,880 and 18,922m^3 day^{-1} respectively.

Recent values for nitrate in tidal waters of the Exe Estuary are shown in figure 47. As is the case for orthophosphate, the more elevated concentrations are recorded in the upper estuary at Lower Wear, below the Countess Wear STW discharge, and levels reduce down the estuary toward the mouth.

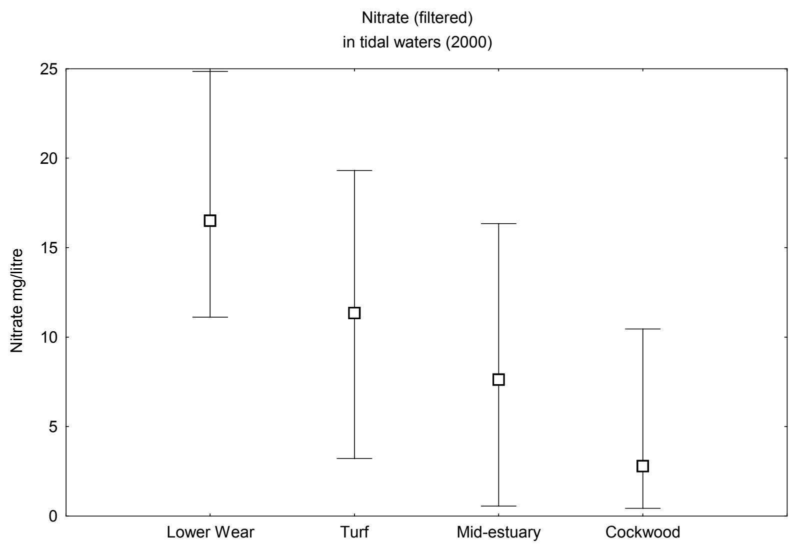


Figure 47. Mean nitrate levels in tidal waters of the Exe. Data are for 2000. Data source EA. Error bars show min and max concentrations

Annual average values for nitrate (expressed as N) in tidal waters are shown in table 27. Values are above 0.144mg l^{-1} N, which indicates hypernutrification (dependant on P levels) as suggested in the North Sea Status Report (see above), and with the exception of Cockwood, exceed the (1mg l^{-1}) effects level suggested by Deegan *et al* (1997) as responsible for poor habitat quality for estuarine fish populations.

Table 27. Nitrate (as N) in the Exe Estuary: Mean annual for 2000.

	Mean annual nitrate (as N) mg l^{-1}
Lower Wear	3.725
Turf	2.562
Mid-estuary	1.722
Cockwood	0.629

6.2.4 Ammonia

Whereas the effects of nitrate and phosphate enrichment tend to be indirect, some forms of ammonia are toxic to marine life. 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 (denitrification). Ammonia as an intermediate stage in nitrogen fixation (conversion of atmospheric N_2

to fixed nitrogen and subsequent incorporation into microbial proteins, etc) is a relatively unimportant source in comparison to mineralisation (Cole *et al.,* 1999).

However, anthropogenic sources are generally more important in estuaries, 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 Sewage Treatment Work (STW) outfalls. The toxicity of ammonia can therefore be a cause for concern in estuarine European marine sites and close to sewage outfalls in coastal waters.

Ammonia is most commonly monitored as N, although it is the un-ionised form of the ammonium ion (NH_3) which is the most toxic. The toxicity of ammonia to aquatic life is affected by 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. Of these three factors, salinity is the least important.

Table 28. Proposed ammonia classification criteria for estuaries in England and Wales (Nixon *et al*., 1995)

Ammonia (as N) - 90th percentile (mg l^{-1})	Class
0.86	A/B
4.7	B/C
8.6	C/D

A proposed GQA classification scheme for ammonia in the estuaries of England and Wales, shown in table 28, is a tiered system with class boundaries derived from a review of toxicity data (Nixon *et al* 1995). This scheme has not been implemented in England and Wales so far but provides a rough guide for comparison of ammonia levels in the marine site.

Atkins (1988) reported high concentrations of ammonia throughout the Exe estuary, which was attributed to the large volumes of sewage entering the system. Ammonia was the most temporally variable form of N in the estuary, concentrations at Topsham in the upper estuary were very high and approached levels which would be toxic to fish. Above Topsham, recorded ammonia levels were even higher and considered 'certainly toxic to fish' and would 'cause migrating fish to avoid the area'. Levels were said to exceed those given by the EEC Directive relating to the quality of water needed to sustain fish life (freshwater). No further references to ammonia levels in the Exe could be found in the literature.

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 the ability of lobsters to adjust to different salinities). Estimated 96-hour LC50s for juvenile school prawns *Metapenaeus macleayi* and leader prawns *Penaeus monodon* are 1.39 and 1.69 mg un-ionised ammonia - NH_3 (as N) l^{-1} - (≡ 26.3 and 37.4mg l^{-1} total ammonia (as N)), respectively (Allan *et al*., 1990). For the nauplius of the marine copepod *Tisbe* *battagliai*, Williams and Brown (1992) estimated a 96-hour LC50 of 0.787 mg NH_3 (N) l^{-1} (≡24.6mg total ammonia (N) l^{-1}), and tests on several life stages showed a No Observed Effect Concentration (NOEC) of 0.106mg NH_3 (N) l^{-1} (≡3.34mg total ammonia (N) l^{-1}). For invertebrates, toxicity appears to increase as salinity decreases (Miller *et al.,* 1990, Chen and Lin 1991), although more work is needed to establish 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.

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). Acute toxicity of ammonia to fish increases with low dissolved oxygen concentrations 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).

Ammonium toxicity to fish is also related to salinity, and appears to be lowest at intermediate salinities (~10psu), but below this may increase as salinity reduces towards freshwater (Seager *et al*., 1998, Miller *et al*., 1990). This may be of relevance, especially in estuaries where DO sags occur at low salinities. In the Mersey, diverse invertebrate populations can survive, and flounder and salmonids can pass through the estuary at a mean unionised ammonia concentration of 0.008 mg NH_3 (N) l^{-1} (Cole *et al,* 1999).

Ammonia does not accumulate in the sediments, although ammonifying microbial activity in sediments can result in ammonia release. Such ammonification activity is greatest when large quantities of macroalgal biomass decline (Owens and Stewart, 1983), and may be a significant source in areas of the Exe Estuary. Additionally, nitrification processes in sediments may be reduced during conditions of low DO and high temperature, (Maksymowska-Brossard and Piekarek-Jankowska, 2001), effectively increasing ammonia concentrations, and potential toxicity to sediment dwelling organisms and those organisms that use water in the boundary layer between the sediment and the water column for feeding or respiration (molluscs, crustacea and most annelids).

Recent data for ammonia (N) indicates that, not surprisingly, concentrations in freshwater entering the Exe estuary from riverine sources are relatively low in comparison to concentrations in discharges (figures 48 and 49, respectively). *However, this does not necessarily reflect ammonia loadings.*

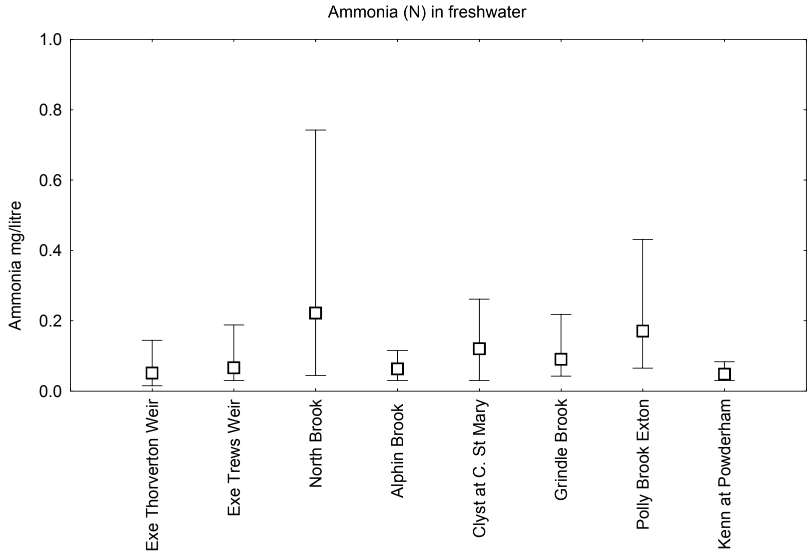


Figure 48. Mean ammonia (N) in freshwater entering the Exe Estuary. Data source EA. Data are for 2001. Error bars show min and max concentrations.

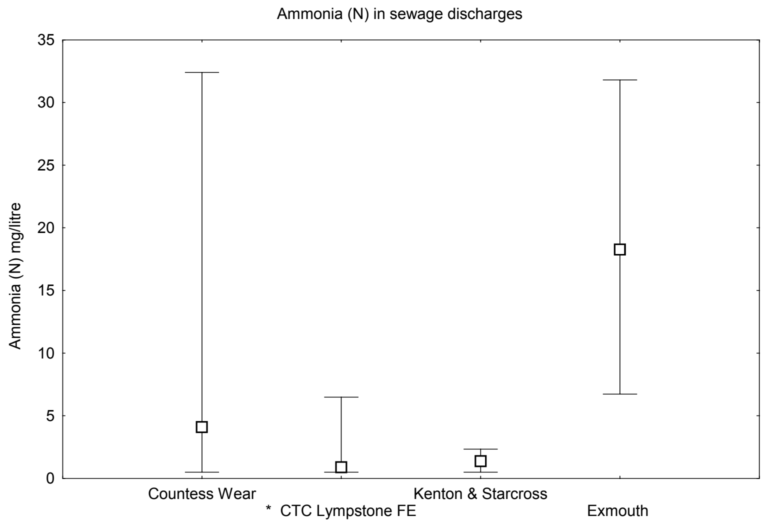
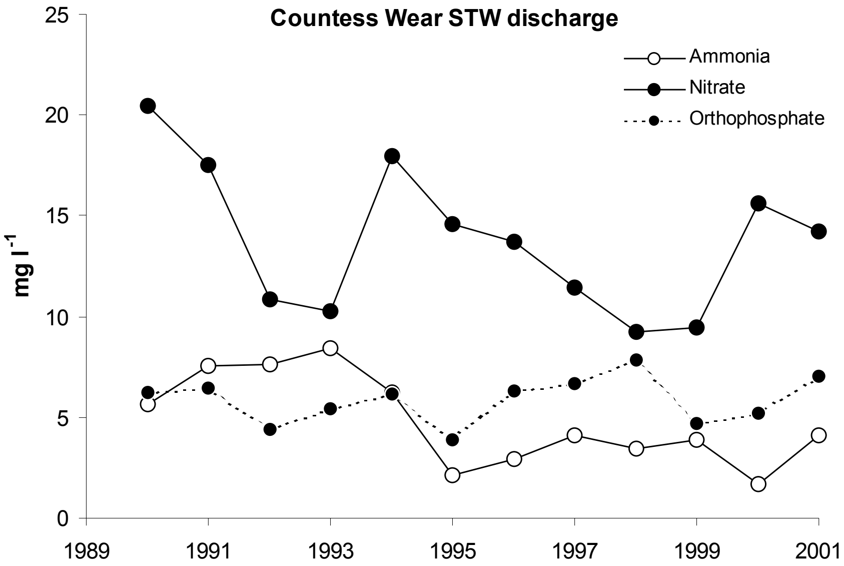


Figure 49. Mean ammonia (N) in STW discharges to the Exe Estuary. Data source EA. Data are for 2001. Error bars show min and max concentrations.

11% of samples (10 out of 93) from Countess Wear STW discharges failed to comply with the ammonia standard of 10mg l^{-1} (95th percentile) in 2001, and the maximum concentration of ammonia recorded was 32.4mg l^{-1} in July 2001.

Ammonia levels in discharges from Exmouth STW are higher than at Countess Wear (mean 18.2mg l^{-1}), although no compliance failures are reported for 2001. This may be due to the nature of the receiving waters (outside the estuary mouth).



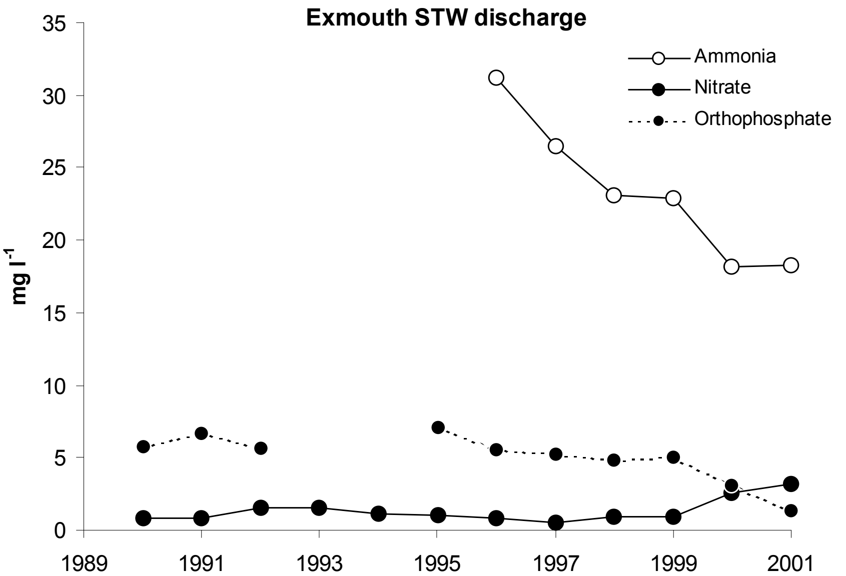


Figure 50. Temporal trends for mean annual concentrations of nitrate, orthophosphate and ammonia (N) in discharges from Countess Wear, and Exmouth STWs. Data source:EA

Information on temporal trends for ammonia in discharges indicate that levels in effluent from Exmouth have been reducing since the Exmouth/Budleigh Salterton scheme was implemented in 1996, and there has been a slight reduction since 1993 for Countess Wear (figure 50).

An ammonia standard (10mg l^{-1} as 95th percentile) has been introduced for discharges to sensitive areas. The aim of this standard is to reduce ammonia in tidal waters in order to comply with the proposed EQS of 0.021mg l^{-1} un-ionised ammonia (NH_3 N) for the protection of saltwater fish and shellfish. The effect of ammonia reduction is a net increase in nitrate concentration as observed in discharges to other southwest estuaries (e g Poole, EA 2001c). This may explain why concentrations of nitrate and ammonia can be seen to co-vary inversely in figure 50.

Recent values for ammonia in tidal waters of the Exe Estuary are shown in figure 51. Highest concentrations are recorded downstream of Countess Wear STW and in mid-estuary (max 0.59 and 0.56mg l^{-1} respectively). Further downstream, concentrations decrease along the estuary toward the mouth.

Note that the ammonia data are totals, and values for unionised ammonia, NH_3 (N), would need to be calculated from the total data, taking account of pH, temperature, and salinity. As a rough guide; for a pH of 8.2, a temperature of 20ºC, and a salinity of about 30psu, 0.44 mg l^{-1} total ammonia (N) relates to about 0.021mg l^{-1} NH_3 (N), which is the proposed EQS. Thus, the potential may exist for this value to be exceeded in tidal waters of the Exe in individual samples, but probably not as an annual average. There may be a case for targeted monitoring of NH_3 (N) in the estuary.

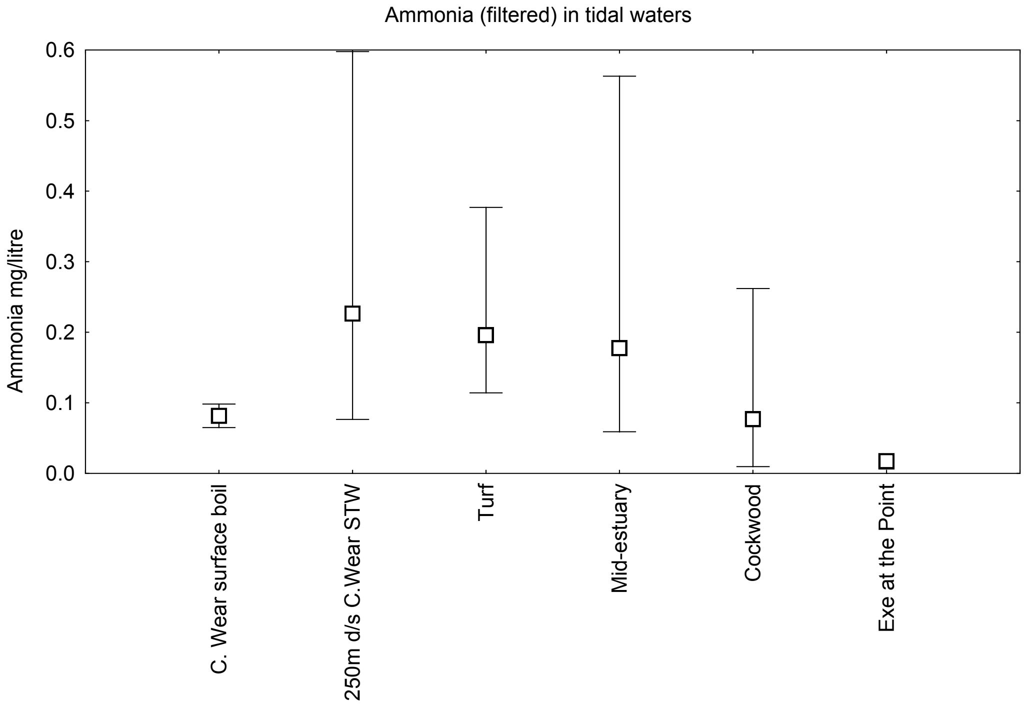


Figure 51. Ammonia (filtered as N) in tidal waters of the Exe Estuary (annual mean). Data are for 2001 except Countess Wear surface boil and Exe at the Point (2000). Data source EA. Error bars show min and max concentrations.

Elevated ammonia levels in the upper estuary probably reflect the fact that STW inputs from Countess Wear discharge in to a relatively enclosed area, whilst for middle estuarine sites the source/s are not so clear. Kenton & Starcross and

Lympstone STWs cannot be ruled out as possible sources, also there are inputs of sewage from Exton (N & S) for which we have no data[1].

Mean annual values for ammonia in tidal waters show that reductions in ammonia concentration occurred between 1992 and 2000, although in 2001 this trend is reversed at the Turf, Mid-estuary and Cockwood sites (figure 52).

This may to be a result of small increases in discharges, and also possibly related to releases from sediment during macroalgal decline (see section 9.2). More work is needed to establish the contribution from this source.

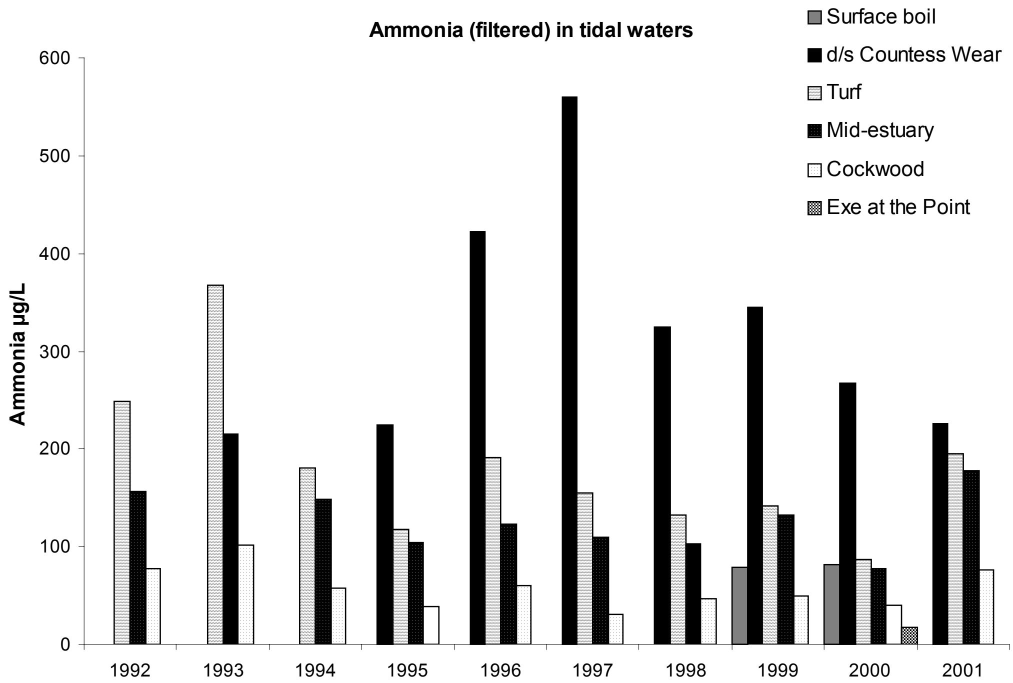


Figure 52. Temporal trends for ammonia (filtered as N) in tidal waters of the Exe Estuary. (Data source EA).

6.2.5 Chlorophyll *a* and micro-algae

Elevated spring and summer levels of chlorophyll *a* are one of the primary symptoms of increased nutrient inputs to estuarine waters and as such are another response variable measurement. Levels of chlorophyll would be expected to increase in spring due to the natural spring bloom. It is pronounced or persistent blooms which cause concern. Chlorophyll *a* is the molecule mediating photosynthesis in almost all green plants, including phytoplankton. Rapid proliferation or blooms of phytoplankton, as reflected in elevated chlorophyll *a* levels, can occur throughout the ocean but are typically associated with temperate coastal and estuarine waters, notably in restricted exchange environments such as estuaries. During winter months growth of phytoplankton populations are at a minimum because of reduced temperature, light availability, and water column stability, and chlorophyll-*a* levels generally remain low. Monitoring of chlorophyll *a* is undertaken more often in spring and summer

[1] The discharge from Lympstone is a private MOD discharge. The discharge of crude sewage from Exton (N) is ~10.8m^3 day^{-1}, and discharge for Exton (S) receives primary treatment and amounts to approximately 40m^3 day^{-1}.

months when estuarine concentrations may exceed 50-80µg l^{-1}, under optimum growing conditions (Monbet 1992).

In the UK, the indicator (mean) value for suspected eutrophic conditions is set at 10µg l^{-1} chlorophyll *a* (Dong *et al.,* 2000; also DoE standard, [EA, 2001c]). Values greater than this, coupled with cell densities of 5 x 10^5 cells l^{-1} (500 cells ml^{-1}) are considered indicative of phytoplankton blooms (EA, 1997).

There are indications that phytoplankton blooms have occurred in the Exe Estuary. In the upper estuary, up to 60µg l^{-1} chlorophyll *a* were recorded in 1987, whereas levels of 0.5 – 1.5µg l^{-1} were found in the inflowing river water and the sea water at the mouth of the estuary (Atkins, 1988).

Algal blooms were also observed in the estuary during the summer months of 1988 and 1999 but were not sustained throughout the summer (EA, 2001b). Algal species recorded in high numbers included *Naviculoid sp., Nitzschia sp.* and *Chaetoceros*; species often associated with brown surface scum. A large bloom of *Nitzschia closterium* was observed at Lower Wear in August 1998, and a large diatom bloom which included *Chaetoceros* occurred in the estuary during July 1999. Cell counts were highest in 1998, and on spring tides (Turf Locks and mid-estuary) in both years. On neap tides, chlorophyll *a* measurements were high but corresponding cell counts low, indicating the presence of dead or dying algae. Figure 53 shows the mean, maximum and minimum values of chlorophyll *a* concentrations recorded during the period 1998-1999. The maximum concentration (101µg l^{-1}) occurred at Turf Locks. With the exception of Cockwood, mean chlorophyll *a* concentrations recorded exceeded the UK indicator mean for suspected eutrophic conditions.

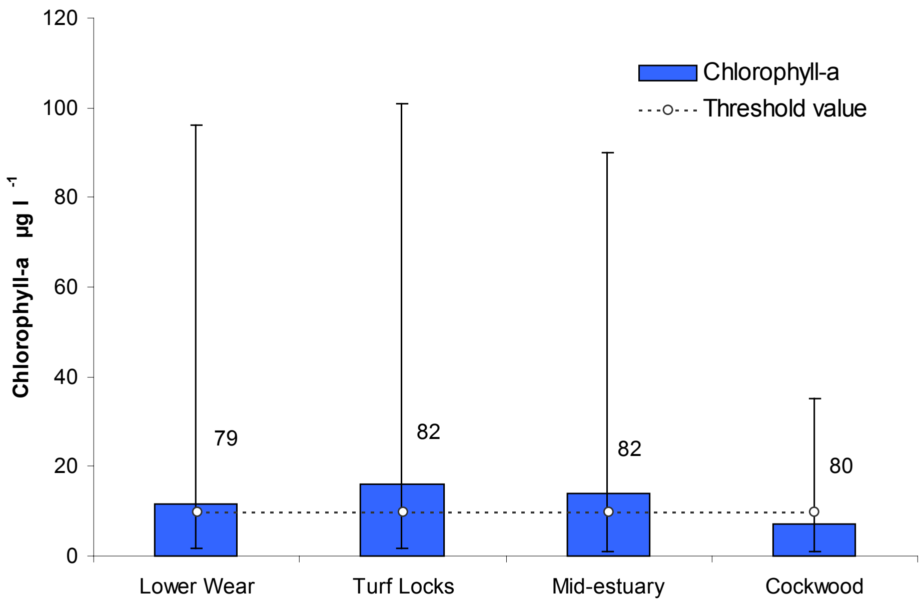


Figure 53. Mean values for chlorophyll *a* in tidal waters of the Exe Estuary 1998-2000; Figures above bars refer to number of samples. Error bars represent min and max concentrations (from EA, 2001b). Threshold value = 10µg l^{-1} - (mean) value for suspected eutrophic conditions (Dong *et al.,* 2000); also DOE standard (EA, 2001b).

Data for chlorophyll *a* concentrations in tidal waters of the Exe in 2001 are summarised in figure 54 and trends generally resemble those in the two previous years. Data are mainly for April-September, although measurements taken in the winter months (Nov, Feb) are included for some sites. The UK indicator value for suspected eutrophic conditions of 10µg l^{-1} chlorophyll *a* (Dong *et al.,* 2000) was exceeded at both Turf Locks and Mid-estuary during 2001 (mean 13.6 and 11.4µg l^{-1}, respectively) with maximum concentrations (58 and 45µg l^{-1}) occurring in April.

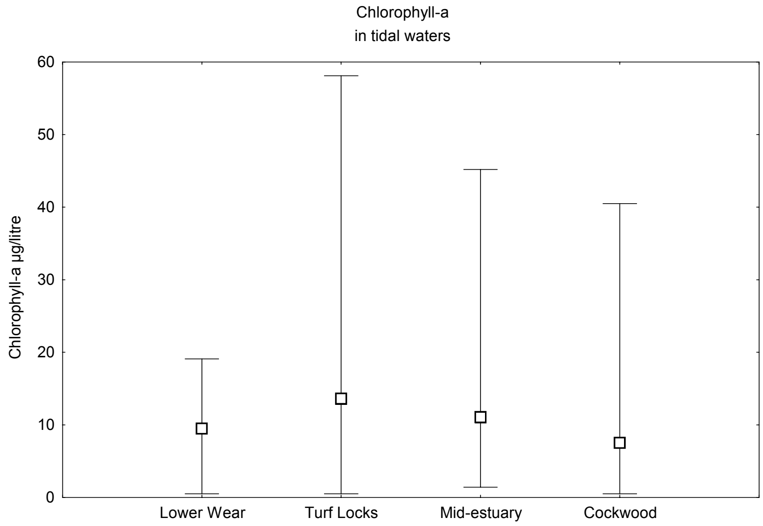


Figure 54. Chlorophyll a in tidal waters of the Exe Estuary. Data source EA. Data is for 2001.

On a longer temporal scale, concentrations have been increasing over the past decade, this trend is exemplified in figure 55 showing measurements in the middle reaches of the estuary taken at Turf Locks. Temporal trends generally show a seasonal pattern for chlorophyll *a* in tidal waters, with the expected spring and summer blooms. The most pronounced of these was during July 1999 when elevated concentrations were recorded at most sites, up to 101µg l^{-1} at Turf. An unusual winter bloom is indicated by high concentrations of up to 44µg l^{-1} recorded at Turf during November 1990. These higher winter levels indicate that potentially eutrophic conditions existed in the estuary more than 10 years ago.

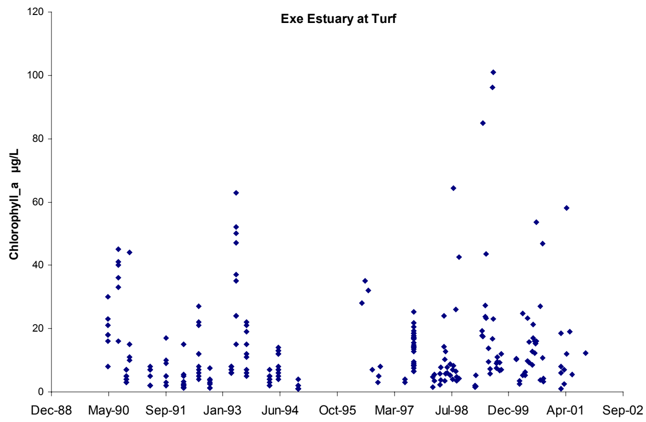


Figure 55. Temporal variations for chlorophyll *a* in tidal waters of the Exe Estuary at Turf Locks. Data source EA.

Recent (2001) values for chlorophyll *a* in freshwaters entering the estuary are summarised in figure 56. Highest concentrations are recorded in the Exe at Trews

Weir with a maximum of 18.3µg l^{-1} in June (presumably freshwater phytoplankton species). Elevated levels of freshwaters plankton may lead to problems following die-off (release of DOC) as they enter more saline waters in any great numbers.

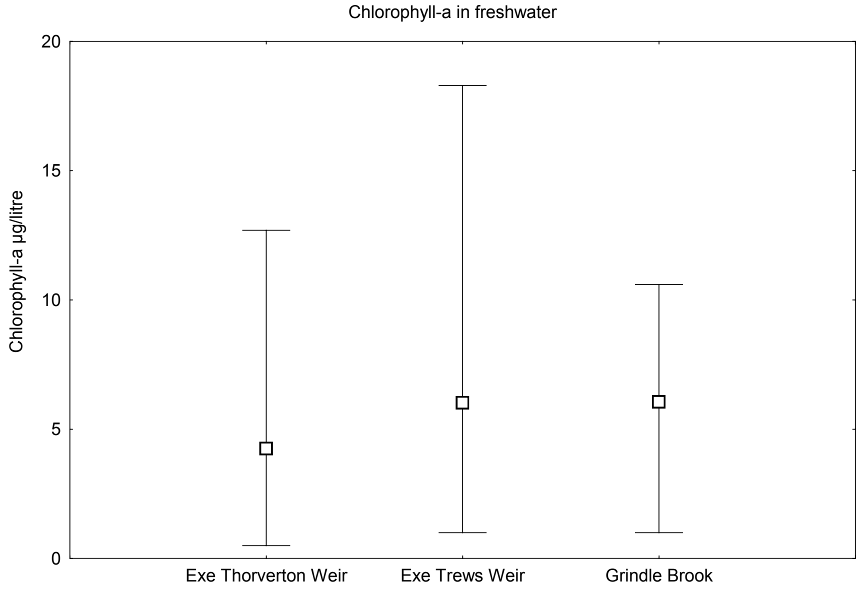


Figure 56. Mean annual values for chlorophyll *a* in freshwaters feeding the Exe Estuary. Data source EA. Data is for 2001.

There have been several complaints by members of the public, concerning the presence of brown foams and scums, indicative of algal blooms, principally in the Topsham and Starcross areas. One incident was investigated and the scum analysed for chemicals and algae in an attempt to establish its source but results were inconclusive (EA, 2001b). Increasingly, therefore, it is important to distinguish between natural blooms and those caused by "artificial" causes, typified by elevated and prolonged spring and summer levels of chlorophyll a. It is also important to try and predict under what circumstances nuisance blooms will occur.

Overall, data for chlorophyll *a* indicate regular phytoplankton blooms which may be increasing in intensity, and that these are probably related to elevated nitrate and phosphate concentrations. Rigorous monitoring would seem advisable to ensure that this trend does not escalate in to nuisance proportions.

NB. It is generally assumed that an N:P ratio of 10:1 is ideal for plant growth. At N:P ratios >10:1 (mainly in freshwater), P is thought to be limiting, and at N:P ratios < 10:1 (mainly in seawater) N is thought to be limiting. However, there are 3 large coastal areas in the UK where P may be limiting – from the Solent to Dartmouth; around the Severn from Padstow to Oxwich, and from the Humber to Essex (Parr *et al,,* 1999).

The N:P ratio in the tidal Exe, based on annual average values (phosphate as elemental P and nitrate as N) for 2000 is >10 at all sites (Lower Wear 47, Turf Locks 42, Mid-estuary 115, Cockwood 15) indicating that N is unlikely to be limiting.

6.2.6 Dissolved Oxygen

DO is measured in estuaries and coastal waters in terms of either a concentration (mg l^{-1}) or as a percent saturation (%). Table 29 shows recommended EQS values for saline waters derived from the review of Nixon *et al.,* (1995).

Table 29. Recommended EQSs for dissolved oxygen in saline waters (from Nixon *et al.,* 1995)

Saltwater use	EQS	Compliance statistic	Notes
Designated shellfishery	70% saturation 60% saturation 80% saturation	50%ile, mandatory standard Minimum, mandatory standard 95%ile, guideline value	EC Shellfish Water Directive
Saltwater life	5 mg l^{-1} 2 mg l^{-1}	50%ile 95%ile	
Sensitive saltwater life (e.g. fish nursery grounds)	9 mg l^{-1} 5 mg l^{-1}	50%ile 95%ile	
Migratory fish	5 mg l^{-1}3 mg l^{-1}	50%ile95%ile	Higher values may be required where fish have to traverse distances >10 km, or where high quality migratory fisheries are to be maintained

Various class thresholds for estuaries in England and Wales, based on DO over a continuous period of >1 hour were proposed by Nixon *et al.,* (1995) (see table 30) and although this scheme has not been implemented, the class thresholds are a useful indication of the levels of DO that are likely to affect organisms which are exposed for long periods.

Table 30. 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^{-}

The principal sources of DO in the marine environment are the atmosphere, via O_2 gaseous exchange across the air-sea surface, and *in situ* production by algae and aquatic plants during photosynthesis. DO levels vary with temperature, with lowest levels in estuaries occurring during the summer months. 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.

Increased levels of nutrients in estuarine waters can stimulate growth of both macro algae and phytoplankton (algal bloom), resulting in an intensification of both seasonal and diurnal variation in DO. Daytime photosynthetic activity may result in O_2 supersaturation of the water column; whilst at night severe depletion can occur due to respiration. These fluctuations can cause problems for fish and invertebrate communities. During bloom die-offs, microbial decomposition of algal cells leads to an increase in oxygen demand and acute DO depletion, which again can result in lethal and sub-lethal effects to fish and invertebrate communities.

Atkins (1988) reported that concentrations of dissolved oxygen were elevated to the point of super saturation (>100% saturation) in some areas of the Exe during a 1987 survey. Such high levels were considered to be a reflection of the high algal density (section 6.2.5). Oxygen content was highest in the upper estuary and on neap tide cycles when minimum water exchange occurs and algal populations flourish. DO increases were observed in the mid- and lower reaches during the ebb tide as highly oxygenated water moved down the estuary. Although it was clear that DO concentrations were sufficient to sustain fish and EEC limits were not approached during the study, Atkins noted that phytoplankton abundance would exert a strong oxygen demand at night during respiration, but to establish the extent of this would require overnight monitoring.

Daytime spot sample measurements during 1998-2000 are summarised in figure 57 and show no noticeable difference between surface, mid-depth and bottom samples indicating that the water column was relatively well-mixed. No close relationship between salinity and DO was found (EA, 2001b).

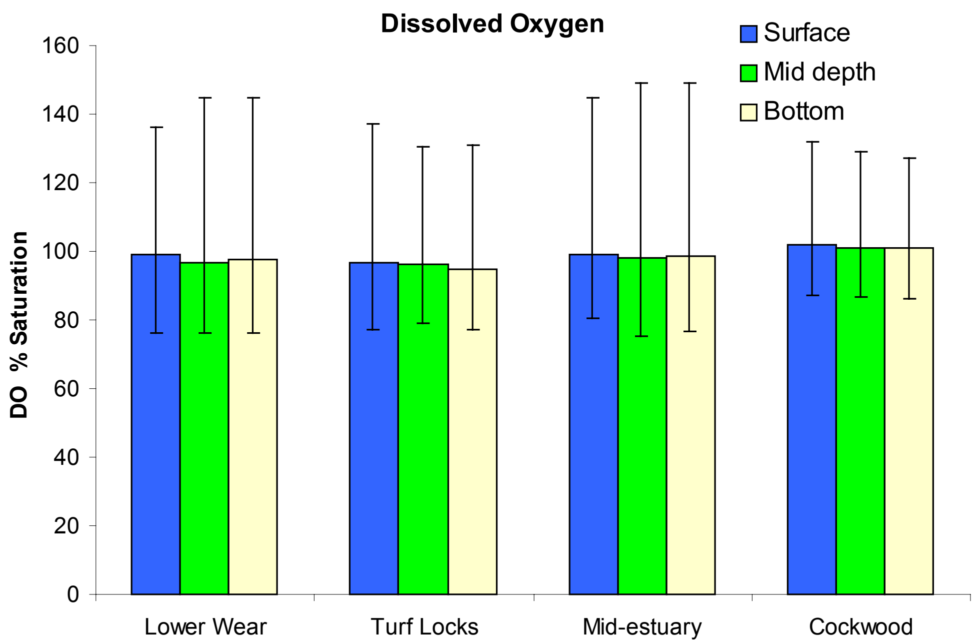


Figure 57. Mean values for dissolved oxygen in tidal waters of the Exe Estuary 1998-2000; Error bars represent min and max concentrations (from EA, 2001)

Continuous monitoring was carried out for much of the period between March and September 2000 at Turf Locks in the estuary (EA, 2001b). Results were similar to that reported by Atkins (1988) and showed that supersaturation (up to 160%) occurred in July. However, dissolved oxygen concentrations fell to almost zero at times in September (presumably at night) and remained as low as 60% for periods in August and September.

Data for DO, expressed as mg l^{-1}, in tidal waters of the Exe (2001) are summarised in figure 58. Overall, mean values are high and similar at all sites, as in previous years. Levels are above the 5mg l^{-1} (median) recommended EQS value for saltwater life and for migratory fish (see table 29). Minimum values during the year do not fall below this figure, although these are a result of spot sampling, presumably during the hours of daylight. It has been shown by continuous monitoring that severe oxygen depletion in the estuary can occur at night (see above).

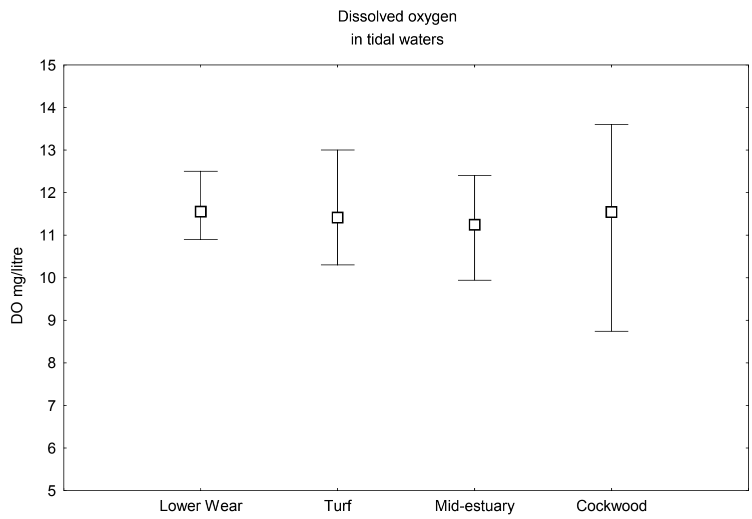


Figure 58. Mean annual values for dissolved oxygen in tidal waters of the Exe Estuary. Error bars represent min and max concentrations Data source EA. Data is for 2001.

There is a general trend toward increasing concentrations of DO at these sites over the last decade, which is probably related to algal activity in the estuary and characterised by exaggerated fluctuations in DO such as those discussed above.

Data for dissolved oxygen in freshwater sources for 2001 show mean concentrations to be between 10 and 11mg l^{-1} for all sites and do not indicate DO depletion, although again, it has been shown that data from daytime spot sampling may not give a clear representation of the situation.

6.2.7 Turbidity and Suspended Solids

Turbidity is a measure of the attenuation of light in the water column and may be defined as the properties of water that cause light to be scattered and absorbed. Turbidity is caused by particles and dissolved substances in water, including organic and inorganic particulate suspended matter, and dissolved substances that contribute to the colour of water. During blooms, the organic component can include significant amounts of algae.

The composition of particulate matter varies but is derived from: directly eroded material, sediments that have settled to the substratum and become resuspended during periods of high flow, dredging, suspended solids in discharges, chemical flocculation (at the salt/freshwater interface) and plankton. Increased or sustained turbidity in the water column may result in a reduction in algal (macroalgae and phytoplankton) growth rates due to reduced light availability. Subsequent adverse effects to zooplankton, benthic communities and fish populations (a general reduction in biodiversity) would be anticipated as particulates are suspended and re-deposited. An accompanying reduction in food availability may have secondary effects on higher trophic levels.

Methods for measuring turbidity vary, utilising different combinations of light transmission and scattering, water transparency (secchi disc), suspended solids (sample filtered and dried at 105°C or 500°C) or remote sensing. The results of these methods are not readily inter-convertible making comparisons problematic, and the only EQS appears to under the Bathing Waters Directive and relates to transparency using a secchi disc (guide value 90th percentile >2m; imperative value 95th percentile >1m). These values are only applicable during the bathing season and may be waived in the event of 'exceptional weather or geographical conditions'.

Atkins (1988) found suspended solids of between 0 and 7.5mg l^{-1} at offshore sites in the estuary, with the higher values recorded close to the estuary bed. In the lower estuary, increased water velocities on spring tides produced higher levels but these did not exceed 11mg l^{-1}. Similar levels were recorded in the Lympstone area where the highest values were recorded during low tide and on the flood. Higher up into the estuary turbidity increased. On spring tides at Turf Locks, suspended solid levels were high, in excess of 25g l^{-1}, and increased further towards the head of the estuary. This was thought to reflect the effects of sediment resuspension in strong currents, coupled with inputs from sewage and river discharges.

The principal method used by the EA for quantifying turbidity in the Exe Estuary is suspended solids (at 105°C) (units: mg l^{-1}). Figure 59 shows suspended solids in freshwater sources of the estuary. Generally, rivers and streams entering the Exe do not appear to comprise a significant source of suspended matter, mean annual values for 2001 are in the range 4.1 to 15.8mg l^{-1} (the Exe at Thorverton and Trews Weir, respectively). A single elevated value for North Brook, which joins the Exe above Countess Wear, is included although there are no other measurements to indicate how representative this value is.

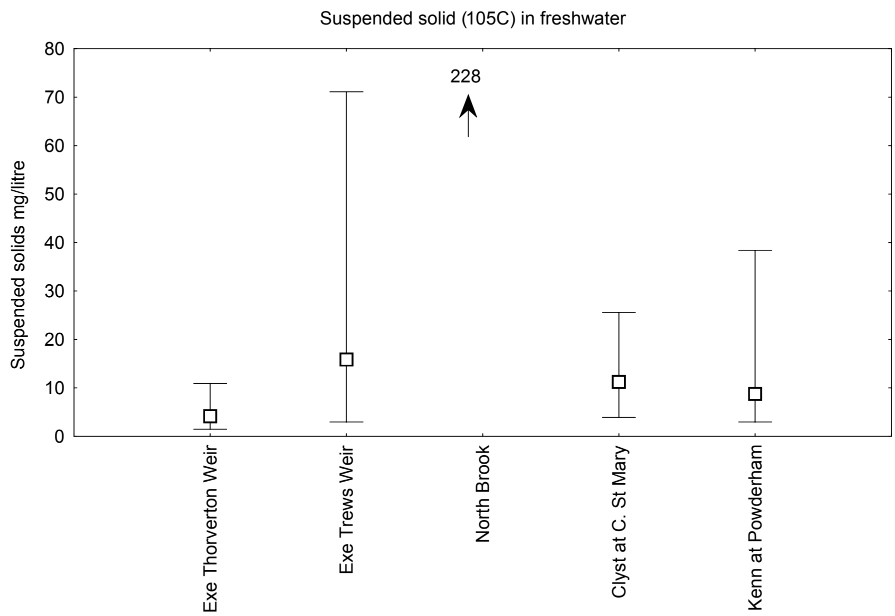


Figure 59. Mean levels of suspended solids @ 105°C in freshwaters entering the Exe Estuary. Data source EA. Data are for 2001. Error bars show min and max concentrations.

For discharges, recent data indicate that highest mean levels occur at Kenton and Starcross. However, levels are low overall (figure 60). EA data indicates that the Countess Wear discharge failed to meet standards on one occasion during 2001, presumably with the maximum recorded value of 27mg l^{-1}. There are few clear temporal trends in the data; however, significant reductions in levels of suspended solids have occurred in discharges from Exmouth STW over past decade, presumably in response to improved waste treatment.

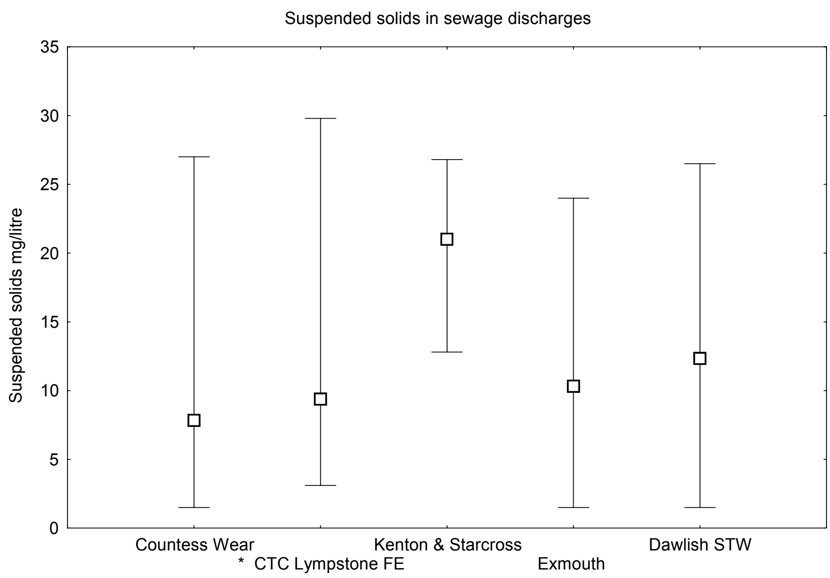


Figure 60. Mean levels of suspended solids @ 105ºC in discharges to the Exe Estuary. Data source EA. Data are for 2001. Error bars show min and max concentrations.

Recent data for suspended solids in tidal waters are summarised in figure 61. Concentrations are moderate to high in places (mean values between 17 and 74mg l^{-1}) and indicative of relatively turbid waters in mid-estuary. Temporal trends for suspended solids in the tidal reaches of the estuary are interesting in that several sites (Countess Wear, Turf, mid-estuary and Cockwood) show gradual reductions between 1990 and 1995. Subsequently, these trends are reversed, with values for the latter 1990s increasing.

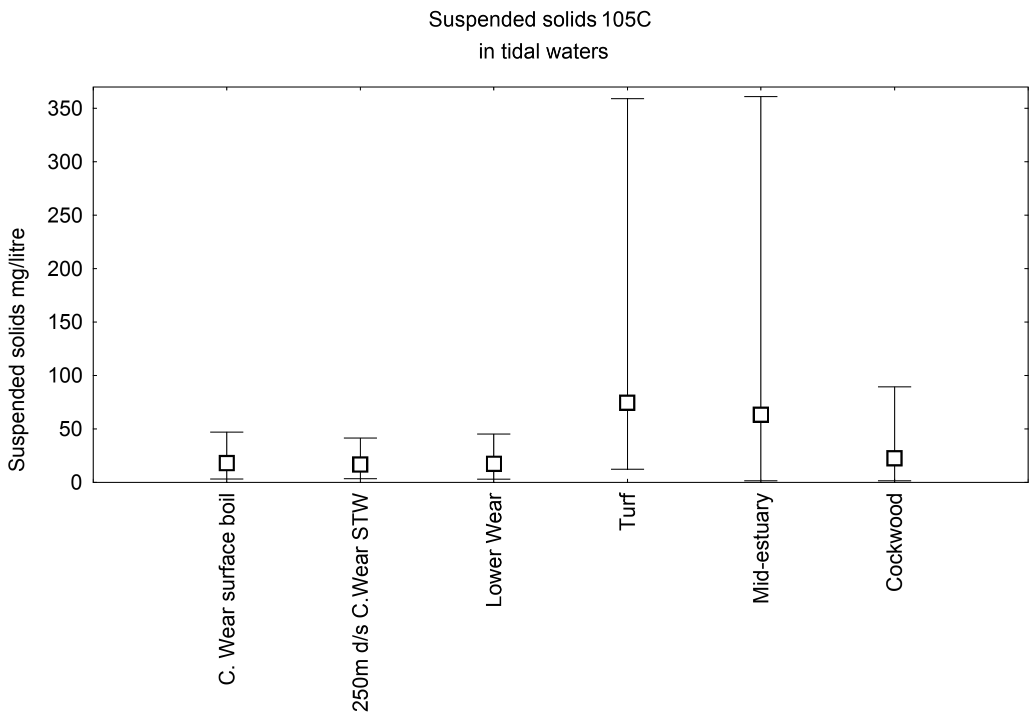


Figure 61. Mean levels of suspended solids @ 105ºC in tidal waters of the Exe Estuary. Data source EA. Data are for 2001. Error bars show min and max concentrations.

Compared with concentrations of suspended solids found in other UK estuaries, values for the Exe are perhaps average. To put these levels into some perspective, Cole *et al* (1998) cited typical mean annual values for suspended solids (105°C) around the English and Welsh coast as 1-110mg l^{-1}, and suggested that anything >100 mg l^{-1} could be considered high.

7. SEDIMENT STATUS AND QUALITY GUIDELINES

At present there are no environmental quality standards for sediments applicable in the UK. However, several guidelines on sediment quality are emerging, and CEFAS has cautiously recommended the Canadian/US effects-based approach (CCME ,1999; Long *et al*., 1995). Threshold Effects Levels (TELs - affecting the most sensitive species) and Probable Effect Levels (PELs - likely to affect a range of organisms) are derived from published toxicity data for a variety of substances in sediments (laboratory and field exposures). TELs are proposed as an Interim Sediment Quality Guideline (ISQG) value. As yet these guidelines have not been validated in the UK, though for many List I substances of the Dangerous Substances Directive a 'standstill' provision applies whereby the concentration of the substance in sediments (and organisms) must not increase with time. Sediment quality is also important under the remit of the Habitats Directive (attainment of Favourable Conservation Status - FCS) which may require improvements to sediments at the site in order to secure long-term sustainability.

There are a number of further caveats to the application of these guidelines, as discussed by Grimwood and Dixon (1997) in the context of List II metals. Foremost are the possible influences due to fundamental differences in sediment geochemistry (as discussed in the footnote below) and the use of non-indigenous test species in deriving thresholds. Nevertheless, in the absence of any UK standards, interim guidelines adopted by Environment Canada (CCME 1999; see Annex 5) serve as a rough indication of the risk to biota from sediment contaminants. Hence, their application will help to identify instances where efforts should be made to minimise further inputs of these substances to the SPA.

7.1 Metals

In general, levels of metal contamination in estuarine sediments decrease significantly towards offshore sites, partly due to distance from major inputs, and partly due to changing characteristics of the sediments. The progression from fine silts rich in binding sites in the upper estuaries, to coarser sediments offshore is usually accompanied by decreasing contaminant loading. Thus, distributions will be governed to a large extent by the hydrodynamic regime in the system and the sorting and redistribution of fines. Sieving and normalisation procedures[1] are advisable to compensate for such granulometric and geochemical effects, to allow meaningful comparison of contamination levels (Langston *et al*., 1999; MPMMG, 1998). In the current report we have used our own data, for sediments sieved at 100µm, to examine

[1] The need to standardise/normalise sediment measurements: This stems from the fact that chemical composition varies according to the sediment type, irrespective of anthropogenic influence. Thus muds and silts naturally have higher metal loadings than coarse sands because of their larger surface area and more extensive oxyhydroxide and organic coatings (capable of sequestering other chemicals). There are various ways in which this granulometric variance can be overcome, including normalisation to geogenic elements such as Al and Li: this may be particularly useful when comparing sediments of totally different geological backgound. An alternative and more direct technique to minimise the influence of grain size in comparisons is to select particles of similar size – hence the use of particles <100µm in the MBA data. A study of microwave-digested Irish Sea sediments has shown that, following sieving at this mesh size, further normalisation confers no significant additional advantage when comparing contaminant trends (Langston et al., 1999). Sieving fulfils a further function - to place emphasis on particles which are accepted by benthic organisms.

sediment quality in the Exe Estuary. Because of the small data set however, we have also incorporated EA data which are presumed to be on unsieved sediment. Provided that the samples are predominantly fines (<100µm), as they may well be throughout much of the estuary, these direct comparisons should be valid.

There are other methodological issues to bear in mind when comparing sediment data sets. Firstly, temporal differences: neither of the data sets used here contains very recent information on Exe sediments. MBA's records are primarily from the 1980s and EA data are for the early 1990's, though, fortunately, sediments tend to integrate contamination over much longer-time scales than water. Secondly, chemical techniques (e.g. digestion and analysis) and quality assurance practices may differ. However since sets of analyses appear subjected to reasonable validation procedures the data are considered acceptable for at least an initial assessment of sediment quality[1].

Figure 62 shows sediment sites sampled by EA and MBA. Metals for which guidelines on sediment quality have been produced include Hg, Cd, As, Cr, Cu, Pb and Zn.

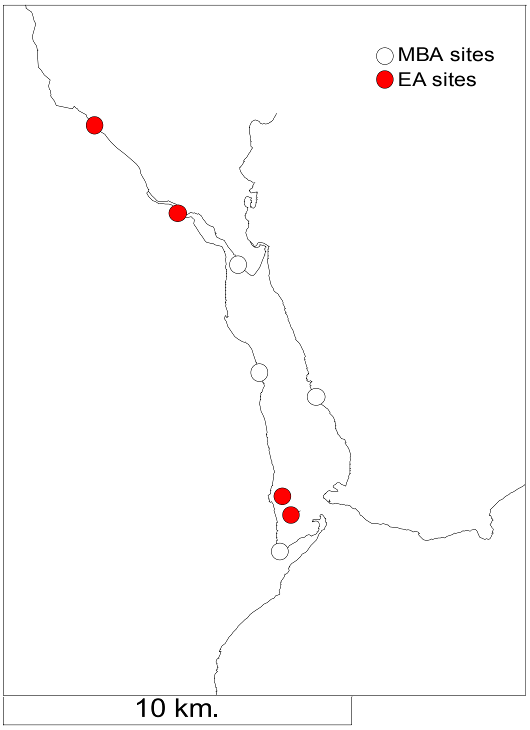


Figure 62. Location of EA and MBA sampling sites used in mapping of sediment quality.

[1] footnote - QA procedures: The Agency has recently (May 2002) been accredited by UKAS to BS EN ISO/IEC 17025. Prior to this formal accreditation (when most of the analyses considered here would have been performed), internal QA/QC procedures and inter-laboratory calibrations were operated. Unpublished MBA metals data on sediments and biota in the European Marine Sites, used in this project, are based on similar internal QA/QC protocols: the methods used have been validated in a number of intercalibration exercises (e.g. Quasimeme) and for the last 10 years has involved regular use of certified reference materials as checks on quality of the data. Samples are expected to be accurate to within ± 10%.

In order to demonstrate graphically the likelihood of biological effects, we have represented data for metals in inter-tidal sediments from the Exe Estuary in map form, classifying sites according to the interim sediment guideline criteria for each metal (figures 63 and 64). Green bars denote sites where no harm to biota is predicted (below Interim Sediment Quality Guidelines, ISQG's), grey bars denote sites where effects cannot be excluded (between ISQG's and PEL's) and red bars represent sediment concentrations where harmful effects might be expected (above PEL's).

The trend in concentrations is very similar for all metals. Levels are low in freshwater at Trews Weir (all below ISQG) and highest at the head of the estuary (probably due to inputs from Countess Wear, coupled with natural adsorptive processes and scavenging by particulates at low salinities). Concentrations generally decrease towards the mouth of the estuary.

Chromium levels in sediments fall below the ISQG value at all sites (green bars in figure 63). Even though they display enrichment upstream in the estuary, none of the sediment Cr values is anticipated to result in biological effects. The pattern for Cd is virtually identical, though at Countess Wear concentrations exceed the ISQG (grey bar figure 63 – biological effects cannot be excluded), but do not exceed the PEL value where effects would be expected.

Mercury, lead and copper sediment concentrations generally fall between ISQG and PEL values at upper and mid-estuary sites (grey bars in figures 63 and 64), but are below ISQG guideline values at the shellfish sites in the lower estuary (green bars). The pattern for Zn is also similar. However at Countess Weir the Zn concentration exceeds the probable effects level, as indicated by the red bar in figure 64.

Despite evidence of enrichment at Countess Wear, the concentrations of As in sediments display least variation throughout the estuary, and according to the CCME criteria are consistently at levels where biological effects cannot be excluded (*see* grey bars figure 64).

It is emphasized that these are guideline values only and, for some contaminants, may tend to be overcautious. Where sediments have exceeded the PEL (in only one case for metals in the Exe) this is usually by a relatively small margin, rather than by orders of magnitude. Effects, if they occur, would be chronic rather than acute.

Although these sediment classifications do not themselves constitute direct evidence for effects (or the absence of effects), the results nevertheless indicate that diffuse source contamination from sediment is unlikely to be of significance throughout much of the Exe SPA. Based on available evidence it is only in the region of Countess Wear near the tidal limit of the estuary, that deterioration due to metals could be expected.

It is stressed that much of the data on sediments presented here is more than ten years old. Re-survey is needed to establish the current status and to evaluate temporal trends. This is seen as a particularly important issue in terms of meeting standstill requirements for sediments under the Dangerous Substances Directive, and attainment of Favourable Condition (Habitats Directive), and may partially drive the requirement to minimise further inputs via aqueous discharges.

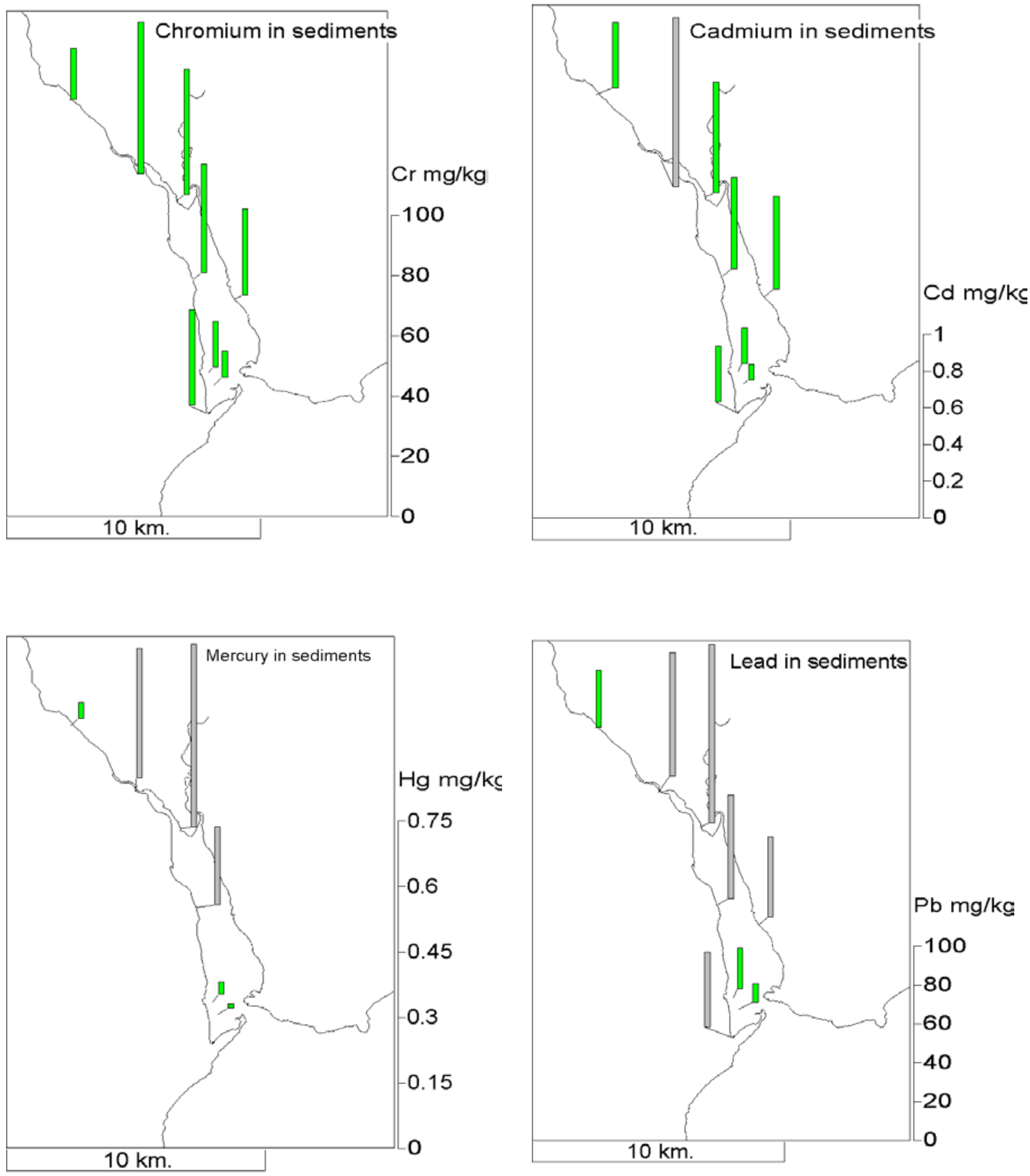


Figure 63. Chromium, cadmium mercury and lead in sediment. Classification of the Exe Estuary SPA based on interim marine sediment quality guidelines (ISQG's) and probable effect levels (PEL's) (from CCME 1999). Red = effects expected; Grey = possible effects cannot be excluded; Green = no harm to the environment expected. (Data Source MBA and EA)

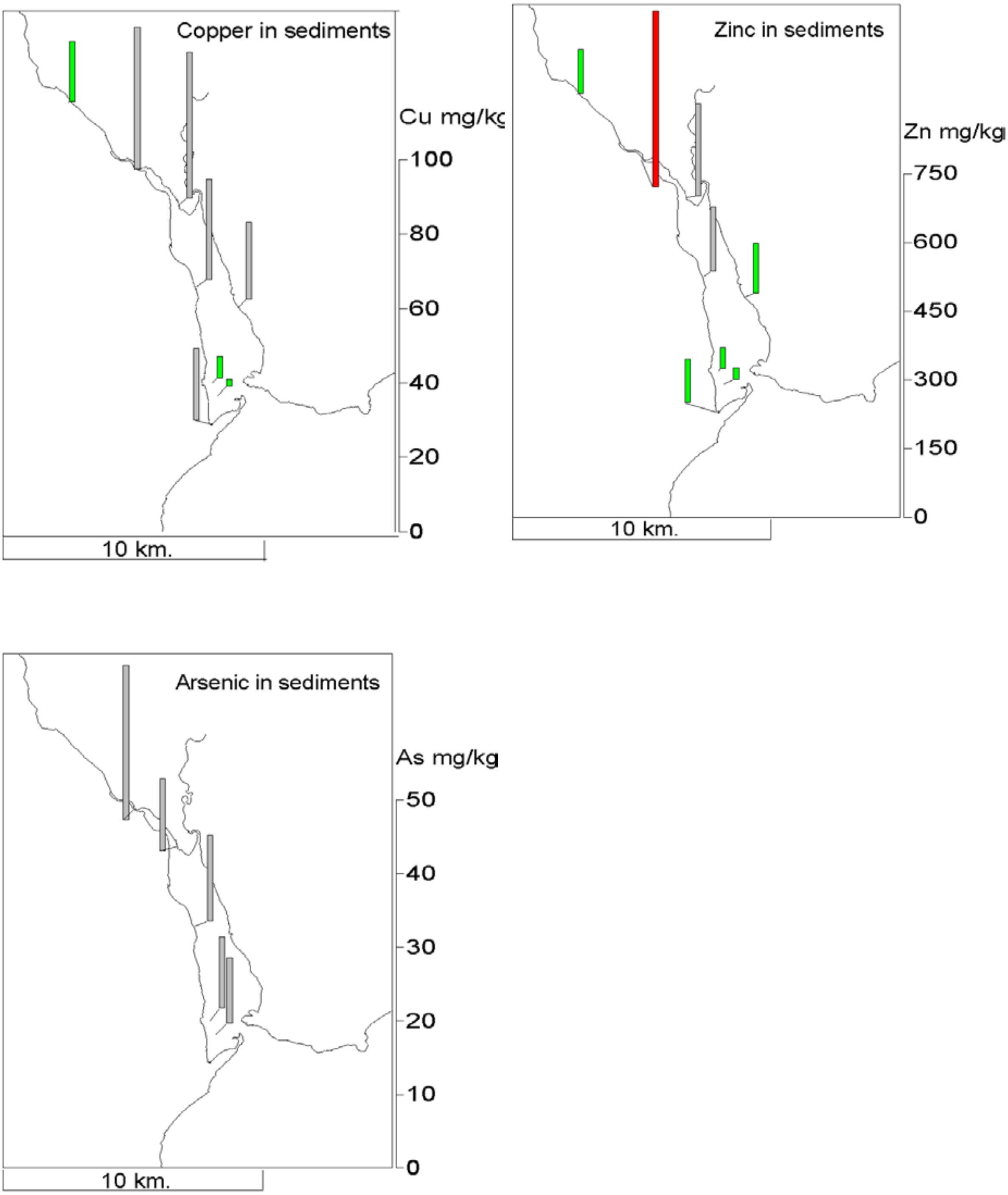


Figure 64. Copper, zinc and arsenic in sediment. Classification of the Exe estuary SPA based on interim marine sediment quality guidelines (ISQG's) and probable effect levels (PEL's) (from CCME 1999). Red = effects expected; Grey = possible effects cannot be excluded; Green = no harm to the environment expected. (Data Source MBA and EA)

7.2 Organic Contaminants in Sediments –PCBs, Pesticides, Herbicides

The only data for organic contaminants in sediments, for values expressed on a dry weight basis (i.e. to compare directly with sediment guidelines), are restricted to two sites, Trews Weir and Countess Wear, mainly in the early 1990s. Thus, there is not enough information to map trends in the distributions of these compounds in Exe sediments, or to give more than a rudimentary evaluation of the impact of these diffuse sources. Concentrations of most organic contaminants were predominantly below detection limits with the exception of γ-HCH. Values for the latter were above the probable effects level for lindane, though it is likely that the PEL may be overcautious (table 31).

Even though the sum of DDT and DDE isomers appears to be above the PEL this is probably artifactual, due to the fact that the majority of values are below detection limits which are themselves often above the guideline value. None of the other compounds exceeded PEL values. Dieldrin exceeds the ISQG though again this appears to be largely a function of detection limits.

Table 31. Organic contaminants in sediments of Exe Estuary at Trews Weir and Countess Wear compared with interim marine sediment quality guidelines (ISQG's) and probable effect levels (PEL's) from CCME, (1999). All units $\mu g\ kg^{-1}$ expressed on a dry weight basis. (Data source EA)

Compound	Mean $\mu g\ kg^{-1}$	Values <DL (%)	ISQG[a] $\mu g\ kg^{-1}$	PEL[b] $\mu g\ kg^{-1}$
ALDRIN	0.80	100%		
DDT (PP)[c]	1.37	88%	1.19	4.77
DDT (OP)[c]	3.53	100%	1.19	4.77
DDE (OP)[c]	1.57	100%	2.07	3.74
DDE (PP)[c]	2.39	62%	2.07	3.74
DIELDRIN	1.64	50%	0.71	4.3
ENDOSULPHAN ALPHA	1.89	100%		
ENDOSULPHAN BETA	2.17	100%		
ENDRIN	0.75	100%	2.67	62.4
HCH GAMMA	4.20	35%	0.32	0.99
HEXACHLOROBENZENE	1.38	77%		
HEXACHLOROBUTADIENE	2.17	92%		
ISODRIN	1.86	100%		
TRIFLURALIN	10.29	50%		

[a] interim marine sediment quality guidelines (ISQG) and
[b] probable effects levels (PEL) (CCME, 1999)
[c] guideline = sum of pp' and op' isomers;
[d] results with '<' sign are halved for calculation

There are some additional EA data on organic contaminants in sediments of the Exe Estuary at Bull Hill and the adjacent non-designated shellfish site, summarised in table 32. These are expressed on a wet weight basis and therefore not directly comparable with interim marine sediment quality guidelines (ISQG's) and probable effect levels (PEL's). However, assuming a wet to dry weight ratio of 1.5 it seems unlikely that these values exceed PEL values, except for γ-HCH. The large proportion of values below detection limits is again a feature. This includes PCBs which, on this evidence, are extremely low. So low, in fact, that concentration units in the data base should perhaps be checked. Even if the values in table 32 are mg kg^{-1} rather than µg kg^{-1}, however, they would still fall comfortably below PELs.

Table 32. Organic contaminants in sediments of Exe Estuary at Bull Hill and adjacent non-designated shellfish site, expressed on a wet weight basis. (Data source EA). Interim marine sediment quality guidelines (ISQG's) and probable effect levels (PEL's) from CCME, (1999) are shown for comparison but are on a dry weight basis. All units µg kg^{-1}

Compound	Mean µg kg^{-1} (wet wt.)	Values <detection (%)	No. of values	ISQG[a] µg kg^{-1} (dry wt.)	PEL[b] µg kg^{-1} (dry wt.)
ALDRIN	1.14	100%	7		
DDT (PP)[c]	1.55	100%	6	1.19	4.77
DDT (OP)[c]	1.43	100%	7	1.19	4.77
DDE (OP)[c]	2.15	100%	6	2.07	3.74
DDE (PP)[c]	1.46	100%	7	2.07	3.74
DIELDRIN	1.55	100%	7	0.71	4.30
ENDOSULPHAN ALPHA	1.40	100%	6		
ENDOSULPHAN BETA	2.50	100%	1		
ENDRIN	1.39	100%	7	2.67	62.4[d]
HCH GAMMA	1.11	85.7%	7	0.32	0.99
HEXACHLOROBENZENE	1.00	87.5%	7		
HEXACHLOROBUTADIENE	1.41	100%	7		
ISODRIN	1.10	100%	7		
PENTACHLOROPHENOL	2.00	0.0%	1		
TRIFLURALIN	9.08	50.0%	6		
PCB NO.28	0.000005	100%	7		
PCB NO.101	0.000005	100%	4		
PCB NO.118	0.000005	100%	6		
PCB NO.138	0.000005	100%	6		
PCB NO.153	0.000005	100%	6		
PCB NO.180	0.000005	100%	6		
PCB Total (Σ above isomers)	0.000030	100%		21.5	189

[a] interim marine sediment quality guidelines (ISQG) and [b] probable effects (PEL) (CCME, 1999)
[c] ISQG and PEL for DDT and DDE = sum of pp' and op' isomers
[d] Provisional; adoption of freshwater PEL.

It is recommended that future sampling programmes incorporate more high quality information on sediment contaminants over a broader range of sites.

8. MODELS

One of the earliest attempts to model the hydrography of the Exe Estuary, from measurements of flow rates and salinity distributions, was described by McCandlish (1980) who established the partially mixed nature of the system and proposed possible uses of the salinity box-model approach in pollution management and control. Subsequently there have been substantial developments on this theme.

A two-dimensional box model, based on the original of Officer (1980) has been used to simulate PAH behaviour, since transport of PAHs in the Exe Estuary has been shown to depend primarily on estuarine hydrodynamics (Herrmann and Hubner, 1982). Reasonable agreement was obtained between computed and measured distributions along the estuary using benzo(a)pyrene as the model PAH. The box model was able to predict reasonably well the position of the PAH concentration maximum, as a function of estuarine circulation of suspended particulates, but tends to underestimate magnitude slightly as resuspension from bottom sediments is not taken into consideration.

Atkins (1988) have undertaken an environmental survey and modelling exercise of the River Exe which included a bathymetric survey, measurement of offshore currents, fixed station measurements of standard physical parameters and water levels, dye tracing, and macrobiological, bacterial and sediment characterisation. The report describes a depth-integrated hydrodynamic, transport and water quality model EXEDOS, which permits simulation of the behaviour of up to ten interacting and decaying pollutants. Thus, the model can be used as a descriptive tool to show the dispersion of sewage and storm water from existing and future outfalls. In addition to bacteria, parameters which can be modeled are BOD, nutrients, DO and soluble metals. Hooper *et al*. (1989) provide further details of the hydrodynamics model, (which draws heavily on earlier developments made by Falconer (1984)), the solute transport model, coliform models and other pollutant applications. Also included is a discussion of deficiencies, which includes the assumption that the estuary is vertically mixed. However, the upper estuary will be stratified under certain conditions, and the use of a 2-D model that included vertical stratification could be preferable.

The EU shellfish waters directive (EEC/79/923/EEC) protects shellfish populations by requiring that a discharge must achieve a 5.25log dilution ($10^{5.25}$) in faecal coliforms between the crude sewage and the edge of the shellfish waters (including treatment and dilution in the estuary/sea; assuming no decay of bacteria). Alternatively the scheme should achieve a standard of 1500 faecal coliforms/100ml for 97% of the time in the long term. Drawing partly on Atkins (1988) bathymetric data and modelling parameters for the River Exe, together with EA data, Sherwin and Torres (2001) have recently produced estimates of dilutions of the Countess Wear STW effluent which impinge on the shellfishery lower down the Estuary. These have been computed using the Estuary CSV model described in Sherwin and Menhinick (2001). This is a 1-D model which predicts the concentration of a decaying pollutant, as a function of salinity (requiring a knowledge of salinity as a function of the cumulative upstream volume). Salinity data suggests that flushing effluent from the estuary usually takes between 2.6 and 11 days. Effluent from Countess Wear STW takes between 0.6 and 6.7 days to reach the shellfishery (depending on tidal range and river flow). The poorest dilution at the shellfishery is a factor of 10 during low riverine flows when the STW is discharging fully. On most occasions however the dilutions are considered to be of the order of at least 20-fold at low water (Sherwin and Torres, 2001).

A further modelling study by Metocean - to assess the potential impact on the marine environment from the (then) proposed Exmouth and Budleigh Salterton Sewerage scheme - was commissioned by SWW in 1992 (Metocean, 1992). This involved the use of three- dimensional solutions to the simplified advection-diffusion equation to predict plume behaviour and the risk of non-compliance (bathing waters and shellfish directives) for different treatment options, meteorological conditions and frequencies of storm discharges. The outputs generally showed that under normal operating conditions the proposed scheme would achieve the objective of 95% compliance, though under worst-case conditions a storm discharge is likely to affect Sandy Bay (considered to be the critical beach), for at least one tidal cycle. As indicated in section 4 of this report, the adoption and completion of this scheme[1] in 1997, and other improvements to coastal outfalls, appears to have improved bathing water quality overall, both to the east and west of Exmouth.

Recently, one-dimensional numerical modelling of environmental quality in the Exe, using the estuarine simulating shell ECoS (Harris, *et al*., 1991), has been tested by the EA in the context of nutrient loadings (nitrogen- as total inorganic nitrogen) and the Urban Waster Water Treatment Directive (Murdoch, 2001). Modelling was used to establish impact on the estuary from Countess Wear STW. The report gives details of the model developed to quantify the relative contribution of the discharge from Countess Wear to nitrogen (TIN) levels in the estuary. As indicated in section 6.2, TIN loadings from the River Exe exceeded STW inputs. Results showed that Countess Wear contributes ~10% of the annual load from the Exe. In summer this rises to 25%, and can be as high as 50% in the worse case. TIN profiles showed that impact is greatest in summer and at Lower Wear.

The impact of Countess Wear STW diminishes along the estuary from approximately 25% at the head, to 10% at the mouth (during the summer). Subsequently, concern was expressed that the model may have underestimated the relative contribution from the STW because storm discharges were found to operate more frequently than expected (EA, 2001b).

Stillman *et al.,* (2001) used a behaviour-based model to explore the effects that the present-day management regimes of the mussel fishery in the Exe Estuary (and a cockle fishery, Burry inlet, UK) have on the survival and numbers of overwintering oystercatchers. It also explored how alternative regimes might affect the birds. Although applied to oystercatchers, the general principle on which the model was based applies widely. The model included depletion and disturbance as two possibly detrimental effects of shellfishing and some of the longer-term effects on shellfish stocks. Birds in the model responded to shellfishing in the same ways as real birds. They increased the time spent feeding at low tide, and fed in fields and upshore areas at other times. When shellfishing removed the larger prey, birds ate a greater quantity

[1] Treatment at Exmouth is now to secondary standard with UV disinfection. The scheme also involved extensive resewerage, extension of the outfall and improvements to CSOs to relieve sewer flooding problems in Exmouth.

of smaller prey. The results suggested that neither shellfishery caused oystercatcher mortality to be higher than it would otherwise be in the absence of shellfishing, and concluded that the current intensity of shellfishing did not significantly affect the birds.

However, they also showed that changes in management practices, such as increased fishing effort, reduced minimum size of shellfish collected or increased daily quota, could greatly affect oystercatcher mortality and population size. Results also indicated that the detrimental effect of shellfishing could be greatly increased by periods of cold weather or periods of prey scarcity. The authors considered that by providing quantitative predictions of bird survival and numbers of a range of alternative shellfishery management regimes, the model could guide management policy in the Exe and other estuaries.

9. CONCLUSIONS AND RECOMMENDATIONS

9.1 Biological Status

Diversity indices are frequently used to assess the effects of environmental degradation on the biodiversity of natural assemblages of organisms. Several indices are used commonly which help to put the biological status of the Exe into perspective:

Species richness is indicated by the number of taxa per unit area (e.g. m^2). Warwick *et al* (1989) recorded 20, 24 and 34 taxa at inner-, mid- and outer-estuarine intertidal sites along the Exe, respectively. This does not appear to be particularly high in comparison with the average of 29 for estuarine sites in the Tamar, although it must be remembered that there is little hard intertidal substrate in the Exe. Atkins (1988) found highest numbers of infaunal species in the outer estuary at Exmouth and Shutterton.

Shannon-Weiner diversity index (H^1) expresses the relationships between the occurrence of species and the apportioning of individuals among those species (relative dominance). The Exe Estuary sub-tidal sites generally scored high on the scale (2.51 – 4.17), and increased along the estuary towards the mouth. The highest score was for a subtidal site in the lower estuary, with a coarse substrate high in organic content (off Exmouth) (Baker, 1993). Two intertidal sites off Exmouth scored lower, 2.8 and 2.5, the latter being fine substrate amongst the Zostera bed. For comparison, the average H^1 for estuarine sites in Plymouth Sound and Estuaries was 2.21, and offshore Plymouth scored >5 (MPMMG, 1998).

Pielou's evenness index (J) compares the diversity of the data with its theoretical maximum, where all species would be equally abundant. Lower values would be associated with samples from sites numerically dominated by only one or two species, which is generally indicative of stressed communities. Again, scores for sub-tidal sites were generally high (0.54 to 0.88) and increased along the estuary with the highest score for a site in the lee of the spit near Dawlish Warren, and intertidal sites scored relatively low (0.58 and 0.55) (Baker, 1993).

The Simpson index relates the contribution made by each species to the total population. Although observing similar aspects of the dataset, this index is unrelated to the Shannon-Weiner diversity index. Higher values in the Simpson index equate to the presence of a few dominant species in the assemblage. Scores were in the range 0.8 to 2.8 with highest values in the intertidal sites. Lower values were found for sub-tidal sites in the lower estuary (Baker, 1993).

Taxonomic distinctness Using data on free-living marine nematodes from 16 localities/habitat types in the UK including the Exe, Clarke and Warwick (1999) looked at the univariate biodiversity index, taxonomic distinctness (TD). This index, which captures phylogenetic diversity rather than simple species richness, is more linked to functional diversity. The Exe (mud, sand and all habitats) was identified as above average in comparison with other UK sites (Fal, Tamar, Clyde, Forth). Subsequently, Clarke and Warwick (2001) refined and developed this index to examine average taxonomic distinctness (AvTD), and variation in taxonomic distinctness (varTD) using the two parameters in combination to pick out degraded locations. Again, the Exe sites (mud, sand, all habitats) were above the theoretical norm for VarTD, although for AvTD, Exe mud was identified as being somewhat degraded. However, when these parameters are viewed in the context of species numbers, no significant difference in taxonomic structure from that of the British Isles as a whole is indicated.

Abundance Biomass Comparison - Warwick *et al.,* (1989) used the Abundance Biomass Comparison (ABC) method (Warwick *et al.,* 1986) to analyse faunal distribution and community structure in several estuaries, including the Exe, in an effort to establish whether observed patterns resulted from the effects of natural environmental variables, or whether they were affected by some unnatural disturbance such as chemical pollution, organic enrichment from sewage, frequent bait digging etc. This method depends on the fact that the distributions of biomass among species in marine macrobenthic communities show a differential response to disturbance, which can be demonstrated by the comparison of k-dominance curves for abundance and biomass. In the Exe Estuary, two thirds of sites sampled (6 out of 9) appeared to be completely undisturbed. Bite, Cocklesand and Ridge (S) were classified as moderately disturbed. The latter three sites are in the Dawlish Warren, Exmouth and Starcross areas, respectively. In this study, the Exe was one, of only two, estuaries sampled, for which there were no 'grossly disturbed' sites identified.

Thus, indices indicate that biodiversity in the marine site is relatively high and increases toward the mouth of the estuary. Abundance may be relatively low for the majority of species though this is probably due to natural factors (Atkins, 1988). In these terms, the Exe appears to be comparable to, or perhaps slightly healthier than a number of other UK estuaries and therefore not significantly degraded by anthropogenic features.

This conclusion is supported by the work of Lindley *et al.,* (1998) which examined the viability of Calanoid copepod eggs hatched from intertidal sediment samples from different estuaries as a technique for in-situ bioassay of fine sediments. The study was primarily concerned egg viability in relation to sediment PAH concentration, but will probably indicate general sediment pollution. Many more nauplii hatched from incubated Exe sediments than from the more polluted estuaries of the Humber and Mersey, reflecting the lower levels of urban pollution in the Exe Estuary.

The intertidal sediments and fauna of the Exe appears to have remained relatively unchanged during the 20th century, though there may have been a decline in the diversity of algal species (Dixon, 1986). There was also sparse evidence to suggest that seagrass beds in the estuary may be declining, although it is difficult to speculate on the exact cause of the decline. An ongoing programme to survey, map and monitor the extent of these important features would seem prudent.

A recent BTO review of bird populations has triggered a 'high alert' for Widgeon (over a 25 year period) though the most recent trends (5 and 10 year) signify partial recovery. 'Medium alerts' were triggered for the Dark-bellied Brent Goose, Oystercatcher (5 and 10 year trends) and Avocet. The decline in the Avocet is for the last five-year period only, however, and is set against a fluctuating trend (Armitage *et al*., 2002). On balance, the trends in bird numbers are not considered sufficiently important to trigger further investigations into the causes of population changes ('Level 2' assessment).

9.2 Chemical Status

At present there is little evidence from chemical data indicating that modifications to biota have occurred, or would be expected to occur, due to contaminants. However the available evidence is very patchy. To address this issue in the future a more subtle, targeted assessment of impact will be required in order to establish cause and effect (discussed in greater detail in section 9.3). Until more appropriate integrated chemical and biological effects monitoring is put in place to answer this challenge it is only possible to assess, subjectively, the possible impact (or lack of impacts) of individual contaminants, or groups of contaminants, based on available evidence. A brief overview of the major water and sediment quality parameters that could, in theory, impinge on benthic communities in the Exe Estuary is given below, and summarised in table 33.

Table 33. A Summary of Water and Sediment Quality 'issues' in the Exe Estuary SPA. (Findings for each of the numbered 'contaminant categories' are explained in more detail in the accompanying text).

'contaminant'	Area	Potential Sources	Most vulnerable features/biota
1) Organotins (TBT, TPT?)	Effects not established but more data required: nb dogwhelks at Maer Rock and Orcombe Pt. and to address TBT persistence in sediment	Mostly historic but possibly some continuing input from shipping. Sediments?	Molluscs
2) Metals (Zn and several other metals).	Effects not established. If they occur probably confined to upper reaches (nb sediment) and localised hotspots (e.g. Exmouth Dock).	Trade discharges (mostly historic), major STWs, boats and ships, sediments	Invertebrates (primarily molluscs and crustaceans), species composition, larval fish and birds
3) Nutrients – esp. Nitrate and ammonia (Problem microalgal blooms)	Upper and mid-estuary.	River Exe, Sewage discharges (esp. Countess Wear STW, also possibly mid estuary discharges – Kenton, Exton?) Diffuse sources Sediments?	Invertebrates, fish (estuarine and migratory, esp. early life stages), seabirds, General diversity
4) Dissolved oxygen fluctuations	Upper and mid-estuary –esp. Turf	Algal blooms (possible nutrient enrichment, - see above)	Fish, (estuarine and migratory) invertebrate communities
5) Hydrocarbons: PAHs, PCB	Poorly defined, probably confined to upper and mid-estuary	combustion, run-off, discharges, boats and ships; sediments	Benthic invertebrates and fish (NB those in contact with sediment)
6) Pesticides and herbicides and other endocrine disruptors	Direct toxicity improbable. Extent of endocrine disruption not known	Discharges, run-off, sediment	Invertebrates (esp. crustacea), fish

1) Organotins

There is no evidence to indicate a threat from TBT throughout most of the Exe Estuary, though the data are inadequate in terms of providing an up to date and accurate assessment.

Estuarine waters sampled by EA were below the detection limit (<28 ng l^{-1}) though this is significantly above the EQS for coastal waters of 2 ng l^{-1}. STW effluent at Exmouth and Countess Wear STW were sampled on several occasions during 1996; most were below detection limits which ranged from 10-68 ng l^{-1}. One sample from Exmouth however, had a positive value of 43 ng l^{-1}.

Impact of TBT appears negligible for the majority of organisms in the Exe estuary. However the extremely sensitive dog-whelk *Nucella lapillus* has disappeared at Maer Rock and Orcomcbe Point (just outside the estuary mouth at Exmouth), where previously they were abundant (Dixon, 1986). Suggested causes include organotin compounds and dinoflagellate blooms. However, the fact that recovery has not been recorded in subsequent surveys tends to implicate the former, since imposex is irreversible and effects on populations are long-lasting. TBT levels measured at Lympstone in 1987, and in some of the samples described above, would have been high enough to induce the phenomenon.

It is likely that sediments on the extensive flats of the Exe Estuary are low in TBT, though data for only one site could be found. There may be localised reservoirs of TBT in sediments, particularly in the upper estuarine silts and close to marinas, which are susceptible to remobilisation by processes including physical resuspension (e.g. dredging, erosion) and bioturbation. It is therefore important to map out potential hotspots and quantify the threats more comprehensively.

2) Metals

There is no indication that rivers entering the Exe Estuary are likely to cause problems with regards metals.

Current monitoring of tidal waters by the EA has established no cases of EQS exceedences in recent years, though for most metals elevated levels are reported near the head of the estuary at Countess Wear, perhaps most notably for Zn.

Metal concentrations in sediments are also highest in the upper estuary (due to proximity to STW, and to enriched organic and oxyhydroxide coatings which sequester metals). The relative abundance of organic and oxyhydroxide coatings will govern the ability of the sediment to act as a sink for contaminants and the extent to which they are remobilised. The only metal above sediment 'probable effects levels' here, was Zn, though Cd, Hg, Pb, Cu and As exceeded the lower guideline value. Concentrations of most elements decrease to background levels towards the mouth of the estuary, as finer muds become diluted with coarser, less polluted, sediment of marine origin. Based on available evidence it is only in the region of Countess Wear, near the tidal limit of the estuary, that deterioration due to metals could be expected. It is stressed that much of the data on sediments is more than ten years old and may not be representative of conditions now. Re-survey is needed to establish the current status and to evaluate temporal trends. This is seen as a particularly important issue in terms of meeting standstill requirements for sediments (Dangerous Substances

Directive), and attainment of Favourable Condition (Habitats Directive), and may partially drive the requirement to minimise further inputs via aqueous discharges.

Bioindicator studies with infaunal species such as worms and clams suggest that, apart from slight enrichment in Ag, Cd, Hg and Sn, there is little significant bioaccumulation above normal for most metals. However, these data are now twenty years old and from two sites only therefore re-evaluation is recommended. Elevated metal levels in mussels close to Exmouth Dock appear to be a localised phenomenon as shellfish from commercial beds nearby display little evidence of contamination. (One exception was Pb, though the high values observed in shellfish data, a decade ago may not be an accurate reflection of current status).

The extent of ecological impact due to metal contamination in the Exe is largely unknown, but at most is likely to be restricted to the upper estuary (largely determined by the STW inputs), and perhaps localised hotspots such as Exmouth Dock.

There is scope for more research to establish the physiological and ecological significance of metal body burdens. Sub-lethal indicators, notably metallothionein induction, provide sensitive and selective measures of metal stress and can help map affected (and unaffected) areas, as well as monitoring temporal trends.

3) *Nutrients*

Nutrient-associated water quality problems in the Exe during the early 1970s appeared to have been alleviated with the opening of Countess Wear STW. However, perhaps due to increasing pressures locally, the estuary is again suffering periodically from eutrophication, and the Countess Wear discharge is implicated as the major offender. Nutrient concentrations generally decrease with distance down the estuary from the discharge. Algal blooms occur (roughly centered in the mid-estuary), which are increasing in intensity over recent years, and although not persistent due to the flushing characteristics of the estuary, are an important indication of enrichment problems. High concentrations of ammonia in the estuary are also a major cause for concern due to the possible toxicity to estuarine organisms. Effluent from Countess Wear STW failed to comply with a recently introduced standard to reduce ammonia in discharges (and thus in tidal waters) in 11% of samples taken during 2001.

In estuarine and marine ecosystems there is a complex interaction of nutrients between sediment and overlying water, which in the case of N, involves a range of processes including nitrification, denitrification, mineralisation, assimilation and fixation which may all vary spatially and temporally. It has been shown that ammonifying microbial activity is greatest when macroalgal biomass declines resulting in ammonification and the release of ammonia from sediment (Owens and Stewart, 1983). It is not known whether this occurs in the Exe, although reports do indicate the presence of a significant biomass of *Enteromorpha spp.* The complexity of the nitrogen (and phosphorus) cycle, and the significance of sediments, has been long appreciated; nevertheless, monitoring still largely involves measurements of nutrients in water. Until more data becomes available for sediments, and the significance of related microbial activity is better understood, any attempt at evaluating the sediment as sources or sinks of nitrogen, ammonia and phosphorus will be difficult.

Hence, the problem persists and if unchecked the situation may deteriorate. The issue has been acknowledged by the EA and the Exe Estuary investigated as a Sensitive Area (Eutrophic). Designation could have facilitated significant reductions in nutrient loadings from significant sources. However, it was not put forward to DEFRA due to the rapid flushing rate and lack of evidence, therefore it will not be designated in the foreseeable future.

Part of the freshwater catchment (the stretch from the River Creedy at Crediton STW to the normal tidal limit of the Exe) has been designated, and the Agency are currently carrying out a study of the trophic status of the Exe from Tiverton to the Creedy confluence. Measures to address diffuse sources of nutrients will only be taken if the area is also designated as a nitrate vulnerable zone (NVZ)

Effects of the high levels of nutrients on individual species in the Exe are largely unresearched. Warwick *et al.,* (1989) found an inverse linear relationship between the abundance of cockles and the nitrogen content in Exe sediments. This may be relevant and warrants further investigation. Diversity may be impaired in localised (intertidal) areas in the estuary, where abundance of individuals is high but dominated by a few species.

In view of the conservation importance of the Exe Estuary, it is evident that any increase in nutrients should be avoided and changes to consents (quantities and location) should therefore be considered carefully to avoid the risk of further enrichment.

4) *Dissolved oxygen*

The limited information available indicates that exaggerated DO fluctuations occur as a result of algal activity in the estuary. Whilst daytime levels are high to the point of supersaturation, DO at night may drop below mandatory levels required by the shellfish directive and possibly those required for sensitive saltwater life. Low DO levels can also have a significant impact on migratory fish; due to the energetic demands of their upstream migration and the increased activity that takes place during spawning, the oxygen requirements of migratory teleosts are very high at these times in the life cycle (Claridge and Potter, 1975). Since the maximum amount of oxygen that will dissolve in water is inversely related to temperature, even in clean turbulent water, oxygen concentrations can fall to below the minimum level for survival. Consequently, any factors that lower oxygen tensions will have a significant impact on fish populations at these critical times (Bird, 2002) and should be minimized.

5) Hydrocarbons, PAHs

The EA database provided little information on hydrocarbons oils in the SPA and so their significance is difficult to assess. Although the majority (68%) of samples were<DL, there were occasional high values, and median concentrations in the Bull Hill samples were elevated, perhaps to levels where tainting could occur in fish. These data are now almost 10 years old however, and in need of updating in order to comment on their potential impact on estuarine biota.

Historical data for PAH concentrations suggest levels in estuarine waters of the Exe, generally, would be expected to fall below ecotoxicological guidelines (though fluoranthene in the upper estuary, near Topsham would have exceeded the lower OSPAR threshold). Concentrations of PAHs in the main channel in the upper estuary tend to be elevated due to the high levels of suspended solids, and decrease towards the mouth of the estuary and over tidal flats (Herrmann and Hubner, 1982). PAH concentration in sediments from Exe sites are highly variable and are low in sandier substrates but moderately high in mud samples upstream (above lower guideline values at the Turf for ΣPAH). The same applies also for most individual PAHs, though concentrations of acenaphthene and fluorene are above probable effects levels, by a small margin. Any effects, if they occur, are likely to be chronic rather than acute and restricted to muds towards the head of the estuary, rather than in sandier sediments further downstream. Natural settling processes at the turbidity maximum probably create a region of high PAH concentration in the upper estuary.

Unfortunately, no body burden data for PAHs could be found. Measurement of PAHs in molluscs (both commercial and native bioindicator species) should be seen as a priority for future monitoring exercises.

6) *Pesticides, Herbicides, PCBs and other organic contaminants.*

Most organic compounds analysed in rivers and tidal waters by the Agency are below detection limits and appear to comply with EQS standards (for the majority of pesticides, herbicides, PCBs, chlorinated solvents and alkylphenols). STW have contributed reckonable loadings of γ-HCH (and probably other pesticides and herbicides) to the estuary in the recent past. These inputs now appear to be declining substantially. We can speculate that risks to biota are likely to be low.

Sediments are a reservoir for many of these compounds, though for most concentrations are reported as not detectable in the EA data-base. The sum of DDT and DDE isomers appears to be above the probable effects level (PEL) in sediments from the head of the estuary, though this is artifactual, due to the fact that the majority of values are below detection limits - which are themselves often above the guideline value. Values for γ-HCH in estuarine sediments measured in the early 1990s were above the PEL as were samples from the early 1980s determined by Herrmann and Thomas (1984). It is possible that the trend in γ-HCH concentrations in Exe sediments may be downwards, in line with waters, though further monitoring is advisable to ensure standstill requirements (Dangerous Substances Directive) and Favourable Condition (Habitats Directive). The distribution of γ-HCH in Exe sediments described by Herrmann and Thomas (1984) was unusual compared to that for other organic micropollutants (PCBs, PAHs): rather than the expected decrease seaward, the pattern of γ-HCH (and also α-HCH, and another OC pesticide hexachlorobenzene-HCB) was characterised by diffuse agricultural inputs from the numerous small streams along the estuary. Concentrations were, in fact, highest at sites just inside the estuary mouth near Dawlish Warren.

During the 1980s it was shown that PCB concentrations in water and sediment increased from the river into the estuarine mixing zone and, in the tidal channel, decreased axially from there towards the sea, and also, laterally, over tidal flats, resembling the behaviour of PAHs (Herrmann and Thomas (1984). Most of the PCB load appears to have originated from the river, carried into the estuary in particulate form which becomes focused by hydrodynamic processes at the turbidity maximum However, there were signs of occasional irregular localised sources of PCB superimposed on the main input(s) from the River Exe. The concentrations in these water and sediment samples appear to be higher by an order of magnitude than in EA samples taken in the 1990s, though it is not clear whether this reflects a genuine temporal trend or methodological variation. Nevertheless, the fact that some of the sediment values in the study by Herrmann and Thomas approach or exceed quality guidelines and PEL, and are therefore of possible biological significance, supports the notion that more extensive monitoring is needed to clarify the present situation.

CEFAS monitors levels of selected pesticides and other potential endocrine disrupting chemicals in bivalves from UK designated shellfish waters. Analyses of cockles, mussels and oysters made between 1995 and 1996 imply that body burdens of α,γ HCH, DDT, dieldrin and PCBs in most shellfish waters in England - including, presumably, the Exe Estuary - were close to or below detection limits and within guideline values for human consumers. Pesticide/PCB levels in designated shellfish areas of the Exe are therefore generally considered of little toxicological importance (CEFAS, 2001). Unfortunately, bioaccumulation data for this group of compounds, specifically relating to the Exe Estuary, is only fragmentary. Because the data are extremely sparse, both numerically and geographically (e.g. for shellfish, two adjacent sites in the lower estuary), a comprehensive risk assessment is not possible, though the predominance of <DL values supports the notion that pesticides, herbicides and PCBs pose little threat to the Exe SPA as a whole. More extensive, targeted sampling will be needed to test this thoroughly, and should incorporate sediments and sediment-dwelling species such as clams and worms.

9.3 Future Research Requirements

Better, more integrated information on the environmental chemistry, 'health' and biodiversity are obvious, generalised top-level needs to address the 'quality' of the Exe Estuary marine site - just as rigorous monitoring of habitats will be needed to provide estimates of 'quantity' and extent.

With regard to the latter, an appropriate surveillance strategy should be adopted to quantify the nature and extent of biotopes in order to fulfil Favourable Conservation Status[1] requirements encompassed in the Habitats Directive. Monitoring techniques are described in detail by Davison and Hughes (1998) in relation to surveillance of *Zostera* beds, but are equally applicable to biotope monitoring in a broader context. These fall into four categories: *aerial remote sensing* (aerial and infrared photography, satellite and multi-spectral scanning imagery (CASI)); *sublittoral remote sensing* (sonar techniques such as RoxAnn™ and side-scan sonar provide maps of substratum types which, with appropriate ground-truthing, can be linked to

[1] Favourable Conservation Status (FCS) for a given habitat/species requires that the condition has to be characterised and, if considered necessary, brought up to a level where the habitat/species is sustainable in the long term. Under the Habitats Directive, Member States must report on the progress towards FCS for all nominated sites. English Nature has produced Favourable Condition tables to aid this process, which encompasses a number of attributes, including the extent and biological quality of the interest features (summarised in Annex 1 for the Exe Estuary).

the distributions of habitats and communities); *underwater video* (e.g. remotely-operated vehicles (ROVs), towed video and drop-down video); *conventional benthic sampling* (e.g. grabs and cores and observations arising from inter-tidal surveys and diving). The first three options have potential for large-scale generalised mapping of distribution and extent, whilst the fourth provides a more detailed synthesis of biotope structure and condition. Ideally the preferred monitoring scheme would probably consist of a blend of these approaches. The selection of techniques will of course have to take in to account questions of scientific objectives, practicality and cost.

The requirement to fulfil FCS and other drivers on water and sediment quality (such as the 'standstill' provision under the Dangerous Substances Directive) may be more difficult to monitor. The fragmented nature of much of the available environmental quality data - much of which has been collected for compliance rather than process-oriented purposes - prevents all but a first approximation of the status of the site. This needs to be addressed if we are to progress our understanding of how environmental quality, and in particular anthropogenic inputs, are affecting the biota and, hence, the status of the marine site.

A major issue central to the current project is how to monitor the health of the environment within the Exe Estuary i.e. to ensure that conditions are favourable for the survival of biota and, if they are not, to establish any cause and effect relationships. An obvious starting point is that, given the continual natural variation which occurs in ecological systems, critical assessments of human impacts (consented discharges, fishing, dredging, boatyards, tourism etc) can only be made against a time series of background data. The question is 'What data best serves this need'?

Without doubt, eutrophication is a priority concern, necessitating careful surveillance of nutrient sources and distributions ('non-toxic contaminants'), together with associated parameters which signify biological consequences (DO, chlorophyll a, turbidity).

'Toxic contaminants' appear to pose less of a threat to the site as a whole but will need continuing appraisal. Some of the classes of contaminants which, in our opinion, should be prioritised in future Exe surveys are indicated above. Traditionally, surveillance of chemical parameters in water has often been carried out by the EA for the purposes of compliance monitoring and is not necessarily intended for survey purposes (or for the type of characterisation being undertaken here). This should perhaps be reviewed in future to maximise the value of the information. Accurate, up-to-date chemical data, on e.g. metals, PCBs, PAHs, organotins and pesticides, are needed to give better impressions of fluxes from rivers and discharges, and to provide details of their current distribution, sources and sinks within the SPA. It is particularly important that future sampling programmes incorporate more information on sediment contaminants and their role as diffuse sources. Concentrations in sediments often consist of both anthropogenic and geogenic components which have yet to be distinguished in the Exe. Methods are becoming available which address this problem and the consequences for bioavailability and re-release. It is recommended that these be applied. Biota should be collected concurrently to try to link sediment loadings and 'speciation' of contaminants with their biological consequences.
The use of a validated suite of indicator species (which must incorporate species capable of reflecting sediment-bound contamination), at a selection of reference sites,

is a useful way of estimating bioavailability around the system. Species which appear to be ideal for this purpose include the ragworm *Nereis diversicolor* and the clam *Scrobicularia plana*, as outlined in section 6.1.1. Other useful indicators are suspension feeders such as *Cerastoderma edule* and *Mytilus edulis*, winkles *Littorina littorea* and seaweed e.g. *Fucus vesiculosus*. An accurate picture of current patterns of bioaccumulation of inorganic and organic contaminants throughout the system needs to be constructed in order to establish the current status of the SPA. This should be repeated at intervals in the future, to ensure bioavailability does not increase. Furthermore, many sediment-dwelling organisms are essential food items for the important bird species and assemblages for which the site was designated. The threat posed by bioaccumulation and food chain transfer of, for example, PAHs, PCBs and metals, needs to be quantified in these species and requires a much more extensive data set.

In recent years, techniques have been developed to assess sub-lethal biological impact in greater detail, which would allow targeted biological-effects screening of the SPA, including possible problem discharges. Also, an important priority is how to assess (and then minimise) the risk from diffuse sources. Current sediment quality criteria are useful initial guidelines to impact, but are not seen as being entirely appropriate for all species or sediment types. Individual site conditions are likely to modify threats considerably, therefore accurate assessments need to be customised to the habitat in question. By selection of an appropriate suite of indicators/biomarkers, a sampling strategy could be tailor-made to establish the causes and extent of damage (if any) in the Exe with greater certainty. This would ideally include; conventional quantitative ecological survey (for identifying changes in the abundance and diversity of species), chemical and biomonitoring procedures as outlined above (for determining the concentrations and bioavailability of anthropogenic contaminants), and biochemical, physiological and behavioural biomarkers which signal exposure to, and in some cases, adverse effects of, pollution (see Annex 6 for examples and further details).

When such procedures are used in combination in well-designed survey programmes, they can provide insights as to whether or not impact is occurring and if so, which pollutants are responsible for environmental degradation. They may also be useful in addressing the long-standing problem of additivity/ synergism. A major criticism of many current statutory monitoring assessments, whether using comparisons with EQS values, sediment quality guidelines, or some other marker, is that they address only single contaminants at a time. Even if individual chemicals do comply with limit values (as most appear to do in the Exe Estuary) it does not necessarily mean the environment is healthy. Biological effects may occur if several contaminants act together. Hydrocarbon residues alone consist of a myriad of individual compounds, most of which have additive toxicity. The majority of outfalls and sediments contain a particular cocktail of chemicals whose true impact can usually only be assessed through a site-specific evaluation, taking into consideration the interactions that occur between different components and also the local environment. By incorporating biological-effects monitoring, alongside chemical surveillance, it may be possible to make substantial progress towards understanding and managing these complex environmental issues and would provide more reliable and objective site characterisations in the future. If such an integrated approach were put in place at an early stage, to provide baselines, it would also be beneficial for the assessment of long-term trends.

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11 ANNEXES

Annex 1. Exe Estuary SPA: Summary Of The Interest Features

EXE ESTUARY SPA: SUMMARY OF THE INTEREST FEATURES AND CONSERVATION OBJECTIVES, (ADAPTED FROM ENGLISH NATURE, 2001)

Internationally important populations of regularly occurring Annex 1 bird species (avocet *Recurvirostra avosetta*), Slavonian Grebe (*Podiceps auritus*)

- Maintain numbers by avoidance (no increase) in disturbance to feeding , roosting and nesting areas: maintain extent/distribution of habitats (Avocets – mudflats, Slavonian Grebe - shallows)

Habitats

- Mudflat and sandflat communities
  - maintain absence of obstructions to view lines and food avilability (avocets – *Gammarus, Corophium, Hydrobia, Cerastoderma, Nereis,* fish i.e. Gobies)
- Saltmarsh communities
  - maintain absence of obstructions to view lines
- Shallow coastal waters
  - maintain food availability (Slavonian Grebe – marine/freshwater fish e.g. gobies, stickleback, scupins, aquatic invertebrates e.g molluscs, crustaceans, insects

Internationally important assemblage of waterfowl (Oystercatcher, Grey plover, Black-tailed godwit, Dunlin) including the internationally important population of regularly occurring migratory species (Dark-bellied brent goose) The estuary supports over 20,000 wintering wildfowl

- Maintain numbers by avoidance (no increase) in disturbance to feeding , roosting and nesting areas: Maintain extent and distribution of habitat (all require extensive mud/sandflats; Brent geese and wigeon require saltmarsh and seagrass; oystercatcher, dunlin and knot require large extent of intertidal and subtidal boulder and cobble scar)

Habitats

- Mudflat and sandflat communities
  - maintain food avilability (waders e.g. dunlin, black-tailed godwit, grey plover, oystercatcher require range e.g. *Gammarus, Corophium, Hydrobia, Cerastoderma, Nereis*) brent geese and wigeon require *Enteromorpha and Ulva*
- Saltmarsh communities
  - maintain food avilability (brent geese and wigeon need soft-leaved and seed-bearing-plants) waders (dunlin, black-tailed godwit, grey plover, oystercatcher) need invertebrates (as above)
  - maintain absence of obstructions to view lines
- Seagrass bed communities
  - (brent geese and wigeon require e.g. *Zostera*, waders prefer invertebrates – see above)
  - maintain absence of obstructions to view lines
- Intertidal and Subtidal boulder and cobble scar communities
  - maintain food avilability (oystercatcher, dunlin, knot feed on molluscs e.g *Mytilus*)
  - maintain absence of obstructions to view lines

Annex 2. Water Quality Standards

List I (EC Dangerous Substances Directive) and list II substances (from Cole *et al.,* 1999, derived by WRc according to the methodology described in Grimwood and Dixon 1997)

List I substances

Parameter	Unit	Water quality standard		Standstill Provision [a]
		Estuary[b]	Marine	
Mercury	µg Hg l-1	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-1	0.03 TAA	0.03 TAA	yes
Aldrin	µg l-1	0.01 TAA	0.01 TAA	yes
Dieldrin	µg l-1	0.01 TAA	0.01 TAA	yes
Endrin	µg l-1	0.005 TAA	0.005 TAA	yes
Isodrin	µg l-1	0.005TAA	0.005 TAA	yes
Hexachlorobenzene	µg HCB/l	0.03 TAA	0.03 TAA	yes
Hexachlorobutadiene	µg HCBD/l	0.1 TAA	0.1 TAA	yes
Chloroform	µg $CHCl_3$/l	12 TAA	12 TAA	no
1,2-Dichloroethane (ethylenedichloride)	µg EDC/l	10 TAA	10 TAA	no
Perchloroethylene (tetrachloroethylene)	µg PER/l	10 TAA	10 TAA	no
Trichlorobenzene (all isomers)	µg TCB/l	0.4 TAA	0.4 TAA	yes
Trichloroethylene	µg TRI/l	10 TAA	10 TAA	no

Notes: Substances are listed in 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
[c] 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".
[d] All isomers, including lindane

Annex 2 (cont.) Water quality standards for the protection of saltwater life.

List II substances

Parameter	Unit	WQS (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 _g 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.
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-1	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-1	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-1	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
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 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.
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.
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 (CNTs)	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.

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 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 mean
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

Annex 3. Quality Standards Stipulated In The Shellfish Waters Directive

(from Cole *et al.,* 1999)

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]
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.

Annex 4. Bathing Waters Quality Standards

Quality standards for fresh and saline waters stipulated in the Bathing Waters Directive (from Cole *et al.,* 1999)

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-1	300 T90[e]	[f]
Phenols	µgC_6H_5OH	5 T90[e]	50 T95[e]
Surfactants[g]	µg l-1 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 1976).
[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 he substance
[f]There should be no film visible on the surface and no odour
[g]Reacting with methylene blue
[k]There should be no lasting foam

Annex 5. Sediment Quality Guidelines

Interim marine sediment quality guidelines (ISQGs) and probable effect levels (PELs; dry weight) [1]: metals and organics (from Cole *et al.,* 1999)

Substance	ISQG	PEL
Inorganic (mgkg^{-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 (µgkg^{-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]	nd[5]

[1] from CCME, (1999)
[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.

Annex 6. Examples of Recommended Biological Monitoring Techniques

Immunotoxicity Assays – these assay measures the immunocompetence of haemocytes from invertebrates, reflecting both the extent of exposure to immunotoxins and the general well-being of the test organism. Various immunological parameters (e.g. cell counts, generation and release of superoxide anions, phagocytosis, lysosomal enzyme activity) have proved useful in monitoring the status of shellfish in response to oil pollution and PAHs (Pipe *et al*, 2000; Raftos and Hutchinson, 1995). An example of the application of these assays in relation to Poole Harbour, is cited in Dyrynda *et al*., 1998.

EROD (ethoxyresorufin-O-deethylase) is a marker for the activity of the mixed function oxidase (MFO) system, whose induction is usually associated with exposure to, and the detoxification of xenobiotics such as PAHs and PCBs. Occasionally these transformations may produce deleterious side effects due to the formation of carcinogenic or genotoxic compounds (e.g. formation of benzo(a) pyrene diol epoxide from the benzo(a) pyrene). Genotoxicicity assays (see below) may help to establish this possibility.

Metallothionein (MT) induction and associated changes in metal metabolism are specifically induced by metals and are sufficiently sensitive to be used to detect elevated levels of bioavailable metal in the field or arising from metals in discharges (e.g. Langston *et al*., 2002). The induction of MT protein, and associated metal-binding patterns can therefore be used to map spatial and temporal trends in biological respones to metals. Examples of the application of this assay in relation to Poole Harbour are indicated in section 5.1.1.

Genotoxicity-The Comet Assay - The single cell gel-electrophoresis (comet) assay is ideal for screening for possible genotoxicity associated with point-source and diffuse inputs to the system.

The CAPMON technique - Cardiac activity in bivalve molluscs and decapod crustaceans – Heart rate provides a general indication of the metabolic status of mussels and crabs. The CAPMON technique (Depledge and Anderson, 1990) permits the non-invasive, continuous monitoring of cardiac activity using infra-red sensors attached to the shell.

Tolerance Studies - More widespread investigations of community tolerance to establish their adaptation to contamination levels. Mapping the genetic composition of tolerant populations of individual species (*Hediste, Littorina* and others) in relation to induction of detoxification systems (such as metallothionein or EROD) should also be considered. This could add an interesting temporal dimension to biological monitoring – e.g. in determining the consequences of anticipated improvements in environmental quality (arising from planned schemes, standstill provisions of the Dangerous Substances Directive, or as required under the Habitats Directive to achieve Favourable Condition).

Toxicity Studies on sensitive species - Toxicity has been studied in a relatively small number of species to date. It would be useful to examine subtle sublethal-effects in some of the less-well represented and, perhaps, sensitive species. Also to include sediment bioassays to look at growth and survival of juvenile bivalves. Compare responses in Poole biota with those elsewhere to look for signs of adaptation.

Multivariate Statistical Analysis of benthic communities and environmental variables in order to examine spatial and temporal trends in communities in relation to contaminants (Warwick et al., 1998).

It is stressed that the above procedures have been selected primarily with regard to their ease of use, low cost and relevance to known environmental problems. Ideally, all components to the scheme need to be synchronised and run in tandem to achieve best value and to provide the most useful information on causal links and mechanisms. The results will assist environmental managers in identifying those consents and activities which most require attention and hopefully may help to decide on the best options for action.

Annex 7. A summary of water company improvements in the Exe Estuary SPA

(Information source - EA)

Asset Management Plans (AMPs) timescale

	Timescale
AMP1	1990 – 1995
AMP2	1995 – 2000
AMP3	2000 - 2005

Exe Estuary

A scheme for Exmouth was identified in the AMP1 investment round to improve compliance with the Bathing Waters Directive at both Exmouth and Sandy Bay beaches. Improvements to the STW were completed in 1997 and the outfall was extended prior to the 1998 bathing season. Treatment is now to secondary standard with UV disinfection. The scheme also involved extensive resewerage and improvements to CSOs to relieve sewer flooding problems in Exmouth.

UV was installed at Countess Wear STW in August 2001. Improved storm storage provisions are planned for 2002. UV has also been installed at Starcross STW. There is no CSO at this works so all flows are treated.

A number of outfalls to the Exe Estuary are to be improved during the AMP3 investment period under the Shellfish Waters Directive. These consist of 8 CSO improvements at Dawlish Northern Villages, Kenton and Starcross by June 2002. Exton North and Exton South STW's are also to be improved by March 2005. A secondary treatment works is to be built at Ebford as part of its First Time Rural Sewerage scheme.

Titles in the current series of Site Characterisations

Characterisation of the South West European Marine Sites: **The Fal and Helford cSAC**. Marine Biological Association of the United Kingdom occasional publication No. 8. pp 160. (2003)

Characterisation of the South West European Marine Sites: **Plymouth Sound and Estuaries cSAC, SPA**. Marine Biological Association of the United Kingdom occasional publication No. 9. pp 202. (2003)

Characterisation of the South West European Marine Sites: **The Exe Estuary SPA** Marine Biological Association of the United Kingdom occasional publication No. 10. pp 151. (2003)

Characterisation of the South West European Marine Sites: **Chesil and the Fleet cSAC, SPA**. Marine Biological Association of the United Kingdom occasional publication No. 11. pp 154. (2003)

Characterisation of the South West European Marine Sites: **Poole Harbour SPA**. Marine Biological Association of the United Kingdom occasional publication No. 12. pp 164 (2003)

Characterisation of the South West European Marine Sites: **The Severn Estuary pSAC, SPA.** Marine Biological Association of the United Kingdom occasional publication No.13. pp 206. (2003)

Characterisation of the South West European Marine Sites: **Summary Report**. Marine Biological Association of the United Kingdom occasional publication No.14. pp 112 (2003)

The Exe Estuary at Topsham
Photograph: MBA

Marine Biological Association of the United Kingdom
(Registered Charity No. 226063)
The Laboratory, Citadel Hill, Plymouth, PL1 2PB
Tel: +44 (0) 1752 633100

www.mba.ac.uk