Characterisation of European Marine Sites

# Plymouth Sound and Estuaries

## (candidate) Special Area of Conservation
## Special Protection Area

Marine Biological Association
Occasional publication No. 9

Cover photographs: Environment Agency

# Site Characterisation of the South West European Marine Sites

## Plymouth Sound and Estuaries cSAC, SPA

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

**April 2003**

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

ACKNOWLEDGEMENTS

Thanks are due to members of the steering group for advice and help during this project, notably, Mark Taylor, Roger Covey and Mark Wills of English Nature and Nicky Cunningham, Sacha Rogers and Roger Saxon of the Environment Agency (South West Region). The helpful contributions of other EA personnel, including Ian Warden, David Marshall and Jess Pennington are also gratefully acknowledged. It should be noted, however, that the opinions expressed in this report are largely those of the authors and do not necessarily reflect the views of EA or EN.

**Plate 1: Some of the operations/activities which may cause disturbance or deterioration to key interest features of Plymouth Sound and Estuaries cSAC, SPA**

**1:** (left) The Tamar valley is highly mineralised and has a history of mining activity. e.g. Gawton mine (now disused) in the Tamar Valley

**2:** (above) Marsh Mills STW, the A38 and other busy road traffic routes

**3:** (above) Devonport Dockyard. The Sound is subject to heavy shipping activity, including naval, commercial and pleasure craft.

**4:** (right) Run-off to the Plym from Chelson Meadows waste disposal site

**Photographs:**
**1: 2: 4**: Steve Johnson (Cyberheritage)
**3:** Ian Britton, Freefoto.com

## Plate 2: Some of the Interest Features and habitats of Plymouth Sound and Estuaries cSAC, SPA

**1:** (left) Mudflats in the River Tamar

**2:** (below) Saltmarsh near Antony, Torpoint

**3:** (left) Shore dock *Rumex rupestris*

**4:** Avocet *Recurvirostra avosetta*

**5:** Little Egret *Egretta garzetta*

**6:** (above) Allis shad *Allosa alosa*

**7:** (right) *Zostera marina* beds

**Photographs :**
**1:** Cornwall Wildlife Trust **2:** Steve Johnson (Cyberheritage) **3:** Roger Mitchell, English Nature
**4**: Eric Isley **5**: Keith Regan **6:** Willy Van Cammeren **7:** Keith Hiscock MARLIN

# 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 Plymouth Sound and Estuaries Special Area of Conservation (cSAC) and 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 Laboratories (PML)), has two main objectives. Firstly, to characterise the site in terms of environmental quality (water, sediments and biota), both current and 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. Brief descriptions of the site's physical setting and uses, major pollutant inputs, and biological communities are also given.

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). Key findings are;

Parts of the cSAC, principally the Tamar and Tavy Estuaries are influenced by past mining activities which continue to affect the area via mine drainage discharges, run-off from spoil heaps and remobilisation of metals from sediments.

Organotin contamination is probably still of significance. The principal sources, from marinas and Devonport Dockyard were probably stemmed in the late 1980's, although sediments now also contribute significantly to the overall burden.

Parts of the system, notably the upper estuaries, are subject to nutrient enrichment. Although the majority of nutrient inputs in the system may be due to diffuse sources such as agricultural run-off, sewage discharges constitute additional loading and result in chronic contamination of the affected areas, and nutrient-associated water quality problems. For example low levels of dissolved oxygen have occurred periodically in the upper Tamar and may be responsible for salmonid deaths.

PAHs, and certain pesticides are reported to be relatively high in parts of the system, notably in some sediment. PAHs, principally from urban run-off, combustion and dockyard activities, may occasionally exceed probable effects levels. Concentrations of phthalates in Plymouth Sound are also reported to be high, though at present the evidence for endocrine disruption is equivocal.

These principal findings are discussed in detail, together with implications for key habitats and species. The ecological significance of potential effects on major interest features of the site is also summarised. Unfortunately, however, many of the studies relating to environmental quality of Plymouth Sound and its estuaries are now over 10 years old, were typically of short duration, and covered limited geographical areas and ranges of contaminants. 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.

TABLE OF CONTENTS

## 2. INTRODUCTION

This review considers the characteristics of the PLYMOUTH SOUND and ESTUARIES cSAC, SPA and how the status of the site is influenced by existing permissions and activities, either alone or in combination. Also considered is possible impact from other factors such as unconsented activities, diffuse sources and natural processes. This includes activities and consents outside the cSAC itself. The purpose is thus to collate and interpret information relevant to the assessment of water quality impacts and risks on the cSAC 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.

## 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 and the NMBL in-house database ISIS.
- Unpublished reports and data-bases: WIMS-Environment Agency (Bodmin); Joint Nature Conservancy Council (JNCC) Coastal Directories Reports (Region 10); Cornish Biological Records Unit; Cornwall Wildlife Trust; Cornwall County Council; The Centre for Environment, Fisheries and Aquaculture Science (CEFAS).
- Information, summary statistics and monitoring data 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, UoP). Published and unpublished information has been drawn upon extensively for the present assessment[1].
- These studies include: measurements and effects of metals and TBT in sediments, water and biota (including modelling of fate and effects); contaminant toxicity, tolerance, and environmental stress studies on estuarine invertebrates and meiobenthos; surveys of macrobenthos and meiobenthos assemblages of the intertidal flats in relation to contaminant concentrations; nutrients and occurrence of dinoflagellate cysts in sediments. The MBA also has contaminant data (principally metals and TBT) for a large range of UK estuaries, including other south-west marine sites (e.g. Fal, Exe, Poole Harbour), which have been used to draw comparisons.

[1] The MBA, PML and UoP have conducted numerous hydrographic, chemical and biological surveys in the western English Channel, including Plymouth Sound and estuaries, stretching back for more than a century ( see Southward and Roberts 1987 for historical perspective). A full review is beyond the scope of the current project and only the most relevant information has been used here. The NMBL at the Citadel Hill Laboratory holds comprehensive archives, in addition to published and unpublished reports, and may be a useful ‘first stop’ for further information. A list of selected data set holdings at the Plymouth Laboratories can be seen in IACMST, 1994.

## 4. THE SITE: FEATURES AND THREATS

Plymouth Sound and its associated estuaries comprise a complex of marine inlets (rias) of considerable biological and historical importance. Much of the site is also a notified SSSI in the British context (Tamar-Tavy, Lynher Estuary, St Johns Lake, Wembury Point, Yealm Estuary and Plymouth Sound Shores and Cliffs), although this does not include the sublittoral. The Tamar River valley, together with that of the River Lynher and River Tavy, is classified by the Countryside Agency as an area of outstanding natural beauty (AONB), and the Tamar Estuaries complex is a Special Protection Area (SPA) designated under the European Commission Directive on the Conservation of Wild Birds (79/409/EEC). Dartmoor, to the north of Plymouth, is a National Park.

**Plymouth Sound**

The Sound itself is an open bay with a steeply sloping, rocky coastline to the east and west, and the inner Sound is sheltered by an artificial breakwater. The River Tamar provides the dominant freshwater input to the Plymouth Sound and estuaries system with an annual average flow of $30m^3 s^{-1}$ (Ackroyd, 1983). Seasonal fluctuations range from 5 - $38m^3 s^{-1}$ (monthly averages for June and January, Uncles *et al.,* 1983) but instantaneous flows can exceed $100m^3 s^{-1}$ (Bale, 1997). On average, the Rivers Tavy and Lynher contribute 30% and 20% (respectively) of the Tamar input, (Uncles *et al.,* 1983) and enter the Hamoaze to the northwest. The Plym and Yealm estuaries open directly onto the Sound in the north- and south-east (respectively). There is a ferry terminal (Millbay Docks) to the north of the Sound, which, in the past was used by cargo vessels, but since 1972 the cross channel ferries mainly transport passengers and vehicles (Duffy *et al*., 1994).

The coastline of the estuaries is generally more gently sloping than that of the outer Sound although rocky outcrops occur and there are steep rock slopes on some river bends. In places, large expanses of intertidal mud overly the bedrock. The area is highly mineralised and the geology of the cSAC is variable with primarily Plymouth limestone to the north and Staddon Grits and mid-Devonian slates to the south.

**The Tavy**

The source of the River Tavy is on north Dartmoor, it runs southwest over granite and slates and becomes tidal at Lopwell Dam on the east of the Bere Ferrers or Birland peninsula. The River Walkham joins the freshwater Tavy north of Lopwell Dam. From that point, the Tavy Estuary is 6.5km long and joins the Tamar 10km upstream from Plymouth Sound. The catchment is largely agricultural with small urban developments and a few old mine workings.

**The Lynher (and Tiddy)**

The source of the River Tiddy is to the south of Bodmin moor in an old copper mining area, and it joins the Lynher in the upper estuary. The River Lynher rises on Bodmin moor to the northwest of Plymouth, and follows the boundary of the granite outcrop underlying the moor as it flows southward. The tidal reach of the Lynher Estuary is 14km. The catchment is primarily agricultural.

**The Plym**

The River Plym, to the east side of Sound complex lies outside the cSAC. Its inclusion in this report stems from the possibility that water/sediment quality issues within the Plym could have a bearing on other parts of the system. Indeed, the two largest (by volume) consented discharges (excluding STW) for the area flow into the Plym.

The source of the Plym is high on the open moorland of south Dartmoor. As it runs seaward, the stream progressively cuts into the landscape of peat and weathered granite. Nine km from its source the Plym is joined by the Blacka Brook and meanders through an almost flat area of alluvium and rock debris, the legacy of centuries of tin mining and china clay working.

'Streaming' for tin began in the 12th century and much of the disturbed appearance of the Moor's surface in this area is due to this process. The Plym was tidal up to a point near Plym Bridge up to the 15th century when the sediment from tin streaming high up on Dartmoor silted up the river. The tidal reach of the estuary is now 5.5km, to just above Marsh Mills. At this point the river is joined by the Tory Brook, which carries sediments from Lee Moor. The large input of china clay wastes from the Lee Moor area has had a major silting impact in the upper Plym estuary where sediments have a high china clay content and the dwindling tidal zone is heavily banked with white clay. Despite this, there are dense populations of crustaceans (especially *Gammarus* species) and the (gastropod) mollusc *Potamopyrgus jenkinsi* in the banks.

Further seaward, there is a wide and shallow section known as The Laira, which is a haven for wading birds. Two wide bays, one on each side, were reclaimed by the erection of embankments early in the nineteenth century. The reclaimed land on the east side, known as Chelson Meadow, is drained by a series of ditches which harbour a characteristic brackish water fauna, grading inland into that of fresh water.

A landfill site is situated on the east bank, on the site of former fresh and saltwater pools and a water meadow (Tamar Estuaries Consultative Forum 1998). Below the Laira road bridge and disused railway bridge the shores of the drowned estuary known as the Cattewater are used for commercial and leisure marine industries and an oil tanker terminal. The catchment of the Plym is thus very much influenced by urban/industrial development.

**The Tamar**

Rising only 4 miles from Bude and the Atlantic Ocean, the River Tamar flows south for nearly 50 miles to the English Channel. The catchment covers an area of approximately 1700km$^2$ (Evans *et al.,* 1993). The middle and upper parts of the Tamar catchment are underlain almost entirely by Upper Carboniferous rocks, known as the Culm Measures, which comprise a succession of folded sandstones and shales. Details of the geology are summarised by (Durrance and Laming 1982), and given in more detail in publications of the Geological Survey (Freshney *et al*., 1972; McKeown *et al*., 1973).

In its middle reaches the River Tamar winds through steep wooded country, an area strewn with the relicts of two centuries of mining. This area is underlain by thick

sandstones and subsidiary shales of the Bude Formation. To the south, the underlying Crackington Formation is characterised by clay shales with subsidiary sandstones. Most of the area is overlain by a drift deposit, varying in thickness from 1-4m, comprising a stony rubble (locally termed head), in the upper part of which the soils have formed. The proportion of sandstone to shale in the soil parent material is a key factor in determining the drainage properties of the soils. Alluvial deposits are mainly silty, or loamy in character, comprising up to about 1m of stoneless material overlying river gravels or cobbles of water-worn sandstone fragments.

Approximately 30km inland, at Gunnislake Weir, the River Tamar becomes tidal, and wide mudflats and saltmarsh support wading birds such as the nationally important little egret *Egretta garzetta*, and avocets *Recurvirostra avosetta* in addition to wintering wildfowl and migratory birds including shelduck, black-tailed godwit *Limosa limosa*, redshank *Tringa totanus*, curlew *Numenius arquata*, dunlin *Calidris alpina* and whimbrel *Numenius phaeopus*. Further seaward the eastern shore of the lower estuary is dominated by the City of Plymouth, Devonport dockyard with its ship and boat-building yards, and the naval base and military port. The Naval Dockyard at Devonport was established in the 1690s and has been developed over a number of years; it now covers 4km of shoreline (Hiscock & Moore, 1986). The most recent relevant changes are the focussing of nuclear submarine maintenance at the site and construction of appropriate facilities. On the opposite side of the river the land is comparatively less disturbed and there are extensive mudflats around the mouth of the Lynher and St Johns Lake.

Mining for metalliferous deposits of tin, copper lead, silver, iron, arsenic, zinc, tungsten and manganese has been a feature of the Tamar and Plym Valleys for at least nine centuries. In the middle of the 19th century the Tamar valley became the richest copper -mining centre in Europe. At that time, there were also at least a dozen mines working silver and lead deposits on the Bere Ferrers peninsula, between the Tamar and Tavy rivers. The river water provided an economical power source, and the estuary, a transport route. The steep sides of the Tamar Valley allowed the development of the adit system which drained water from the mines directly into the river. The tin works of Devon were mostly abandoned early in the 19$^{th}$ century as the Cornwall mines became more productive, although some of the old tin mines have since been re-worked, and several new ones opened during the last century. Heavy metals are known to occur at varying concentrations in sediments across the cSAC due to these historic mining activities (see later sections of this report; EA, 1996). Extraction activities over the years also included granite quarrying, mining of the china clay deposits (this being the decayed felspar within the granite) and peat works.

The catchment of the upper estuary is thus very much influenced by agriculture and old mines whilst the lower estuary is subjected to substantial urban/industrial development.

Sediment and contaminant movements in the tidally energetic Tamar Estuary are governed by a mixture of tidal and freshwater flow variations. Net transport of chemicals is often determined by the fate of suspended particulate matter (SPM) and complicated by the presence of a turbidity maximum which occurs in the low salinity region of the estuary (<5 ‰). At times of low river flow the influence of saline water

(>5‰) may extend within 5km of the weir at Gunnislake, whereas during high flow conditions salt water sometimes does not extend further than ~15km from the mouth of the estuary. The position of the turbidity maximum varies accordingly, and also depends on the stage in the tidal cycle (Bale *et al.,* 1985; Uncles *et al*., 1985). Increased tidal pumping at spring tides can result in concentrations of SPM between one and two orders of magnitude higher than at neap tides; in the upper estuary SPM concentrations may vary between 0.05 and >1g $l^{-1}$. Intensity of the turbidity maximum is also governed by river flow: as well as moving downstream under high run-off conditions, suspended matter concentrations at high water are generally lower (Uncles and Stephens, 1989).

**The Yealm**

The Yealm estuary, to the southeast of the Sound, is a narrow, wooded, steep-sided inlet roughly 6.5km long. There is a limited amount of freshwater inflow from several small tributaries and the sand bar at the mouth shelters the lower estuary from wave action caused by the prevailing southwesterly winds. A small laboratory was established by The International Paint Company in 1920 (now International Coatings), who have three testing rafts along the estuary. With the exception of aggregate extraction at Steer Point brick works, and oyster beds south of Steer Point, there are no industrial activities on the shores of the Yealm and the only populated banks are those of Newton Creek to the east. The Yealm catchment is therefore primarily agricultural.

The diverse fauna of the estuary includes a range of sponge- and worm-dominated communities on lower shore mixed sediments. Atlantic salmon *Salmo salar* and sea trout *Salmo trutta* migrate to the inlet and spawn upriver, the estuary is also a major bass nursery area and the mudflats of the inlet are of national importance to overwintering greenshank *Tringa nebularia*. There is a seagrass (*Zostera*) bed at Misery Point with associated fauna including the greater pipefish *Sygnathus acus.* Just to the west of the estuary mouth is Wembury Voluntary Marine Conservation Area. The marine life at Wembury has been well studied for many years. The gullies and ridges provide protection from wave action for a variety of organisms. Two fresh water streams flow over the tidal zone creating a greater diversity of habitat (Tamar Estuaries Consultative Forum, 1998).

The cSAC area has a long history of marine biological study, both for research and education. The range of habitats and communities reflect the changing salinity gradient from upper estuarine to open coast, across sediments and bedrock. The biodiversity of the area is also influenced by the warm westerly climate.

The cSAC supports an extremely rich marine flora and fauna, which include abundant southern Mediterranean-Atlantic species rarely found in Britain, such as the carpet coral *Hoplangia durotrix*. Particularly notable are the littoral and sublittoral limestone reefs extensively bored by bivalves *Hiatella arctica* and harbouring a rich fauna. The reef habitats support some unique seabed communities, and include the nationally rare species, sponge *Axinella damicornis*, brittlestar *Ophiopsila aranea* and sea fan *Eunicella verrucosa.* The Sound, and the rivers Tavy, Walkham and Yealm are migratory routes used by salmon on their way to Dartmoor spawning grounds. In

addition, the cSAC is a designated bass *Dicentrarchus labrax* and Dover sole *Solea solea* nursery area.

Plymouth Sound and Estuaries have a long history of management, the majority of which falls under the jurisdiction of the Royal Navy. The Dockyard Port of Plymouth Order (DPPO) 1999 is primarily designed to allow for the timely conduct of Naval activities and shipping movements, however, many of its regulations also directly benefit the conservation interests of the site. Similarly the Yealm Estuary is managed by a Harbour Authority, in a manner which aims to help establish and maintain its conservation features. Additionally, the European marine site is covered by a number of fisheries byelaws, which, amongst other activities, prohibit trawling. Recently, the Tamar Estuaries Consultative Forum, which encompasses all statutory and byelaw-making bodies, has developed a single scheme of management to respond to, and deliver, the requirements of the Habitats Directive. This scheme can be found in the Tamar Estuaries Management Plan 2001-2006. Objectives from the scheme are addressed in the current project and include the review of water quality and the identification of additional research and monitoring requirements.

The boundaries of the Plymouth Sound and estuaries marine site are shown in figure 1. Maps of communities and features within the site can be found in greater detail elsewhere (English Nature, 2000).

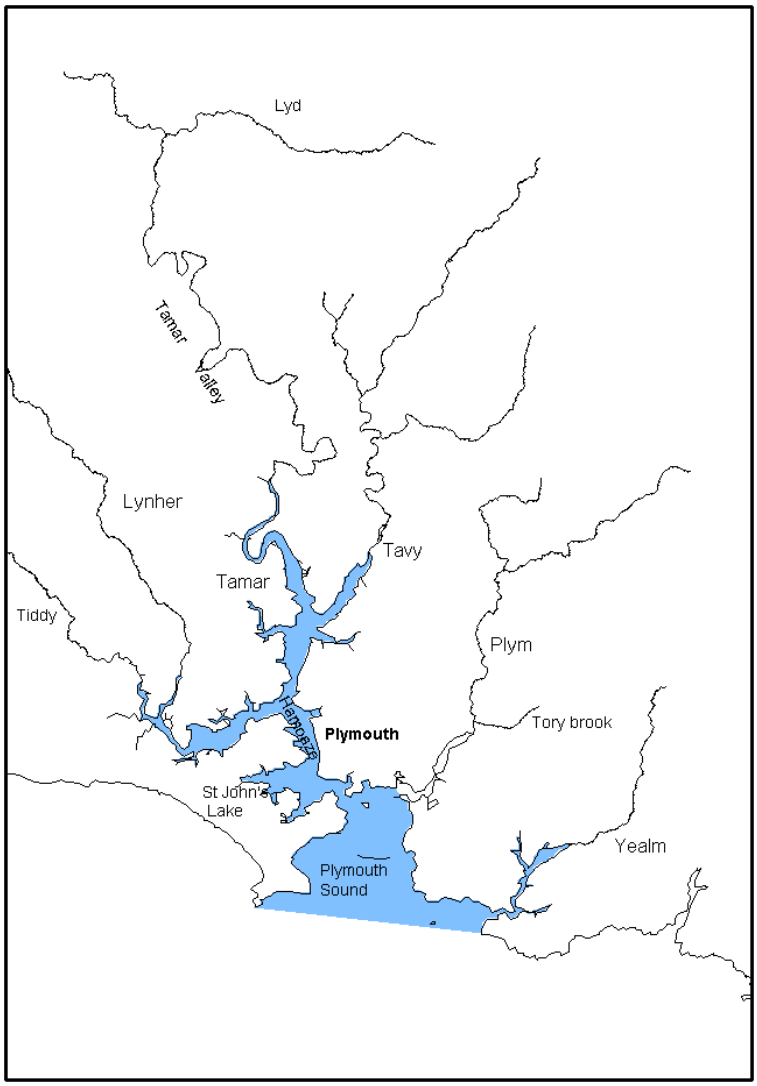



**Figure 1. Plymouth Sound and Estuaries cSAC**

There are a large number of discharges into the system of varying sizes (see full list in the accompanying database). Total consented volumes of sewage and trade effluent discharged either directly into the SAC or through adjacent estuaries are estimated at 95,304 and 121$m^3$ $d^{-1}$ (Allen *et al.,* 2000). Sitings of some of the more important (by volume) discharge consents impacting on the Plymouth Sound and estuaries system are shown in figure 2.

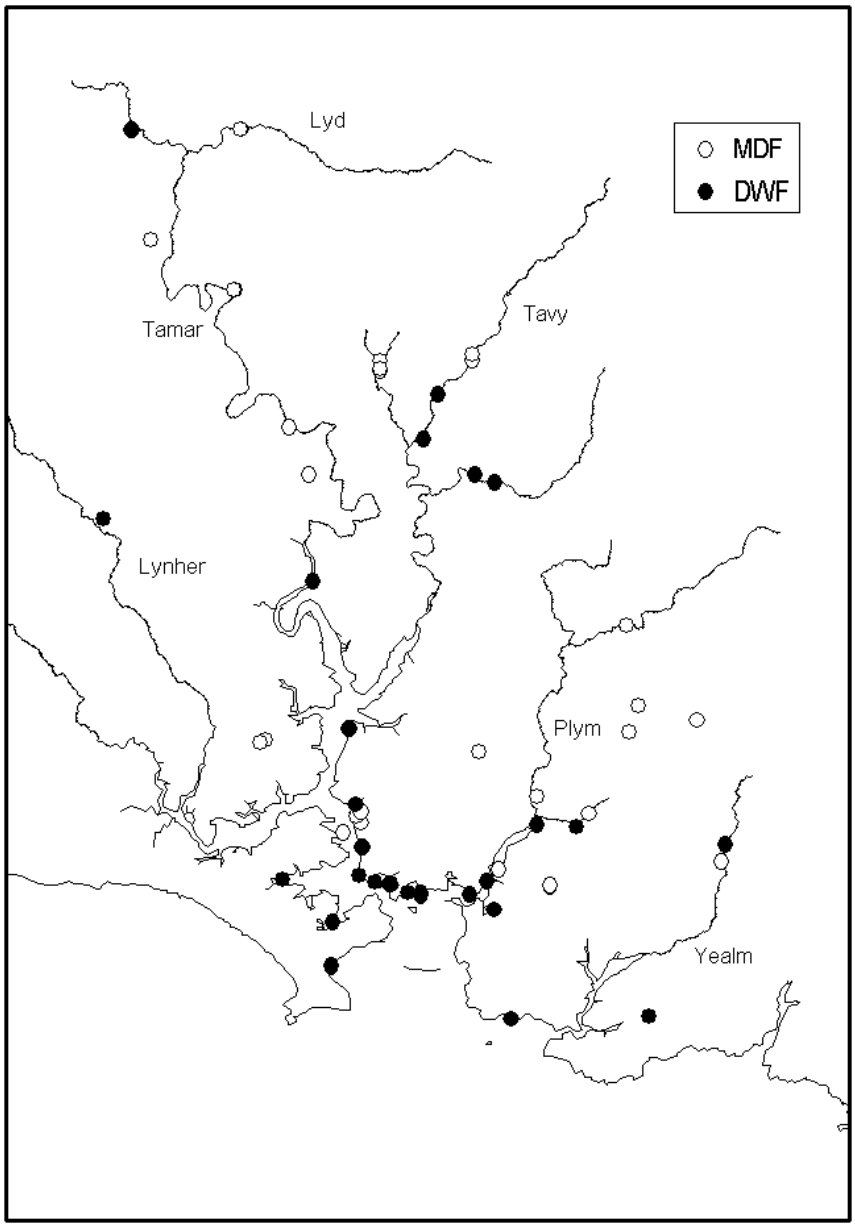



**Figure 2. Locations of some of the larger discharge consents to the Plymouth Sound and estuaries system. Consents shown for the discharge of sewage (generally set for SWW) are those >356 $m^3$/d DWF (closed symbols). Trade consents, and miscellaneous sources of effluents shown (open symbols) are those > 500 $m^3$/d MAX (Data supplied by Environment Agency 2002).**
**NB No distinction has been made between continuous and intermittent discharges. Details of specific discharges should be clarified with the Environment Agency**

English Nature has provided advice on the Plymouth Sound and Estuaries site, given under Regulation 33(2) of the Conservation Regulations 1994 (English Nature 2000). A summary of the interest (or qualifying) features, and conservation objectives for the site is given in Annex 1. Table 1 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 and site characterisation, we will focus on the areas vulnerability to toxic and non-toxic contamination, unless any of the other threats are seen as highly relevant.

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/CCW 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

**Table 1. Summary of the operations, which, in ENs opinion may cause disturbance or deterioration to key interest features. Toxic and non-toxic contamination are the principal threats considered in the current project. (table adapted from English Nature, 2000) ***

| Standard list of operations which may cause deterioration or disturbance | INTEREST FEATURES | | | |
|---|---|---|---|---|
| | **Large shallow inlets and bays** | **Sandbanks which are covered by seawater at all times** | **Estuaries** | **Nationally important Annex 1 birds (avocet, little egret)** |
| **Physical loss** | | | | |
| Removal (e.g. land claim, development) | ✔ | ✔ | ✔ | ✔ |
| Smothering (e.g. artificial structures, disposal of dredge spoil, outfalls) | | | | |
| **Physical damage** | | | | |
| Siltation (e.g.dredging, spoils, outfalls) | ✔ | ✔ | ✔ | |
| Abrasion (e.g. boating, anchoring, trampling) | ✔ | ✔ | ✔ | |
| Selective extraction (e.g. aggregate dredging, entanglement, bait digging) | | | | |
| 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, endocrine disruptors) | ✔ | ✔ | ✔ | ✔ |
| Introduction of non-synthetic compounds (e.g. heavy metals, hydrocarbons) | ✔ | ✔ | ✔ | ✔ |
| Introduction of radionuclides | | | | |
| **Non-toxic contamination** | | | | |
| Nutrient enrichment (e.g. agricultural run-off, outfalls) | ✔ | ✔ | ✔ | ✔ |
| Organic enrichment (e.g. mariculture, outfalls) | ✔ | ✔ | ✔ | ✔ |
| Changes in thermal regime (e.g. outfalls, power station) | | | | |
| Changes in turbidity (e.g. dredging, outfalls, agricultural run-off) | ✔ | ✔ | ✔ | |
| 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: recently, additional interest features have been submitted to the EU. These include; reefs, Atlantic salt meadows, mudflats and sandflats not covered by seawater at low tide (all probably subject to the same threats from toxic and non-toxic contamination as other features). The shore dock *Rumex rupestris* and the Allis Shad *Alosa alosa* have also been added as interest features of the cSAC (see Annex 1).**

# 5. STUDIES ON CONTAMINANTS

## 5.1 Toxic Contaminants

The tentative conclusions from the National Monitoring Programme Survey of UK (Marine Pollution Monitoring Management Group, MPMMG 1998) coastal waters highlighted few issues of concern regarding the Plymouth area. Amongst these were high levels of metals (As, Hg) and PAHs in Tamar sediments, and levels of lindane in water, which were sometimes in excess of the EQS (20ng $l^{-1}$). Pesticides Atrazine and Simazine were also considered to be elevated, though below the statutory EQS. It is perhaps worthwhile reiterating some of the more generalised comments on pollution trends in UK marine waters, arising from the NMP programme:

- Biological effects were of most significance in known industrialised estuaries – many appear to be polluted to an extent which could be harmful to phytoplankton (due to a combination of contaminants rather than single chemicals)
- Benthic biodiversity is low at the head of most estuaries but increases offshore. Much of this is due to natural stressors such as salinity and sediment instability/local hydrographic regimes (particularly pertinent in the Tamar).
- Concentrations of contaminants in water and sediments are generally highest in estuaries and decrease offshore. The relatively high levels of metals in sediments of some estuaries are likely to reflect current and historical anthropogenic inputs (again particularly pertinent in the Tamar).

Though the Tamar has been an obvious 'test-bed' for more detailed estuarine studies by the marine laboratories in Plymouth (and elsewhere) most published work relating to environmental quality is now 10 years old or more, and has often focused on a limited range of contaminants. However, some of these studies address estuarine processes which control environmental quality and may help to define the issues of most concern and to 'fine-tune' future monitoring programmes. The following review of potential key toxic features is therefore broken down into major categories of contaminants.

### 5.1.1. Metals

Studies on metals relate principally to the Tamar, the largest of the Plymouth Sound Estuaries. The catchment area of the Tamar has long been associated with the mining and smelting of metal ores (principally Cu and As, and to a lesser degree Sn, Zn, Pb, As and W which have been mined since at least the thirteenth century) - in particular the Gunnislake-Kit Hill mineral complex. This was, in the later part of the nineteenth century, the scene of half the world's arsenic production and a substantial proportion of the global output of Cu. Although the majority of this activity ceased at the end of the 19$^{th}$ century, drainage from sulphide loads, adits and spoil heaps still contribute to elevated concentrations in waters, sediments and biota, adding to that released by weathering and erosion.

Elevated arsenic concentrations in freshwater immediately upstream the of the SAC (Tavistock-Gunnislake area) were described in a study by Aston *et al* (1975) and by

WRc some 15 years ago, the latter mainly with a view to assessing risks for drinking water (Cole, 1988). Arsenic has been related to carcinogenesis in man. Although 'normal' levels were within the prescribed limit of 50µg (total dissolved) As $l^{-1}$ it was suggested that the history of sporadic rises in concentrations (occasionally > 250 µg $l^{-1}$ from arsenical mine wastes and drainage) merited continued surveillance. This still holds true today. Tributaries of the River Lyhner, though less obviously contaminated than the Tamar, may still contain As concentrations in the range 10-50µg $l^{-1}$.

In comparison with these historic sources, current industrial process probably have a low impact in terms of discharge of metals to the site.

*Estuarine Chemistry of Metals*

The most significant feature for many metals (and nutrients such as phosphate and ammonia) is the pronounced reactivity of dissolved forms with particles, brought about by tidally induced sediment mobility.

The EQS for dissolved As is 25µg $l^{-1}$. Interpretations of As profiles in the estuary are made difficult by the complex nature of inputs which include adit drainage, run-off from spoil heaps and sediment pore-water inputs. By contrast, present-day industrial and domestic sources do not appear to be a major influence.

A typical profile for dissolved As in the Tamar Estuary (downstream of Gunnislake to Plymouth Sound) is shown in figure 3. Dissolved As concentrations are elevated in the upper part of the tidal Tamar (and in the Tavy and Lynher), though generally not exceeding 10µg $l^{-1}$. Enrichment occurs as the river flows through the mineralised area between Gunnislake and Calstock which is littered with old mine workings, spoil heaps and adits. This area was the site of the world's largest concentration of As refineries, capable of producing more than 300 metric tonnes of refined arsenic oxide per month in the late 1800s. Apart from a brief reopening at the time of the first world war there has been little activity subsequently.

The majority of the dissolved As in the estuary is as arsenate ($As^{5+}$) however the more toxic reduced form, arsenite ($As^{3+}$), may be encountered (up to 1µg $l^{-1}$) above Calstock. This is consistent with observations of localised inputs (50µg $l^{-1}$ $As^{3+}$) from adits in the Gawton area (Langston 1983). There is evidence of seasonal biomethylation of ($As^{5+}$) at the seaward end of the estuary. Concentrations of dissolved monomethylarsenic and dimethylarsenic up to 0.46 and 1.27µg As $l^{-1}$ (typically 15% of the total As concentration) have been recorded in summer months, associated with proliferation of marine phytoplankton (Howard *et al.,* 1988).

Upon mixing with salt water (figure 3) some removal of dissolved As (~30%) may take place, at low salinities, in conjunction with Fe removal and oxhydroxide formation. Further down stream, organic-rich sediments are periodically stirred into the water column particularly on a spring tide and the interstitial water released can have a significant impact on the dissolved components in the water column. For arsenic an extended maxima (typically not exceeding 10µg $l^{-1}$) may occur in mid-estuary, as a result of tidal mixing and injections of pore water enriched in As (up to 50 µg $l^{-1}$ arising from the dissolution of hydrous Fe and Mn coatings). The bulk of this

introduced As is released on the outgoing tide, at the mouth of the Tamar, where estuary water is considerably diluted with sea water: As a result, arsenic concentrations in the Sound are seldom significantly above background (~1-2 μg $l^{-1}$). Occasionally, however, in periods of high run-off, low salinity water and entrained suspended solids may extend as a surface plume into Plymouth Sound and beyond, into the English Channel. This will result in corresponding elevated transport beyond the mouth of the Tamar, though concentrations of dissolved As are unlikely to exceed EQS values. The consequences of tidal/seasonal influences on As profiles and a simple model of As cycling in the Tamar Estuary is described by Knox *et al.,* (1984).

The low salinity region of the Tamar Estuary and in particular its 'turbidity maximum' is highly influential in structuring the distributions of other contaminants (both toxic and non-toxic) - for example removal of dissolved silicate, phosphate, and various metals. Laboratory experiments performed by Bale and Morris (1981) confirmed the coagulation and precipitation of phosphate at low salinities (in association with removal of colloidal Fe). Phosphate and arsenate would be expected to behave alike, as a result of their similar chemical properties. In contrast, removal of Mn onto particles, although an estuarine-induced phenomenon, occurs primarily in the freshwater region above the interface with salt-water and is probably related to oxidative removal of hydrous manganese oxide coatings on particle surfaces. Extended maxima of Mn and ammonia in the mid-estuarine region of the Tamar (Bryan and Hummerstone 1973a; Knox *et al* 1981) are very similar to those described for As and reflect the common influences of physical mixing processes in this area.

Removal of dissolved Zn and Cu from Tamar water occurs at low salinities, suggesting rapid absorption onto suspended particulates forming in the region of the turbidity maximum (Ackroyd *et al*., 1986). A combination of pore water infusions and desorption from tidally re-suspended sediments probably explains the mid-estuarine maxima for both metals (as for As), though the position of these maxima occurs at slightly different regions of the salinity profile (Cu-1-8‰ salinity; Zn 3-20‰) and is sometimes virtually non-existent. As for other metals the variable magnitude and location of the peak signal is determined by the degree of sediment disturbance in response to run-off conditions and the tidal energy oscillation during the spring-neap cycle. Though elevated, maximum concentrations of Cu and Zn reported in the literature *usually* fall below EQS values (5 and 40μg $l^{-1}$ for Cu and Zn, respectively). Compliance is particularly high at sites near the mouth of the estuary and in Plymouth Sound. At upstream sites in the Tamar, however, Cu concentrations may sometimes exceed the EQS. Significant amounts of 'dissolved' metal near the turbidity maximum may in fact be colloidal - associated with ligands of sediment/pore water origin - whereas at higher salinities the Cu complexing capacity of organic matter decreases (Berg *et al.,* 1986). This may increase the proportion of biologically-available Cu at the seaward end of the estuary even though concentrations of 'total dissolved' Cu are lower.

In view of the toxicity of Cu and the persistent reservoir contained within Tamar sediments, (together with extensive usage in antifouling preparations) some re-evaluation of estuarine distributions is perhaps timely. Furthermore if proposals to lower the Zn EQS to 10μg $l^{-1}$ were to be adopted, parts of the estuary might fall above the standard under certain conditions of tide and run-off. It is also worth noting that

pore waters in the Tamar may contain concentrations of Cu (13-200µg $l^{-1}$) and (Zn 13-910µg $l^{-1}$) which are between one and two orders of magnitude higher than overlying water and are themselves of possible toxicological significance for infauna (P Watson, unpublished data; cited in Ackroyd *et al*., 1986). As and Mn in pore water are of the order 20-40µg $l^{-1}$ (Knox *et al*. 1984).

Thus, distinct features of the Tamar are; stripping of dissolved contaminants towards the head of the estuary, and maxima for dissolved Mn, $NH_4^+$ and As in mid-estuary resulting from pore water injection and desorption from suspended sediments (see figure 3). Zn and Cu display similar traits, as do a number of other contaminants such as Al (Morris *et al*., 1986), though the relative importance of pore water infusion rates, sorptive exchange processes and dissolution reactions may well vary. Therefore, both physical and chemical aspects of this cyclical behaviour are likely to impact on biological communities and influence the character of the site. For the above elements, however, these processes appear to be largely acting on historic or natural sources and are largely independent of current discharge consents.

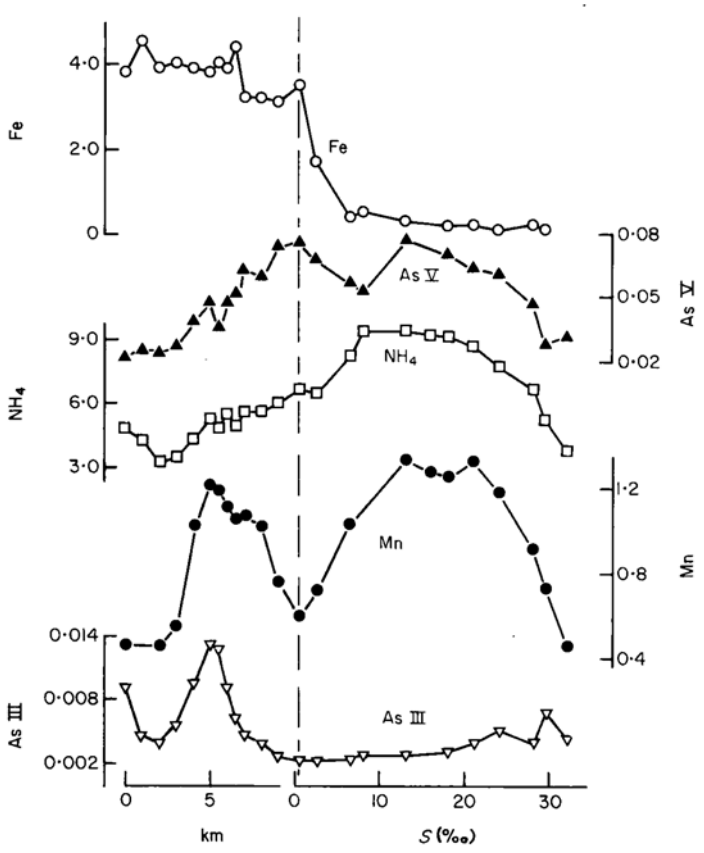



**Figure 3. Profiles for dissolved As (III and V), Fe, Mn, $NH_4^+$ in the Tamar Estuary (2/7/1980) showing many of the features discussed in the text. The vertical line indicates the location of the freshwater/brackish water interface (freshwater to the left, saline water to the right). All concentrations are in µmoles $l^{-1}$ and are plotted against distance from the weir (freshwater), or against salinity for saline water. (From Knox *et al.*, 1984; with permission from Academic Press).**

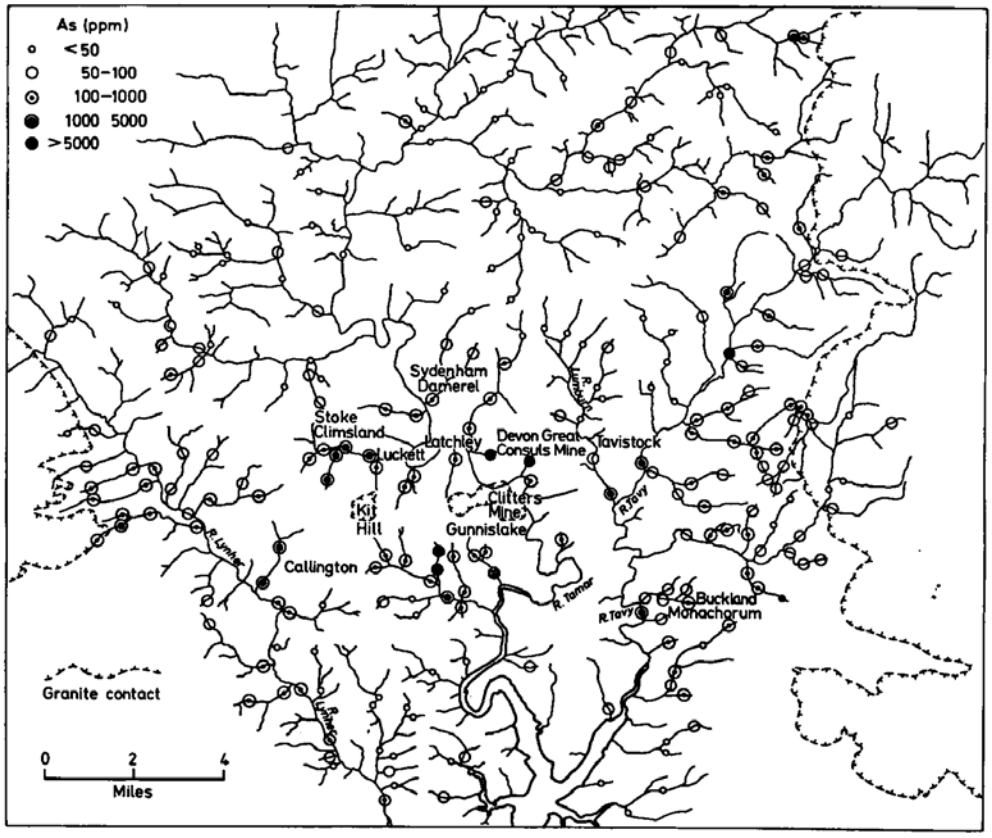
These studies emphasise that careful selection of chemical determinands and simple analogue calculations can provide useful information on apparently complex estuarine profiles. It is unfortunate that many of the above data are now almost two decades old. A similar approach should be considered for future surveys to update understanding of contaminant behaviour in estuaries of the Plymouth Sound SAC and to evaluate changes that may have occurred in the intervening period.

Studies on the behaviour of other metals include Ni, Sb, Se, Sn, U and V (Berg *et al* 1991). Antimony and Uranium profiles indicate some reactivity, as displayed for the group of metals in the previous section, i.e. concentrations governed by pore-water infusions or release from suspended particles in mid-estuary (Sb) and/or removal to sediments at low-intermediate salinity (Sb and U). Similar reactivity occurs for labile Ni. Tin concentrations increased seawards, dominated by inputs at the mouth of the estuary, (presumed to derive from TBT from antifouling paints) and appeared to behave fairly conservatively in the estuary, as did 'total dissolved' V (though desorption of the latter may occur from particulates at low salinities). 'Total dissolved' Ni and Se decreased from freshwater to the sea with little evidence of reactivity in the estuary. It is unlikely that this group of elements, in inorganic form, poses a hazard to the SAC, at the concentrations found. The threat from organotins, i.e. TBT, are discussed in more detail in section 5.1.2.

It needs to be stressed that the behaviour of elements in the water column of the Tamar may be highly variable, depending conditions of tide and river flow. This is further demonstrated by the survey of the behaviour of uranium isotopes by Toole *et al.,* (1987) which, undertaken at a time of abnormally high run-off, indicated virtually no reactivity or inputs - in contrast to the results of Berg *et al*., (1991), described above. Thus in the study by Toole and co-workers, the concentrations of U increased linearly with salinity, from a low value of 0.04 $\mu g\ l^{-1}$ in freshwater of the Tamar to 2.83 $\mu g\ l^{-1}$ at the mouth (29 ‰) and was projected to meet the open ocean value of 3.35 $\mu g\ l^{-1}$ at 35‰. The significant effect of river and tidal conditions on a range of determinands, including As, ammonia, Fe and Mn is described by Knox *et al.,* (1984).

*Metals in Sediments*

Mapping of As in stream sediments in the UK by Aston *et al* (1975) indicted the influence of mineralisation in the southwest and in particular the catchment of the Tamar/Tavy/Lynher (figure 4). Here concentrations >70$\mu g\ g^{-1}$ are widespread (90% of samples would classify as anomalous, compared to background values of 5-15$\mu g\ g^{-1}$, indicating the wide scale of contamination). Occasionally, samples exceed 5000$\mu g$ As $g^{-1}$. Locations of some of the major sources in the area are discussed above and also reviewed by Aston *et al* (1975); generally, the highest concentrations are in the Gunnislake-Callington areas of the Tamar and Lynher catchments. In the Tavy catchment there is a small hotspot for As around Tavistock.




**(Figure 4. Arsenic distributions (µg $g^{-1}$ dry weight) in stream sediments from the Tamar, Tavy and Lyhner catchments. (From Aston *et al*, 1975; with permission).**

Arsenic concentrations in sediments of Plymouth Sound Estuaries exceed baseline levels for the UK by an order of magnitude (Langston 1980). Again this is due to the mineralised nature of much of the region, combined with the historical legacy of inputs from old mines, refineries and spoil heaps, rather than modern day activity. Concentrations of As in surface sediments are typically of the order of ~40µg $g^{-1}$ but may exceed 100µg $g^{-1}$ in some parts of the upper Tamar and Tavy. Put in context, however, enriched though these values may be, they are an order of magnitude lower than As concentrations in sediments from parts of the Fal System, Hayle and other heavily mineralised regions of SW England.

Arsenic concentrations in Tamar estuary sediments are strongly correlated with Fe. This is explained by the fact that dissolved iron precipitates rapidly upon contact with seawater and any accompanying arsenic is actively scavenged by freshly formed particulate Fe oxyhydroxide. Through similar mechanisms of reactivity, sediments – and particularly their surface coatings - are important in controlling the transport and dispersion of numerous contaminants.

A series of axial profiles of Cd, Cu, Fe, Mn, Pb and Zn concentrations in sediments were constructed for the Tamar in an attempt to reveal seasonal trends and spatial variability (Ackroyd and Marsh 1981; Ackroyd *et al*., 1987). These appear to be controlled by fluvial inputs of new material (highest in periods of high run-off) and by seasonal fluctuations in tidal pumping and movement of sediment (also highest in

winter). The distributions of many metals appear correlated (decreasing downstream from the head of the estuary), though this is only apparent by standardising to silt content (Ackroyd *et al.,* 1987) demonstrating that grain size has a significant bearing on contaminant levels.

Under typical summer low flow conditions, fines (usually rich in metals) tend to accumulate at the head off the estuary (transported by tidal asymmetry) whilst proportionately more coarse material (lower in metals) is distributed at lower estuary sites. During winter high river flows there is tendency towards an increase in percentage fines in the mid-lower estuary, which includes fresh recharge from riverine sources as well as downstream fluxes of estuarine material. Peak metal concentrations in sediments upstream can therefore occur (commonly) in summer, as a result of tidal pumping, and in winter, occasionally, from an influx of contaminated land-based material. By comparison the effect of seasonal variations in sediment movement on metal concentrations in the lower reaches of the estuary are less pronounced.

The overall effect on metal accumulation at the head of the estuary is dependent on the reactivity of the metal. Mn is readily adsorbed/desorbed and shows largest responses to variations in flow - and sharpest gradients from river to the sea (concentrations in sediments decreasing exponentially, by almost an order of magnitude). In contrast to the steep gradient for dissolved Fe in overlying water, Fe in sediments is less variable and probably controlled more by physical transport process: gradients in sediment Fe are therefore far less severe (Ackroyd *et al.,* 1987). Zn is not strongly affected by redox chemistry and displays similar behaviour to Fe (fairly uniform concentrations of ~250µg $g^{-1}$ Zn throughout the estuary), whilst Cu profiles indicate intermediate behaviour – affected by a combination of physical and chemical processes. Nevertheless as a general rule metals in sediments, in total and readily- extractable form, increase in an upstream direction. One exception may be Pb, where the proportion of easily-leached metal was reported to be highest towards the mouth of the estuary (Bryan and Uysal, 1978), indicating possible anthropogenic Pb sources in the lower reaches (road run-off, atmospheric?).

Some of the data for sediment metals is depicted in table 2 and indicates considerable enrichment in the Tamar Estuary for As, Cu, Fe and Zn compared to background values (North Sea, Tees Bay), though this is clearly less severe than in parts of the Fal (Restronguet Creek). In contrast to these metals, enrichment of Hg and Pb have been reported to occur around the Hamoaze, nearer to the seaward end of the estuary indicating sources other than geological.

**Table 2. Metals in sediments (µg $g^{-1}$ dry wt): Plymouth Sound Estuaries and other sites (based on Bland *et al*, 1982)**

| *site* | *Cu* | *Zn* | *Pb* | *Cd* | *Mn* | *Fe* | *As* | *Hg* | *Ref* |
|---|---|---|---|---|---|---|---|---|---|
| ***Lynher*** | 274 | 317 | 150 | | 289 | 23120 | 50.7 | 2.1 | 1 |
| ***Tamar*** | 145-545 | 221-605 | 19-239 | | 105-1500 | 21000-49000 | 25-236 | 0.2-1.5 | 2 |
| ***Plym*** | | 256 | | 9.3 | 171 | 12100 | 41 | 0.35 | 3,4,5 |
| ***Restronguet*** | 1690 | 1540 | 684 | 3 | 1030 | 54000 | 1080 | | 6 |
| ***Tees Bay*** | 8 | 74.1 | 45.4 | 0.2 | 242 | | | 0.1 | 7 |

[1]Bland et al 1982;[2] Ackroyd et al 1987; [3]Langston, 1980; [4]Millward and Herbert 1981; [5]Bryan and Hummerstone 1973b; [6] Aston et al 1975; [7]Taylor 1979

Millward and Herbert (1981) studied Hg in Plym estuary sediments in relation to their geochemical characteristics. Hg concentrations varied between 0.018 and 2.61µg $g^{-1}$ but did not appear to covary with characteristics such as Fe, Mn, organic carbon or clay content; nor did they relate to sample location in any obvious way. Deposition of particulate Hg from industrial sources, rather than in-situ scavenging from solution, was suggested as a possible explanation for distributions, though unequivocal evidence for such a source could not be found (including Chelson Meadow waste disposal site). It was speculated that Plympton and/or Hooe Lake sewage works could have been a source of particulate inputs, a fraction of which might be retained by the estuary and the remainder transported to Plymouth Sound. However, sediments were not sieved in this survey and Hg concentration could be influenced by the degree of sorting. Nevertheless, there is an indication of some enhancement in Hg levels in sediments at certain sites, which would merit further investigation. It would be useful to attempt to separate anthropogenic fractions from the geological background signal in sediments, and to establish the biological consequences of such enhancement.

Cadmium concentrations in the upper part of the Plym were also reported as being relatively high some 30 years ago (upto ~9µg $g^{-1}$) and believed to have originated from industrial sources (Bryan and Hummerstone 1973b).

There is an indication that As concentration in upper Tamar Estuary sediments increases with depth – perhaps by as much as two-fold at depths of around 70cm (Lindsay and Bell, 1997) – reflecting the peak in mining activity in the nineteenth century. Attempts to date sediment cores (by $^{210}$Pb profiling) have also revealed relationships between metal concentrations and industrial activity in the region (Clifton and Hamilton, 1979). Figure 5 illustrates this history for a core from St Johns Lake in the lower estuary; levels of Zn, Pb and Cu rise sharply approximately 25 years after the onset of peak mining and appear to have been maintained to the present day as a result of run-off and leaching.

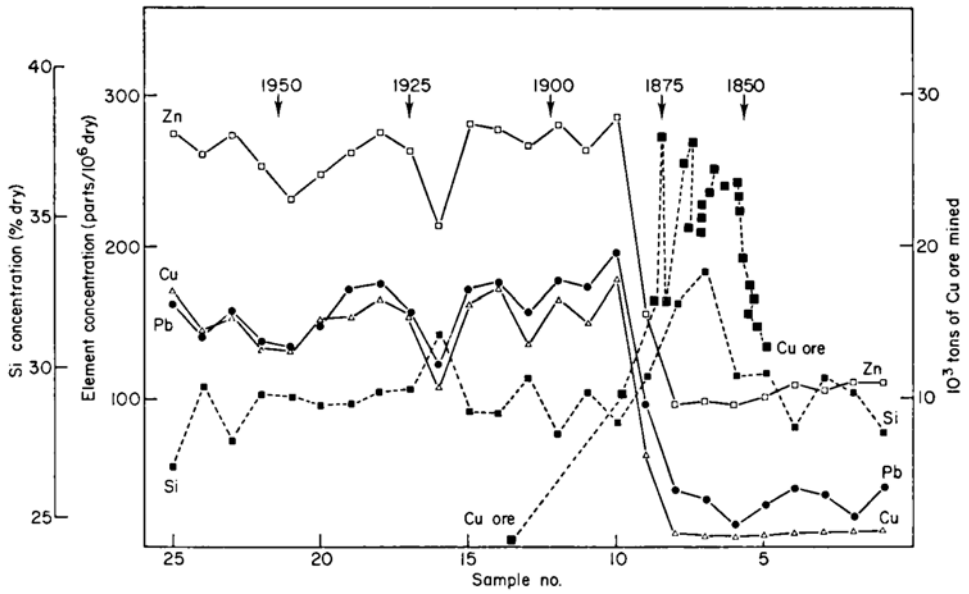



**Figure 5. Tamar Estuary: Metals in sediments over time, in relation to Cu ore production (reproduced from Clifton and Hamilton, 1979 with permission, AP)**

Organisms have therefore been exposed for more than a century to these conditions and no doubt have become partially adapted. It would be useful to conduct further coring at other sites in the SAC to characterise impacts from historical and present-day activities. (This applies to metals, TBT and selected organic contaminants).

*Metals in Estuarine Biota*

A considerable amount of baseline data exists on the distribution of key indicator species (e.g. *Fucus* spp, *Nereis diversicolor*, *Scrobicularia plana*, *Mytilus edulis*, *Cerastoderma edule*, *Littorina* spp.) and the bioavailability and impact of metals in UK estuaries, including the Plymouth Sound Estuaries. Much of this has been collected by MBA staff over a period spanning three decades (see Bryan *et al.,* 1980, 1985; Langston *et al*., 1994b). This provides a useful background to assess characteristics of the site and a valuable baseline for future changes. A synthesis of some of the information for different bioindicators is given below.

Polychaetes are among the most widespread inhabitants of contaminated and uncontaminated sediments, and Nereids such as *Nereis diversicolor* accumulate a number of metals in amounts which reflect their bioavailability in their (sediment) environment (Bryan *et al.,* 1980; 1985; Luoma and Bryan 1982; Langston *et al*., 1980, 1982). Tolerance to a wide range of salinity also makes them extremely useful for monitoring in estuaries (e.g. present in the Tamar from the mouth upstream as far as Calstock). This species provides a useful basis for comparative study in Plymouth Sound Estuaries. It should be noted however that Zn and Fe are partially regulated and therefore body burdens can underestimate contamination with these metals. It is also important to recognise again that sediment conditions can modify availability somewhat (e.g. high sediment Fe and organics can reduce uptake of As, and Hg, respectively: Langston *et al.,* 1980; 1982).

**Table 3. *Nereis diversicolor*. Metals concentrations (µg $g^{-1}$ dry weight) in Plymouth Sound Estuaries.** (Langston, Burt and Chesman, unpublished data)

| | Ag | Cd | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn | Hg | As | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Tamar** | 0.94 | 0.64 | 6.39 | 0.42 | 131 | 570 | 18.7 | 4.60 | 6.79 | 188 | 0.13 | 14.4 | 0.36 |
| **Lynher** | 1.80 | 0.78 | 7.72 | 0.39 | 202 | 497 | 14.9 | 4.73 | 6.37 | 184 | 0.16 | 17.3 | 0.45 |
| **Tavy** | 1.57 | 1.58 | 8.45 | 0.69 | 183 | 417 | 14.4 | 5.25 | 12.9 | 185 | 0.47 | 16.7 | 0.17 |
| **Plym** | 0.62 | 2.51 | 3.89 | 0.58 | 30.6 | 358 | 8.47 | 6.08 | 5.18 | 189 | 0.35 | 15.9 | 1.06 |
| **Yealm** | 0.20 | 0.30 | 6.07 | 0.56 | 41.9 | 477 | 10.3 | 2.80 | 3.12 | 199 | 0.19 | 10.1 | 2.62 |
| **UK Min** | 0.06 | 0.02 | 0.83 | 0.03 | 7.69 | 210 | 4.03 | 0.630 | 0.16 | 87.8 | 0.02 | 3.22 | 0.05 |

Table 3 shows summary statistics of our own unpublished data for metals in *Nereis diversicolor* in Plymouth Sound Estuaries (mean values spanning ~25 years, therefore incorporating the recent history of contamination rather than current status). For comparison, the average of the lowest ten sites in our UK data set is shown (UK min). These indicate some enrichment for all the Plymouth estuaries compared with UK baselines. Within the Plymouth subset however the Yealm is consistently lower than the other estuaries for 'pollutant metals' Ag, Cd, Ni Pb and As. Copper bioavailability in both the Yealm and the Plym is low in comparison to the Tamar complex. In contrast, these data indicate elevated Sn bioavailability in the Yealm which could represent historic inputs of TBT from small vessels, prior to the TBT legislation in 1987, and perhaps a contribution from the International Coatings discharge (see section 7.1.2). Zn concentrations in *Nereis* are remarkably consistent in the Plymouth SAC as a result of the ability of *Nereis* to regulate body burdens of this essential element.

In the Tamar Estuary above Saltash there is a sharp increase in concentrations of Cu and several other metals in *Nereis* (by 2-3 fold) which does not appear directly related to sediment concentrations. The precise cause of this increase in bioavailability is not fully understood but is perhaps a function of the mid-estuarine peak observed in profiles of dissolved metals (see earlier sections). The source of this, in turn is suspected to be related to re-suspended sediments and associated porewater injections, mediated by conditions of tide and flow. Alternatively the step increase in metal availability in *Nereis* could be related to the salinity changes in mid-estuary (pore waters), perhaps acting on metal speciation and permeability in worms. In particular Mn bioavailability in *Nereis* is greatly enhanced by lowered salinity; it may be this factor rather than 'pollution' which governs Mn burdens in *Nereis*.

The deposit-feeding clam *Scrobicularia plana* has proved to be a valuable indicator species, particular in terms of understanding trends in sediment metal bioavailability. Its range in the Tamar –upto ~19Km upstream of the mouth, encompassing most of the Estuary – is exceptionally useful in this respect. Its ability to survive so far upstream 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 4. *Scrobicularia plana.* Metals concentrations (µg $g^{-1}$ dry weight) in Plymouth Sound Estuaries. (Langston, Burt and Chesman, unpublished data)**

| | Ag | Cd | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn | Hg | As | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Tamar** | 0.22 | 2.64 | 16.5 | 2.5 | 32.7 | 2177 | 48 | 5.25 | 73.0 | 1552 | 0.19 | 45.5 | 1.38 |
| **Lynher** | 0.19 | 2.05 | 13.8 | 1.94 | 33.3 | 1643 | 50.1 | 4.36 | 63.6 | 1450 | 0.20 | 37.1 | 1.14 |
| **Tavy** | 0.60 | 6.20 | 27.8 | 2.53 | 96.2 | 1278 | 41.6 | 9.22 | 79.1 | 2611 | 0.24 | 40.2 | 0.75 |
| **Plym** | 0.25 | 14.9 | 5.06 | 3.93 | 24.5 | 751 | 16.9 | 2.41 | 20.5 | 1400 | 0.24 | 28.2 | 0.87 |
| **Yealm** | 0.27 | 0.74 | 11.2 | 2.23 | 32.5 | 945 | 35.9 | 6.58 | 48.8 | 960 | 0.43 | 19.4 | 2.63 |
| **UK Min** | 0.05 | 0.13 | 1.5 | 0.26 | 9.50 | 226 | 4.8 | 0.89 | 3.79 | 193 | 0.04 | 5.7 | 0.08 |

Table 4 shows summary statistics of our own unpublished data for metals in *Scrobicularia plana* in Plymouth Sound Estuaries (mean values spanning ~25 years, again reflecting the recent history of contamination rather than current status). For comparison, the average of the lowest ten sites in our UK data set is shown (UK min). These indicate some enrichment for all the Plymouth estuaries compared with UK baselines. Within the Plymouth subset, however, the Yealm is consistently lower than the other estuaries for Cd, Zn and As. Pb is also relatively low. In contrast, these data indicate elevated Sn bioavailability in the Yealm (as also indicated in *Nereis*) which could reflect historic inputs of TBT. *Scrobicularia,* like *Nereis,* is considered to be a reasonable indicator of sediment-bound metals.

Availability for Cd again appears to be highest in the Plym. Co, Cu and Zn were highest in clams from the Tavy, whilst Fe, Mn, Pb and Zn where generally high in the Tamar complex probably as a result of regional mineralisation and historic mining activities.

Partitioning of metals between the digestive gland and other tissues in clams may be useful in indicating the relative importance of contamination in water and sediment as vectors for uptake. In the Tamar the digestive gland is the target organ for many metals (Cd, Co, Cr, Ni, Pb and Zn) signifying a dietary (particulate) source. In contrast the presence of a significant proportion of Mn (also Fe, and to a lesser extent Cu and Ag) in mantle and siphons, is an indication that dissolved forms of these metals are important, at least at upstream sites (Bryan and Uysal , 1978). Year-on-year bioavailability, as diagnosed by burdens in *S.plana,* appears to be reasonably consistent, though seasonal variability is indicated for some metals. In the case of Mn and Fe this is almost certainly due to the seasonal/climatic influence of flow conditions and tidal state on the relative adsorption/desorption characteristics in sediments.

Bioavailability of Mn and Fe invariably increases upstream reflecting overall increased levels of dissolved forms. Zn in clams also increases upstream, but as Zn is probably assimilated in dietary form, this pattern is thought to reflect the increase in readily extractable Zn towards the head of the estuary (Bryan and Uysal , 1978). Patterns for a number of other elements suggest less severe gradients in bioavailability, superimposed by occasional peaks which, for Ag, Cr and Pb, are attributed to the old South Tamar Mine some 12.5Km from the mouth of the estuary.

Arsenic in infaunal species such as clams *Scrobicularia plana* reflect sediment As contamination (especially weak acid extracts), although As (and Pb) burdens in these

deposit feeders may also be modified by other metals, notably by the amount of Fe in sediment (normalisation of sediment As (or Pb) values with respect to Fe has proved to be the best model for predicting bioavailability – see Bryan and Langston, 1992). Clams from the Tamar contain between 28 and 65µg $g^{-1}$ As compared with UK baselines of ~5µg $g^{-1}$.

*Fucus vesiculosus.* *Fucus* is generally considered to be a reasonable indicator of dissolved metals. Table 5 shows summary statistics of our own unpublished data for metals in *Fucus vesiculosus* in Plymouth Sound Estuaries (mean values spanning ~25 years, together with the UK minimum). These indicate some enrichment for all the Plymouth estuaries compared with UK baselines. Within the Plymouth subset however the Yealm is consistently lower than the other estuaries for Ag, Cd, Pb Cu and Zn.

Availability for Ag and Cd appears to be highest in the Plym, and for Cr in the Lynher, which, along with the Tamar and Tavy, is also relatively high for Cu and Zn.

**Table 5.** ***Fucus vesiculosus*.** **Metals concentrations (µg $g^{-1}$ dry weight) in Plymouth Sound Estuaries.** (Langston, Burt and Chesman, unpublished data)

| | Ag | Cd | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn | Hg | As | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Tamar** | 0.33 | 1.57 | 5.23 | 2.52 | 74.8 | 1631 | 425 | 5.17 | 37.4 | 318 | 0.11 | 53.3 | 0.82 |
| **Lynher** | 0.32 | 2.38 | 3.06 | 28.4 | 93.0 | 3073 | 430 | 3.97 | 33.3 | 715 | 0.06 | 39.8 | 1.08 |
| **Tavy** | 0.30 | 1.77 | 9.69 | 3.33 | 65.7 | 1232 | 314 | 6.70 | 18.3 | 379 | 0.02 | 59.9 | 1.37 |
| **Plym** | 0.56 | 4.69 | 7.39 | 4.34 | 25.0 | 1188 | 253 | 6.98 | 20.4 | 395 | | | |
| **Yealm** | 0.20 | 0.92 | 4.25 | 8.20 | 11.4 | 730 | 306 | 6.63 | 6.35 | 139 | 0.10 | 37.7 | 0.85 |
| **UK Min** | 0.04 | 0.12 | 0.19 | 0.10 | 2.85 | 37.7 | 10.5 | 1.26 | 0.27 | 36.3 | 0.01 | 4.6 | 0.01 |

In the Tamar concentrations in macroalgal samples *generally* increase in an upstream direction (Bryan and Hummerstone, 1973a). Mid estuarine peaks are distinct for Mn however, which almost certainly reflect the release and diffusion from sediments in this part of the estuary. Such peaks in *Fucus* profiles are less obvious for other metals. This probably reflects the fact that of all metals, dissolved Mn profiles in the estuary are affected most noticeably by the adsorption/desorption processes in sediments. Not surprisingly, seasonal changes in *Fucus* metal burdens in the Tamar are most significant for Mn.

One apparently anomalous observation concerns the trend for high levels of Zn to occur in macroalgal samples towards the mouth of the estuary, a pattern which does not appear to conform with that of water. Perhaps there are other localised sources of Zn in the lower estuary (Hamoaze) which merit investigation.

Experimental studies suggest that *Fucus vesiculosus* from the Tamar Estuary may have developed a degree of tolerance to metals as a result of the long history of exposure. After being subjected to 100µg $l^{-1}$ Cu, growth of Tamar plants is still able continue on return to clean sea water. In contrast, plants from a clean site (Avon, Devon) are unable to recover from such a toxic shock. The mechanism for this tolerance may involve a reduced permeability to metal (Bryan, 1984).

Arsenic concentrations in seaweed in the Tamar are in the range 38-60µg $l^{-1}$ and predominantly reflect levels of dissolved As. However some competition for uptake between arsenate and phosphate is likely which can modify burdens in these macroalgae on a site-specific basis.

Biomonitoring potential of winkles such as *Littorina littorea* has been reviewed by Bryan *et al.,* 1983 (again from MBA data) who suggest they may be reasonable indicators for some metals. Table 6 shows summary statistics of our own unpublished data for metals in *Littorina littorea* in Plymouth Sound Estuaries (Tamar, Plym and Yealm only) over the last 25 years together with UK minimum values. These indicate some enrichment for all the Plymouth estuaries compared with UK baselines. Within the Plymouth subset, the Yealm is consistently lower than the Plym or Tamar for Cd, Co, Cr, Cu and Pb. Sn bioavailability in the Yealm (as also indicated in *Nereis* and *Scrobicularia*) appears to be anomalously high.

Cadmium bioavailability again appears to be highest in the Plym though it is stressed that these data are now 20 years old and in need of updating.

**Table 6. *Littorina littorea*. Metals concentrations (µg $g^{-1}$ dry weight) in Plymouth Sound Estuaries.** (Langston, Burt and Chesman, unpublished data)

| | Ag | Cd | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn | Hg | As | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Tamar** | 2.80 | 2.39 | 2.16 | 2.06 | 169 | 391 | 72 | 8.34 | 10.9 | 109 | 0.45 | 31.7 | 0.25 |
| **Plym** | 1.82 | 7.08 | 2.92 | 2.30 | 220 | 452 | 80 | 4.15 | 23.3 | 140 | 0.31 | 13.3 | 0.47 |
| **Yealm** | 2.44 | 1.60 | 1.12 | 0.99 | 91 | 347 | 28 | 3.07 | 6.3 | 94 | 0.49 | 20.1 | 2.91 |
| **UK Min** | 0.39 | 0.43 | 0.17 | 0.03 | 39 | 140 | 13 | 1.01 | 0.22 | 62 | 0.07 | 6.9 | 0.01 |

**Table 7. Metals in oysters *Ostrea edulis* (µg $g^{-1}$ dry wt): Plymouth Sound Estuaries and other sites (based on Bland *et al*, 1982)**

| | Cu | Zn | Pb | Cd | As | Hg | Ref |
|---|---|---|---|---|---|---|---|
| Lynher | 610 (115-1840) | 3280 (690-9150) | 0.6 (0.15-5.0) | 7.4 (3.5-29.7) | 9.1 (6.9-10.7) | 0.23 (0.17-0.31) | 1 |
| Mylor | 1489 | 7828 | 2.92 | 6.52 | 23 | | 2 |
| Restronguet | 1256 | 8408 | 1.5 | 5.23 | 10.9 | 0.08 | 2 |
| Poole | 40 | 4502 | 0.35 | 1.56 | 3.8 | 0.16 | 2 |

[1]Bland et al 1982;[2] own unpublished data except for Hg ( - MAFF)

There has been a traditional oyster fishery and breeding ground for oysters at the confluence of the Tamar and Lynher for 700 years. Despite the introduction of depuration procedures, this fishery was closed in 1966, due to concerns surrounding gastroenteritis outbreaks. In 1980, with a view to re-opening the fishery, analysis of metals and bacteria were performed in samples of *Ostrea edulis* collected between Henn Point and Wearde Quay. Results suggested that faecal coliforms (>1000 per ml tissue) were the more likely to represent a threat to human health (Bland *et al* 1982). Though, as shown in table 2, sediments contained relatively high levels of Cu, Fe, Pb and Hg (the latter attributed to sewage inputs, since there are no natural sources of Hg

in the catchment) only Cu and Zn concentrated significantly in tissues (table 7). Oysters are known to be natural accumulators of these metals, particularly Zn (Langston *et al.,* 1998).

A study of metals in polychaetes from coastal (as opposed to estuarine) areas in SW England included Rame Ground and Cawsand, off Plymouth, and the Fal, together with relatively 'clean' sites in the Yealm and Torre Sands (Bryan and Gibbs, 1987). This demonstrated that some species (notably members of the Nephtyidae) are useful indicators of sediment contamination. For example, significant relationships exist between concentrations of Ag, Co, Cu, Fe, Pb and, to a lesser extent, Zn in *Nephtys hombergii* and those in surface sediment extracts (Bryan and Gibbs, 1987). Other species, including *Owenia fusiformis, Melinna palmata* and *Tharyx marioni*, though useful for some metals, were less satisfactory all-round bioindicators.

**Table 8. Metals in polychaete worms (µg $g^{-1}$ dw) from Plymouth Sound and other sites in the south west** (data from Bryan and Gibbs, 1987)

***Nephtys hombergii***

| Site | Ag | Cd | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| **Torre Sands ('clean')** | 0.02 | 0.98 | 1.49 | 0.21 | 12.7 | 400 | 3.8 | 2.5 | 3.5 | 260 |
| **Cawsand** | 0.23 | 0.22 | | | 38.5 | 616 | 8.6 | | 4.6 | 178 |
| **Fal (Restronguet -contaminated)** | 3.27 | 0.57 | 3.98 | 2.43 | 2230 | 3260 | 7.5 | 4.7 | 44.7 | 518 |

***Owenia fusiformis***

| Site | Ag | Cu | Fe | Mn | Zn |
|---|---|---|---|---|---|
| **Rame (RM1)** | 0.24 | 11.9 | 341 | 8.5 | 72 |
| **Cawsand** | 0.51 | 32.6 | 352 | 4.3 | 247 |
| **Fal (Place Cove)** | | 526 | 373 | | 430 |

Not surprisingly, concentrations of Ag, Cu, Zn and Pb in *Nepthys* were extremely high (by more than two orders of magnitude for Cu) in parts of the heavily mineralised Fal, compared to those at, for example Cawsand, in Plymouth Sound. In turn, levels at Cawsand display enrichment relative to Torre Sands (for Ag, Cu, Fe, Mn and Pb), though by a relatively small margin (table 8).

The Rame ground was, until recently, used for sewage sludge dumping and disposal of dredged material and though outside the cSAC (just to the south west of Rame Head), has the potential to influence the marine site itself. Unfortunately *Nepthys* were not sampled here by Bryan and Gibbs (1987) though their results for other species such as *Owenia* (table 8) suggest that, compared to the Fal, metal bioavailability at the dumping ground is low in comparison, at least for Cu and Zn.

Cawsand, within Plymouth Sound again appears to represent an intermediate level of contamination.

In the 1980s, a transplant experiment using caged mussels was carried out to study sub-lethal effects of metals along a transect from just off the Plymouth breakwater out to the Eddystone (Johnson and Lack, 1985; figure 6). Cages were deployed along a metal contamination gradient, with concentrations in sediments (as signified by Zn in figure 7 - bottom) generally decreasing off shore, with the exception of a small increase in the area of the sewage sludge dumping ground off Plymouth Sound (Johnson and Lack, 1985; Eagle *et al.,* 1979). Accumulation of Zn in mussels after 60 days generally mirrored this distribution (figure 7 - top) and was highest at the site closest to the shore (within the cSAC, and associated perhaps with influence of metal-rich Tamar sediment). A secondary peak at the disposal ground, outside the cSAC, may have been due to the influence of sewage sludge particles. The importance of sediments, as sources, is supported by the fact that mussels in cages deployed just above the sediment displayed greater responses than those maintained at the surface. Tentative observations of induction of a metallothionein–like protein in caged mussels (a biomarker for metal exposure) also appear to reflect the trends in Zn contamination (figure 7 - middle). Since these observations were made prior to the cessation of sewage sludge dumping it would be useful to conduct similar type surveys using improved metallothionein assays (Langston *et al.,* 2002), and possibly other biomarkers, to gauge the success of legislation on recovery of the site. A similar procedure could be used to evaluate the spatial extent of 'biological responses' throughout the SAC.

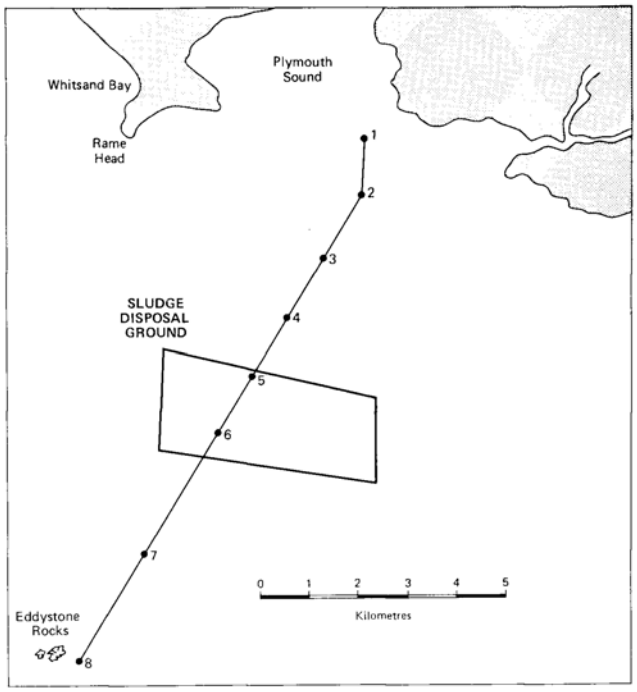



**Figure 6. Map showing positions of mussel transplant and sediment sampling sites off Plymouth** (Johnson and Lack, 1985; reproduced with permission from Elsevier)

Metal concentrations in sediments from Whitsand Bay (offshore, west of the dumpsite), taken in 1995, appear to be scarcely more contaminated with metals than in samples from the central North Sea. Furthermore, there are indications from experimental studies that bioavailability may even be higher at the latter site because the form of metal in the sediment is more labile than in sediments off Plymouth (Langston *et al.,* 1999).

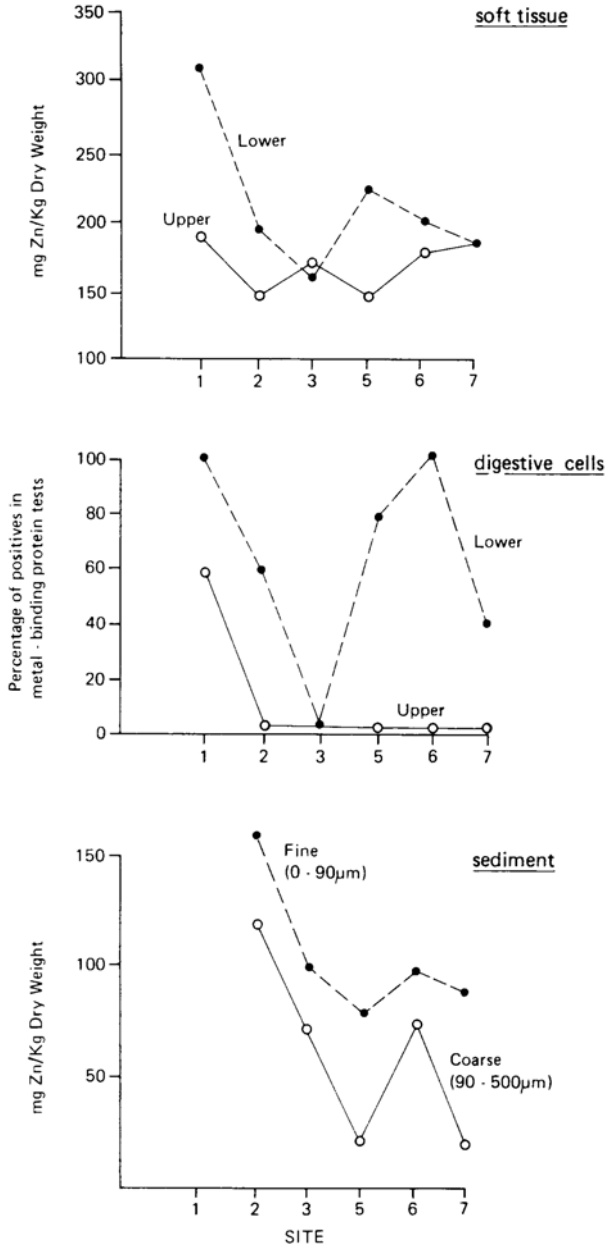



**Figure 7. Zn concentrations in transplanted mussels (top); presence of metal-binding thiolic proteins in transplanted mussels (middle); Zn concentrations in sediment from transplant sites (bottom). (Johnson and Lack, 1985; reproduced with permission from Elsevier)**

In an early attempt to detect possible biological effects of inshore water quality, Stebbing *et al* (1983) tested several responses in the hydroid *Campanularia flexuosa* (specific growth rate, gonozooid frequency and stolon curving frequency) to water samples from the lower Tamar, Plymouth Sound and Cattewater, using Eddystone water as a control. Though restricted to these high salinity waters, tests showed responses in some samples and suggested that Cu and occasionally Cd (though probably not Fe, Mn, Ni, Pb and Zn) may reach concentrations in the lower estuary that could elicit impact. (Experimental studies had previously shown gonozooid production could be stimulated by concentrations of 0.1µg $l^{-1}$ Cu and 0.5µg $l^{-1}$ Cd). Local sources were suspected of initiating effects, however, firm conclusions about the origins of these metals were not possible. Indeed, since the peak in impact occurred in the area of the Devonport dockyard it may well be that other toxicants besides metals could have been responsible for impact. The most obvious of these would appear to be TBT which would probably have been high in the region at the time of sampling (1981).

Such results indicate that a more extensive biomarker type approach may well be useful to visualise responses across the SAC as a whole, and may help to apportion the relative importance of different sources. Assays to test water quality in low salinity regions also need to be considered, since bioavailability may be greatest here.

Reports of metal concentrations in higher organisms associated with the Plymouth Sound cSAC are rare. Results from the National Monitoring programme suggest levels in dabs in the Channel off Plymouth are comparatively low (for example Hg is in the range 0.01-0.02mg $kg^{-1}$ wet wt compared to a maximum permissible level of 0.5mg $kg^{-1}$ in fish products under EC legislation 93/351/EEC). Pb, As and Cd in these samples also appear to be unremarkable compared with those found at other UK sites (MPMMG, 1998). Furthermore, flounder from the Tamar Estuary appear not to concentrate metals to the same extent as some of the invertebrate species described above.

These conclusions tend to be backed up by a review of EA/CEFAS fish data between 1995-1999 carried out by CEFAS (Allen *et al*, 1995). Table 9 summarises these results. However, it should be noted that these summary statistics are derived from a small sample size (n=3-6) and are from unspecified species and tissues. Clearly more thorough monitoring is needed to provide a better risk assessment.

**Table 9. Summary of EA/CEFAS metals data for fish (µg $g^{-1}$ wet weight), Plymouth Sound and Estuaries 1995-99.** (from Allen *et al.,* 2000).

| | **As** | **Cd** | **Cu** | **Hg** | **Pb** | **Zn** |
|---|---|---|---|---|---|---|
| 25th percentile | 2.8 | 0.25 | 0.31 | 0.04 | 0.2 | 6.3 |
| **median** | **2.9** | **0.3** | **10.31** | **0.05** | **0.2** | **20.8** |
| 75th percentile | 3.15 | 0.3 | 20.0 | 0.05 | 0.2 | 35.8 |

### 5.1.2. TBT

Gibbs and Langston (1994) and Langston *et al* (1994a) report on a number studies in Plymouth Sound and the Tamar Estuary, conducted at the Citadel Hill Laboratory of the MBA. These provide an early indication of the success of moves in the late 1980s to reduce contamination; underpin understanding and predictions of the behaviour of TBT in the estuary, particularly the role of sediments; examine impact on neogastropods (imposex). These studies are summarised below.

*Effect of legislation and remediation on TBT contamination*

Prior to 1987, principal TBT sources were assumed to include moored leisure vessels and the naval dockyard, situated toward the mouth of the estuary (figure 8). TBT data for individual sites in June 1986 and September 1988 are compared with 1991 values in table 10. Based on this limited data set there have been large reductions in TBT at the Torpoint site, opposite to the naval dockyard (previously the most contaminated site). Reductions at other sites, though significant, were much less pronounced. It would seem that the combination of national legislation in 1987 and stopping TBT usage on leisure vessels (<25m), combined with the introduction of containment procedures at the naval base in 1988 have been successful, to a large extent, in reducing inputs to the estuary.

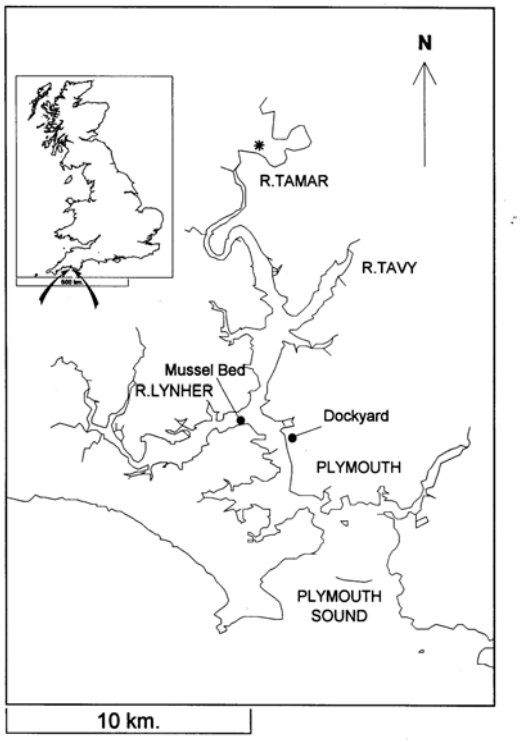



**Figure 8. Map of Tamar Estuary and Plymouth Sound showing position of naval dockyard, mussel bed and approximate limit of saline intrusion (*) in TBT surveys.**

**Table 10. A comparison of TBT in Tamar Estuary waters (0.5m), 1986, 1988 and 1991.**

| | TBT in water ng Sn $l^{-1}$ | | | | |
|---|---|---|---|---|---|
| | June 1986* | Sept 1988 | April 1991 | June 1991 | Oct 1991 |
| Cargreen | 9 | 2.4 | 1.2 | 6.1 | 0.7 |
| Saltash | 10 | 2.2 | 7.0 | 1.9 | 1.0 |
| Torpoint | 112** | 5.6 | 4.7 | 1.6 | 0.8 |

* from Harris *et al* 1991 ** average subsurface values.

Further evidence for this trend in contamination comes from a time series of measurements of TBT in Plymouth Sound waters and TBT (and DBT) residues in mussels, *Mytilus edulis*, sampled from a population at the confluence of the Lynher/Tamar Estuaries opposite Devonport dockyard (see figure 8. for locations), established in the 1980s. In addition to assessment of the benefits of TBT restrictions, the study assesses whether mussel residue data might be used as an integrator of levels of dissolved TBT (Gibbs and Langston, 1994; Page, 1995).

Data for 1988, the first year in which legislation was fully implemented, revealed a pronounced seasonal cycle in TBT residues in mussels, with a peak in late spring - early summer (figure 9A). This may have been due to seasonally-reduced freshwater flow in summer months (effectively concentrating TBT in the estuary), combined with a continuing influence of peak activity of leisure vessels (some of which would still have been painted with TBT-based antifoulants) at that time of year. Since naval dockyard activity was year-round, its influence on seasonal patterns was probably not great. Further summer maxima in TBT residues in mussels were observed in 1989 and, to a lesser extent, in 1990 and 1991 samples, though these appear to have been super-imposed on an overall temporal reduction in baseline concentrations. The data for mussels therefore resembles a damped oscillation function (see better in figure 10).

For DBT in mussels (figure 9B), seasonal trends were somewhat less obvious, and if anything were out of synchrony with TBT (figure 9A), with minimum values tending to occur during summer months. Generally however there was a significant trend with time towards lower levels for both DBT and TBT.

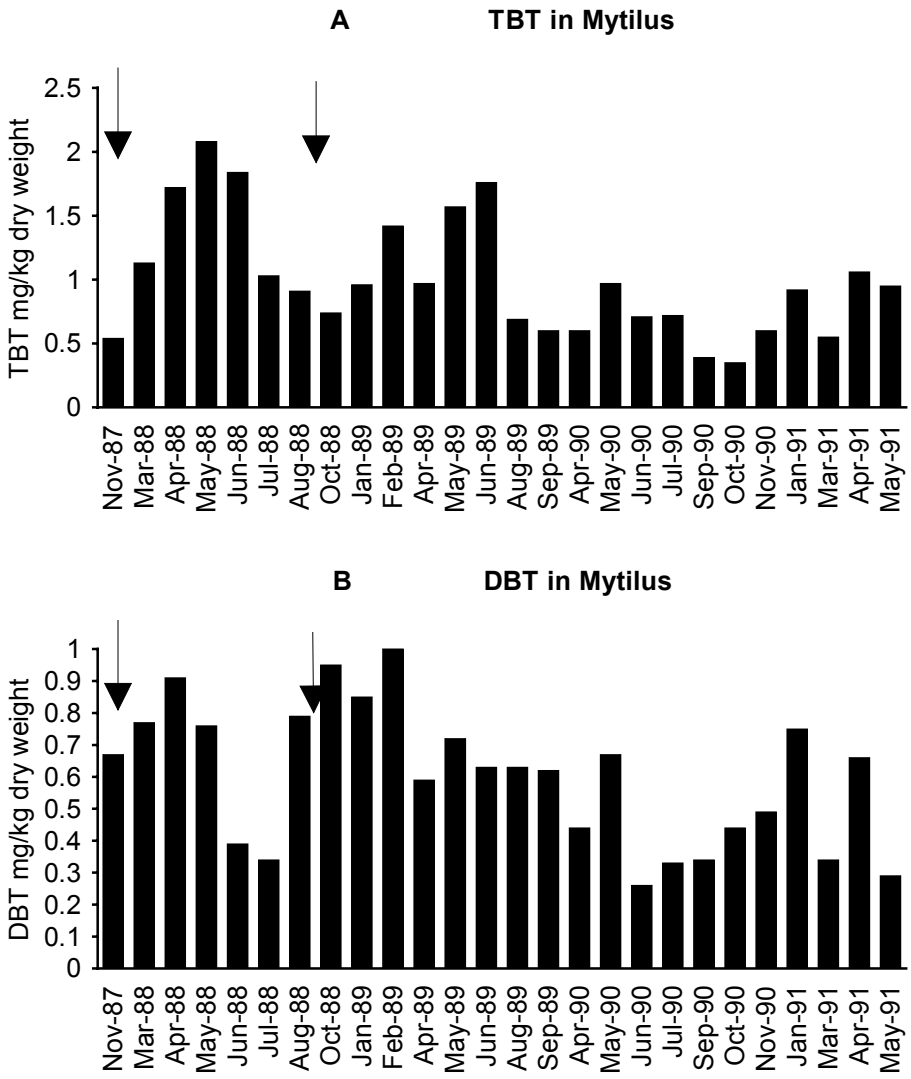
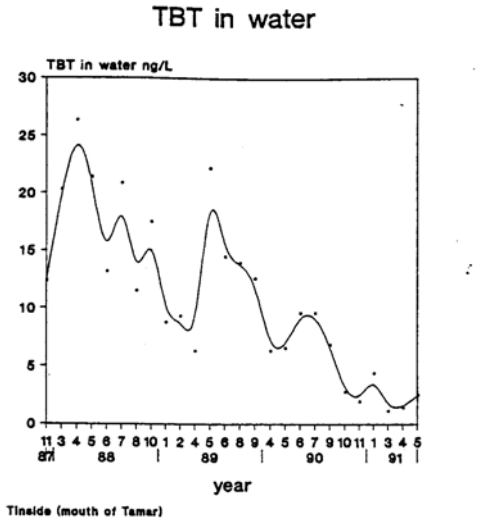



**Figure 9. TBT (A) and DBT (B) in mussels, Mytilus edulis, Tamar Estuary. Arrows indicate national legislation on TBT (1987) and introduction of Dockyard containment procedures (1988). Organotin values expressed as TBT or DBT.**

The pattern of TBT 'decay' in water (measured at the mouth of the Tamar), though of much shorter half-time (12.5 months), resembles fairly closely that of TBT in mussels (figure 10). The correlation between the two ($r = 0.5884$, $P < 0.005$) suggests, therefore, that *Mytilus* may indeed be of value as a means of determining and predicting averaged data for TBT in the water column.



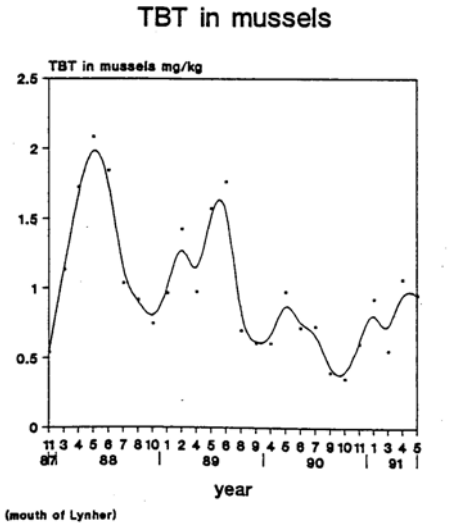




**Figure 10. Seasonal trends in TBT concentrations in mussels and water, Tamar Estuary/Plymouth Sound. (from Gibbs and Langston, 1994)**

*Estuarine behaviour and modelling of TBT (Tamar)*

Clearly, significant reductions in dissolved TBT took place as a combined result of legislation and improved containment procedures introduced in the late 1980s. Following the initial success of these measures, studies focused on the subsequent fate of TBT and the issue of 'diffuse sources', the hypothesis being that concentrations and distributions of TBT would probably be governed by particle water interactions and internal cycling within the estuary, rather than by the inputs from dockyards and leisure vessels. This was backed up by observations that, in the early 1990s, peak TBT concentrations in water (still exceeding the EQS by ten-fold

on occasions) occurred toward the head of the estuary, apparently remote from previous sources towards the mouth.

The primary objective was to answer questions about benthic-pelagic fluxes and partitioning and bioavailability of TBT in particulate-bound form, so that a complete TBT budget for the estuary could be estimated and the long-term toxicological risks to the biota (especially benthic infauna) assessed (Gibbs and Langston, 1994)

A combination of field observations and laboratory experiments with $^{14}$C-TBT were used to show that removal of TBT to particulates results in sediment concentrations between $10^2$-$10^5$ times higher than in water (=partition coefficient, $K_d$). Such partitioning is reversible and therefore, in the event of declining inputs, release back to the water occurs. Partitioning, and hence desorption, was shown to be dependent on contamination level, suspended solid concentration salinity and related pH changes (Langston and Pope, 1995). Sediment characteristics also modify adsorption/ desorption: desorption is least likely to occur from organic-rich silts in sheltered areas but may be rapid in well-scoured, sandy sites. The association of TBT with particulate material, and the presence of paint particles themselves, may delay recovery due to slow degradation rates compared with overlying water, representing an ongoing environmental risk.

Study of the above variables was used to refine a PC-based model (EcoS) and hence to provide a more realistic simulation of TBT behaviour in estuaries following TBT legislation in 1987. Profiles of TBT in the Tamar Estuary were used to estimate transport mechanisms and rates, and to provide validation.

As described for metals in the previous section, significant changes in reactivity of contaminants often occur at very low salinities near the freshwater-seawater interface (FSI), coinciding, in macro-tidal estuaries such as the Tamar, with a region of maximum turbidity caused by tidal resuspension of particles at the salt-wedge. On several occasions, in 1991 TBT surveys in water and sediment were carried out in the along the length of the Tamar Estuary from Plymouth Sound upstream, almost to the weir (see map, figure 8). Parameters likely to control TBT behaviour (e.g. pH, temperature, salinity, suspended solids) and measurements of major sediment components anticipated to affect the adsorption/desorption behaviour of TBT (e.g. readily-extractable Fe and Mn and particulate organic matter) were also taken.

TBT profiles in water exhibited variability, spatially and temporally, though some consistent patterns emerged. Data for one transect (15/10/91) are shown in figure 11. Notable features illustrated in figure 11 are: i) the virtual absence of a fresh water input for TBT and ii) A distinct maximum at very low salinities i.e. at the freshwater-brackish water interface (FBI) followed by progressively decreasing concentrations of TBT in an downstream direction in the estuary (with perhaps a slight upturn towards the mouth).

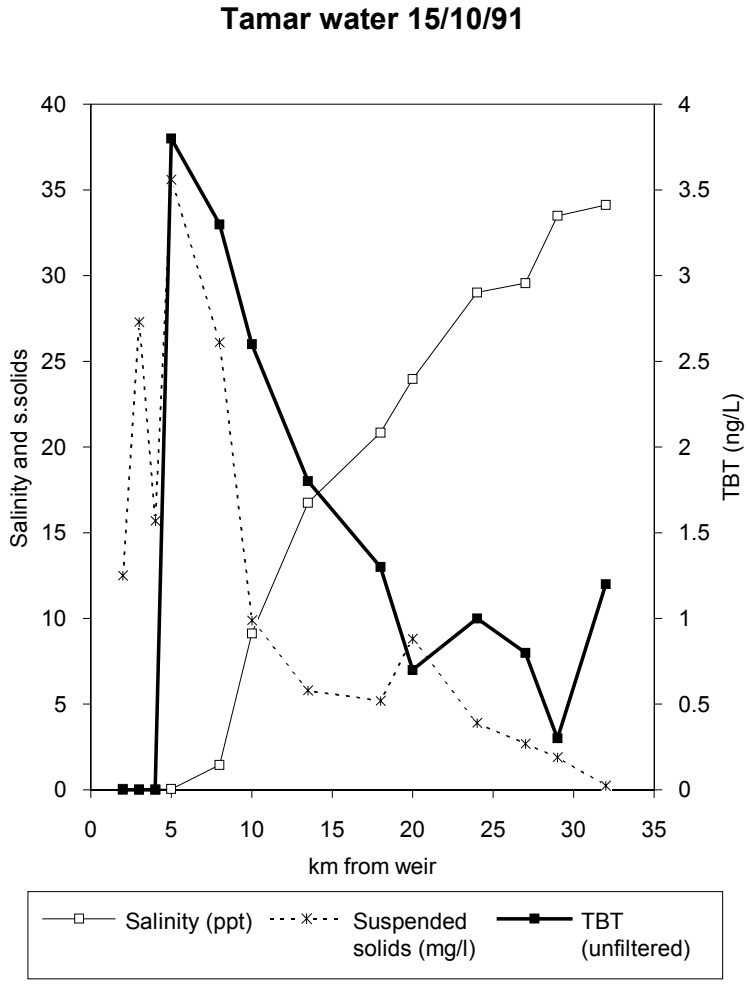



**Figure 11. TBT concentrations, salinity and suspended solids in the water column of the Tamar Estuary, 15th October 1991.**

Since there are no obvious inputs from riverine sources it is assumed that the origins of organotins in the Tamar are (or were) the dockyards, boatyards and marinas situated at the mouth of the estuary (from 24km downstream). The type of profile exhibited for TBT in the Tamar must therefore be generated internally by interactions taking place in the estuary, involving transport upstream, subsequently modified by transfer and remobilisation of TBT from sediments.

TBT adsorption is greatest in freshwater (characteristic of metal cations), decreases at low-intermediate salinities, and increases again at high salinities (characteristic of hydrophobic organics) (Langston and Pope 1995). Thus, release of TBT from tidally-resuspended sediment particles (perhaps supplemented by exchange processes within benthic sediments) would be expected to occur predominantly at the head of the estuary, consistent with the profile in figure 11. It has been calculated that concentrations of sediment-bound TBT present in the estuary could certainly account for part, if not all of the maximum concentrations released into the water column at

the turbidity maximum. Maintenance of peak TBT levels at the turbidity maximum can be envisaged, primarily, as a continuous balance between recruitment from and deposition in estuarine sediments. This advective process would seem a more effective means of transferring TBT from the sediment to the water column than pore-water diffusion alone. An input of TBT at the head of the estuary cannot be ruled out though no additional sources have been identified. One other possible explanation for the retention of elevated levels of TBT in the water column upstream is a high level of dissolved organic matter (complexes with TBT). The source of this DOM may be natural or sewage-derived. However, as DOM is inversely related to turbidity (Miller 1999, see section 5.2.1) the siting of the TBT peak at the turbidity maximum makes DOM an unlikely prime component in determining TBT distribution. Further work is needed to quantify the relative importance of these mechanisms

The type of reactivity exhibited by TBT in the Tamar thus appears similar to a number of other contaminants and is consistent with a highly dynamic, internally cyclic, suspended sediment system (Bale *et al*, 1985, Uncles *et al*, 1985). Tidally resuspendable sediment is net transported to the head of the estuary by ebb-flood tidal asymmetry. Resuspendable sediment continuously accumulates in the upper estuary turbidity maximum zone at the expense of mid- estuarine material. The associated upstream flux of resuspendable sediment particles provides a continuously renewed supply of particulate material, at least under summer conditions, and hence provides a mechanism for TBT transport up the estuary. In winter much of the sediment which has accumulated at the head of the estuary is subsequently flushed downstream to recharge the mid-estuarine region and the internal route for cycling within the estuary is complete.

It should also be noted that these TBT surveys were conducted a decade ago and in the spring-autumn period when freshwater run-off has been low-medium, i.e. relatively stable conditions. Even under these conditions the profiles for TBT are somewhat variable due, probably, to factors related to oscillations in spring/neap tidal energy inputs. Climate extremes would perhaps be expected to have an even greater influence on the TBT profile, and future studies on TBT behaviour should incorporate sampling under winter flow conditions.

The two profiles of TBT (and DBT) in benthic sediments from the Tamar (figure 12), confirm the presence of TBT along the length of the estuary, transported upstream away from the major sources at the mouth. It is likely that differences between the two sets of data are determined by the seasonal changes in sediment behaviour described above. Higher TBT values in October samples (relative to April), particularly at upstream sites, may reflect the net transport of particulates in that direction during the drier summer conditions. In contrast, the lower values for April samples (nb at the head of the estuary) could be a reflection of the post-winter situation, following high run-off conditions and associated scouring of sediments towards, and out of, the mouth. Thus although April 1991 sediments have lower TBT levels ($m=0.008 \pm 0.005 \mu g\ g^{-1}$) than in the following October ($m=0.023 \pm 0.008\ \mu g\ g^{-1}$) these changes may be a consequence of physical processes and do not necessarily imply an increase in inputs to the estuary. It is also interesting to note that October 1991 sediment values are virtually identical to samples collected in October 1988

(m=0.024 ± 0.005µg $g^{-1}$). Significant (P<0.01, <0.05) correlations between TBT and organic content were found, implying that organic coatings (rather than Fe/Mn oxyhydroxides) dominate partitioning behaviour (see also Langston and Pope, 1995).

DBT was present at roughly similar concentrations as TBT in Tamar sediments (figure 12B) and was highest in mid-estuary. DBT levels in sediments changed little between Oct. 1988 (0.012 ± 0.003 µg $g^{-1}$) and Oct. 1991 (0.011 ± 0.005 µg $g^{-1}$).

The similarity in organotin values in 1988 and 1991 implies that, overall, steady-state conditions were maintained in Tamar sediments (i.e. inputs matched losses) during the period. This is in contrast with TBT concentrations in seawater in Plymouth Sound which declined consistently during the same period, following legislation in 1987 (figure 10).

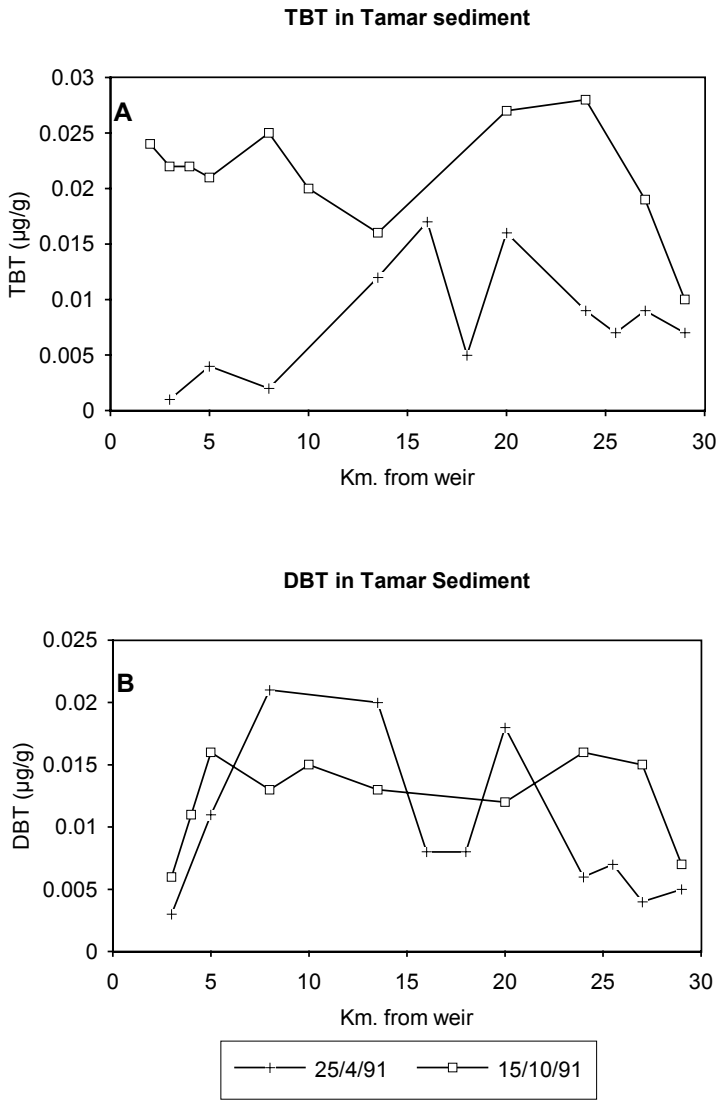



**Figure 12. TBT (A) and DBT (B) concentrations in the sediment of the Tamar Estuary, 25th April 1991 and 15th October 1991.**

*Estuarine simulations of TBT*

In order to comment on the overall TBT budget in the Tamar Estuary, and the prognosis for recovery, laboratory partitioning, leaching and persistence studies and field data were used to fine-tune the estuarine simulation shell, EcoS (Gibbs and Langston, 1994). The model used is similar to that described in general terms by Harris *et al.* (1991).

For the purpose of modelling a half-life of 20 days was set for TBT in the presence of suspended particulates. Degradation rates in unmixed benthic sediments are much slower (approaching zero in anoxic conditions). With a small input of TBT (0.3 micrograms/s) to the estuary the simulation gave realistic values for ratios between dissolved and sedimented TBT, and between DBT and TBT in the sediment. This allowed sensible allocation of losses and reservoirs of TBT and DBT.

Figure 13 shows the calculated losses of TBT (as a proportion of input) for a simulation of conditions in the Tamar for 1991. Under winter conditions of high fresh water flow, losses by flushing across the mouth of the estuary tend to predominate, but under low-flow conditions in summer, degradation losses, enhanced by a more marked turbidity maximum, far exceed the reduced flux of TBT to the sea.

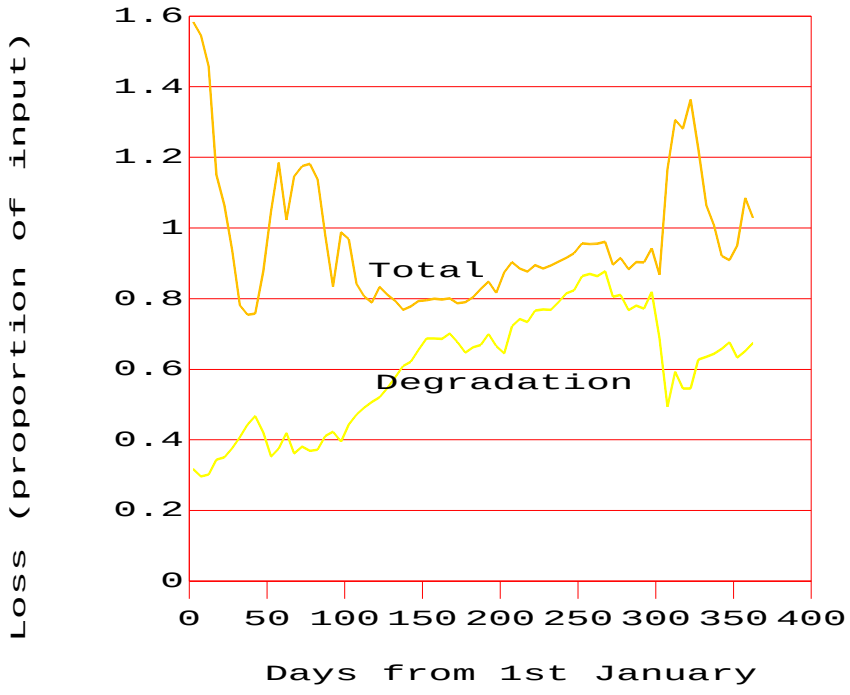



**Figure 13. Losses of TBT from the Tamar Estuary during 1991, according to the simulation described in the text. The lower line indicates degradation to DBT; the upper line includes losses from the mouth.** (From Gibbs and Langston, 1994)

As a result of degradation, rather more than half of the tin originally input to the estuary as TBT is lost from it as DBT (figure 14).

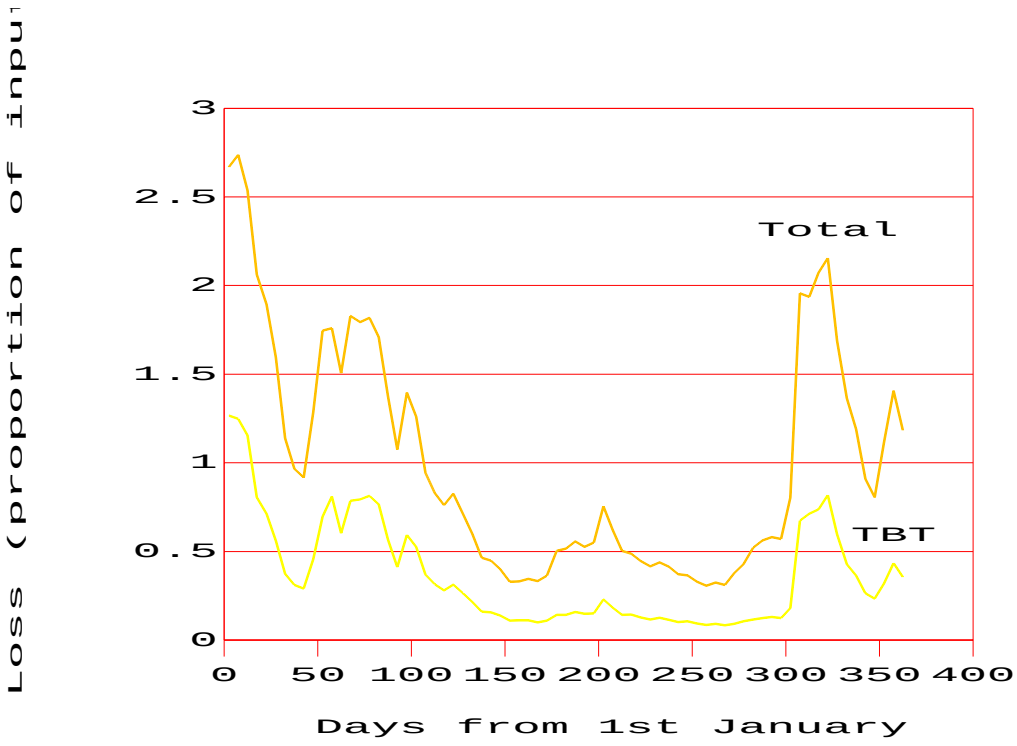



**Figure 14. Losses of tin from the Tamar Estuary during 1991, according to the simulation described in the text. The lower line indicates losses of TBT, largely across the mouth, the upper line includes also losses of DBT.**

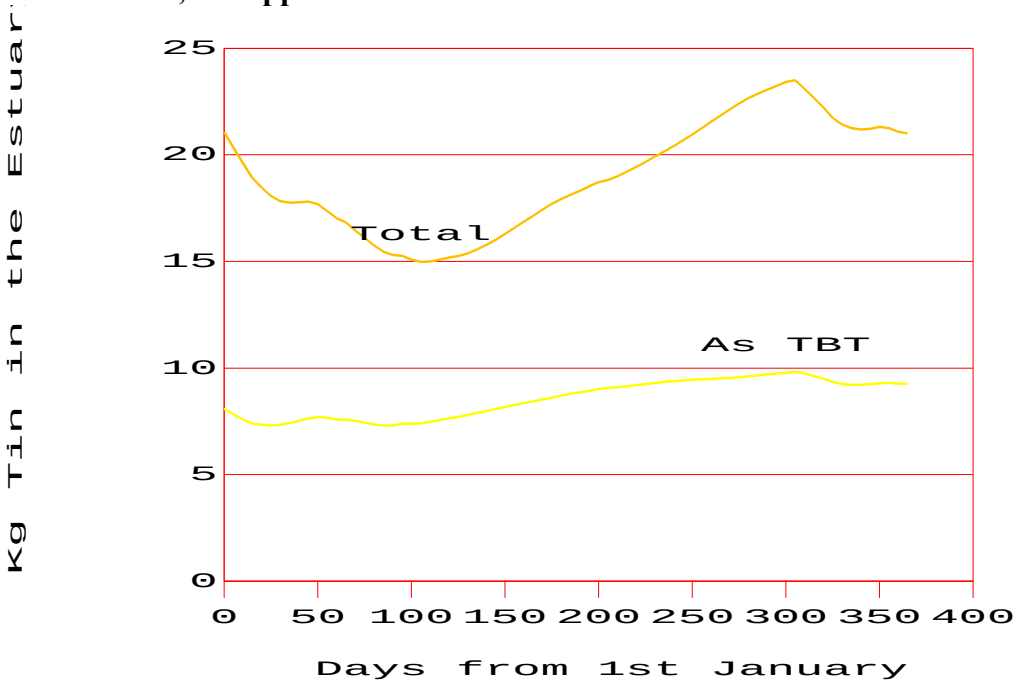



**Figure 15. Variation in butyl tins in the Tamar Estuary during 1991. The lower line indicates TBT, the upper TBT plus DBT. The major portion of both occurs in the bed sediment.**

Simulations using ECoS confirm the approach of steady-state conditions for TBT in the Tamar during 1991 (figure 15).

These simulations imply that TBT losses would be offset by relatively small inputs of the order of 0.3µg TBT/second, which should be compared with the input of perhaps 1 mg/second of TBT thought to have entered the estuary prior to the 1987 legislation. Clearly, legislation and DML's containment practices have reduced new inputs: however, the estuarine process involved, particularly the persistence and cycling of sediment-bound TBT, may result in relatively slow recovery. These simulations therefore confirm trends observed in sediments i.e. that, in 1991, the losses were balanced by inputs to the estuary, resulting in approximately steady-state conditions. This evaluation should now be reassessed, using recent data.

Bioturbation increases the rate of TBT release to overlying water. This has been demonstrated with Tamar (St. Johns Lake) sediment spiked with $^{14}$C-TBT (0.3 mg kg$^{-1}$ as Sn) seeded with ragworm (*Nereis diversicolor*) or clams (*Scrobicularia plana*) where of TBT losses to overlying water increased by 2-3 fold relative to diffusive losses from undisturbed sediments (Gibbs and Langston, 1994). The actions of these particular organisms may not represent a significant influence on the total TBT budget of the estuary though it is possible that other species (e.g. burrowing shrimps) cause more significant releases of TBT from sediments and this should be tested.

The presence of TBT in sediments therefore does not necessarily herald its indefinite removal out of harms-way: remobilisation by physical or biological process is possible. Furthermore, studies have also shown that sediments may in fact be the principle vector for bioaccumulation in species such as the clam *S. plana* (Langston and Burt, 1991). Typical TBT levels found in the Tamar in the above surveys do not appear to represent an acute threat, however a broader discussion, based on additional unpublished data from other sites within the SAC is presented in sections 7 and 8 of this report.

**Imposex in gastropods: dog whelk *Nucella lapillus* and netted whelk *Nassarius (=Hinia) reticulatus***

Consequences of the early endocrine-disrupting effects of TBT on gastropod populations in Plymouth Sound, and recovery following 1987 legislation, fall into two categories originating from studies at the MBA

The first, concerning surveillance of imposex in *N. lapillus* populations between 1985-1993 (reported in Gibbs and Langston, 1994) indicated post-ban improvements to the breeding capacity of partially-sterilised populations. Nevertheless, imposex was still prevalent in 1993, even in areas of low boating activity; visibly-unaffected females were still a rarity; and significant recolonisation of areas denuded of *N. lapillus* had yet to occur.

Secondly, information on the use of *Nassarius (=Hinia) reticulatus* as an alternative indicator of TBT pollution in Plymouth Sound, before and after TBT restrictions, has been described by Bryan *et al* (1993) and Langston *et al* (1994a).

Details of these surveys on 'imposex' (the imposition of male characters on females) are provided below.

*Nucella lapillus:* It was a study of *N. lapillus* in Plymouth Sound in the late 1960's by Blaber (1970) that first indicated the presence of a penis in female dogwhelks, though it was not until the mid 1980's that the link between imposex and TBT was first demonstrated by Bryan et al (1986). At that time the incidence of imposex in female dog-whelks was virtually 100%. Monitoring of TBT levels in the water of Plymouth Sound and also of imposex levels in populations of *N. lapillus* at selected sites was begun in 1985/86 i.e. before 1987 legislation on TBT.

The RPSI (ratio of female penis size: male penis size) in front of the MBA Laboratory, Plymouth Hoe, in 1985 was 67% compared with a projected value of less than 5% in 1969-70 (Bryan *et al* 1986). Dog-whelks from other sites around Plymouth Sound exhibited degrees of imposex (RPSI) ranging from 64% at Mount Edgcumbe, 55% on Drakes Island, and 48% at Batten Bay decreasing to 23% at Renney Rocks near the Mew Stone and 15% at Rame Head (more open coastal sites).

TBT concentrations in water from Batten Bay and at Renney Rocks are illustrated in figure 16. During the period 1990-93, TBT values for Batten Bay show a general amelioration when compared to the previous three-year period. Since October 1990, concentrations have generally remained below 5ng $l^{-1}$. Over the same period, Renney Rocks values show the same downward trend, generally remaining below 2ng $l^{-1}$ but reaching 4-5ng $l^{-1}$ on two occasions. Overall, the EQS of 2ng $l^{-1}$ has been generally exceeded at Batten Bay but has been met at Renney Rocks.

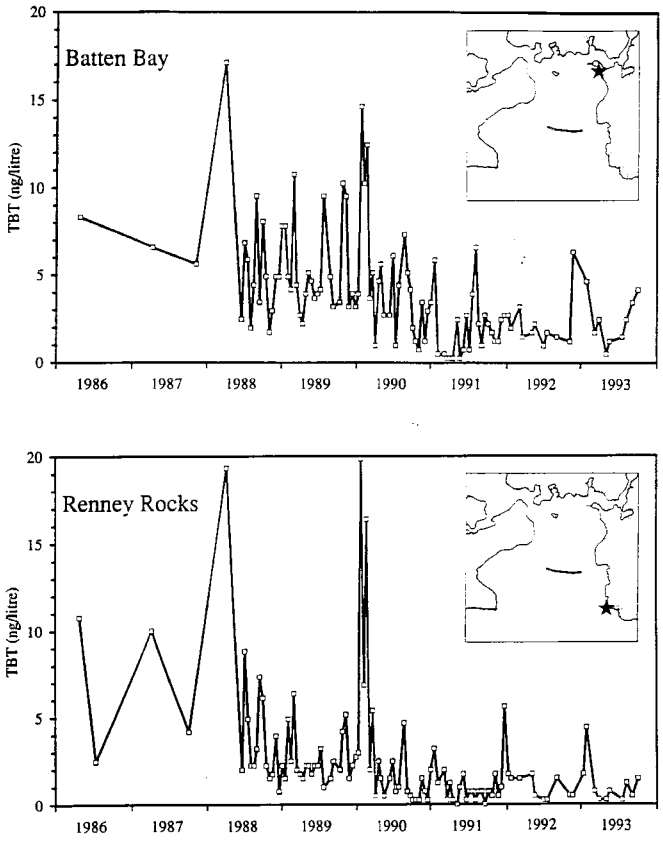



**Figure 16. Plymouth Sound. TBT concentrations in water at Batten Bay (top) and Renny Rocks (bottom).**

The *Nucella* population at Renney Rocks was sampled on an annual basis between 1986 and 1993. Adult penis length dropped from the range of 2.6-2.9 mm in '86-'90 to 2.1-2.2 mm in '92-'93. Similarly, subadult penis length has declined from 2.2-2.4 mm to 1.7-1.9 mm. These data accord with the general observation of an improvement in the breeding condition of this population. Thus, frequencies of Vas Deferens Sequence stages (VDS – see Gibbs et al., 1987) in annual samples of adult females from the Renney Rocks population from 1986 to 1993 confirm a general trend of improvement in the water quality. The imposex level in the late 1980s had advanced to the stage where the survival of the population was in doubt, *i.e.* some 70-80% of the females were sterilised (VDS stages 5 and 6). However, the effect of the improvement in water quality (figure 16) on the breeding capacity of this population has been quite dramatic. A sharp drop in the proportion of sterilised females to below 50% was noted in 1991, further declining to about 30% in 1992 and to below 10% in 1993. A corresponding and significant decrease in the concentrations of TBT in the body tissues of females was also detected (figure 17). Despite improvements, there were, at the time few, visibly-unaffected females and no unequivocal evidence for recolonisation of areas denuded of *N. lapillus* along the inner shores of Plymouth Sound from Edgcumbe to Batten Bay. The latter bay is in close proximity to a small enclave at Jennycliff (0.5km to the south) but no detectable immigration appears to have occurred.

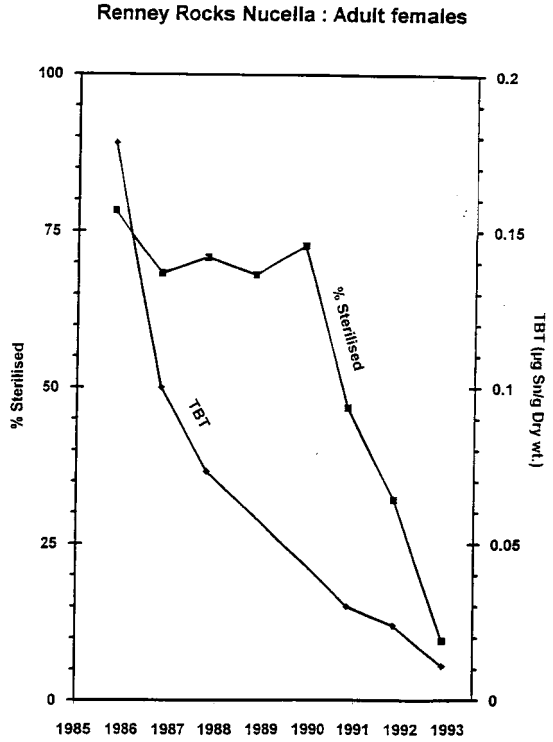



**Figure 17. *Nucella lapillus:* % sterilisation in relation to concentrations of TBT in body tissues of females in the Renney Rocks population 1983-1993.**

There is little information on the community-level effect of TBT impact though experimental removal of dog-whelks from an area of shore (simulating severe imposex) has been shown to increase prey items including limpets and, to a lesser extent, mussels and barnacles. The increase in limpets subsequently led to a decline in macroalgae (Spence *et al.,* 1990).

*Nassarius (Hinia) reticulatus*: Studies on dog-whelk*,* above, showed that, sterilization of females by TBT-induced imposex, had caused populations to decline in Plymouth Sound and in estuaries including the Yealm (Bryan *et al*., 1986; Gibbs & Bryan, 1986; Gibbs and Langston, 1994). Imposex was also found in the netted whelk *Nassarius (Hinia) reticulatus* but did not appear to cause sterilization of females. As a result, this snail was investigated as a possible long-term (1985-1992) indicator of TBT pollution in localities where *N. lapillus* had been eliminated (Bryan et al 1993; Langston *et al*., 1994a). Intersite comparisons of imposex were based on the relative penis length (RPL) index (female length/male length x 100) or, at individual sites, temporal changes were expressed in terms of penis lengths in females. Sampling sites within Plymouth Sound SAC are shown in figure 18.

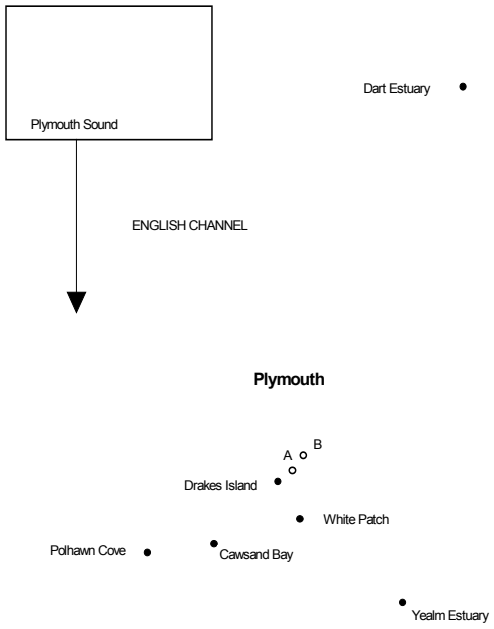



**Figure 18. Maps showing positions of *Nassarius reticulatus* sampling sites (•) in Plymouth Sound and the Yealm estuaries. Also marked are TBT Water sampling sites (o) in Plymouth Sound at (A) Mayflower Steps and (B) Tinside.**

*Drakes Island*, opposite the Millbay ferryport and downstream of the naval dockyard and several marinas (figure 18), was the most TBT-contaminated site in Plymouth Sound. Concentrations of TBT in water and *N. reticulatus* tissues are shown in figure

19. Following the introduction of TBT restrictions in 1987, concentrations in seawater and tissues declined slowly. In part this is may be attributable to the continued presence of TBT antifouling paints on large ships to which the regulations do not apply. In the water, TBT levels were generally higher in summer and lower in winter reflecting seasonal boating activity. This seasonality was seen clearly in water samples from nearby sites at Tinside and Mayflower Steps (see Tinside data shown earlier in figure10).
Compared with the TBT data (tissues and water), post-1987 changes in female penis lengths in the Drakes Island *Nassarius* population were comparatively modest (figure 19).

*Cawsand Bay* lies to the west of the main shipping channel and yachts are moored there in the summer (figure 18). Water samples were not collected frequently and variations in TBT concentration were erratic: the mean 1986-87 concentration was 7.2 ng Sn/l compared with a 1988-93 mean of 2.4 ng Sn/l. Pre-1987 tissue TBT concentrations were roughly half the Drake's Island values and declined appreciably following the restrictions (figure 19). The penis-length data (figure 19) displayed greater variation than at the Drake's Island sites. From 1987 onwards there were smaller fluctuations but no significant decline in female penis length was observed.

Recently (January 2002) the grounding of the *MV Willy* on the western coast of the Sound resulted in locally high levels (~25ng Sn $l^{-1}$) in Cawsand Bay, illustrating that the influence of individual ships close to the shore could (still) contribute to observed fluctuations in response.

*White Patch* lies to the east of the main shipping channel (figure 18) and was less contaminated than the Drakes Island site. Pre-1987 tissue concentrations were not measured but values in 1988 and 1989 were about two-thirds those of Drake's Island animals. Levels at the two sites were comparable in 1992. After 1987, penis lengths of White Patch females declined significantly (figure 19).

*Polhawn Cove* lies just outside the cSAC, near the western entrance to Plymouth Sound (figure 18) and was the least TBT contaminated site studied. Some exposure is inevitable, since this entrance to the Sound is used by large ships still treated with TBT antifouling paints. In water samples collected from the shore, the pre-1987 mean TBT concentration was 1.6 ng Sn $l^{-1}$ and the post-1987 mean (1988-93) was 0.9 ng Sn $l^{-1}$. No clear trend emerged from TBT analyses of the tissues (figure 19). Similarly, the female penis-length data displayed no obvious trends (figure 19). In some samples most females lacked a penis, but in other samples about two-thirds bore a small penis. These results suggest that initiation of penis development in females occurs at a seawater TBT concentration of roughly 1 ng Sn $l^{-1.}$

*Yealm Estuary* (figure 18) shelters many small boats and the small International Coatings Laboratory and test rafts. One to two km upstream of the *N. reticulatus* site the mean seawater TBT concentration for the 3 months following the TBT ban in 1987 was 26 ng Sn $l^{-1}$. In the summer of 1989 lower concentrations of 4 and 6 ng Sn $l^{-1}$ were observed and by 1993 values were around 1 ng Sn $l^{-1}$. In females the tissue TBT concentration in January 1985 was 238 ng Sn $g^{-1}$ but 8 years later had fallen to 8

ng Sn $g^{-1}$. Penis lengths in females also declined significantly after 1987 though at slower rates.

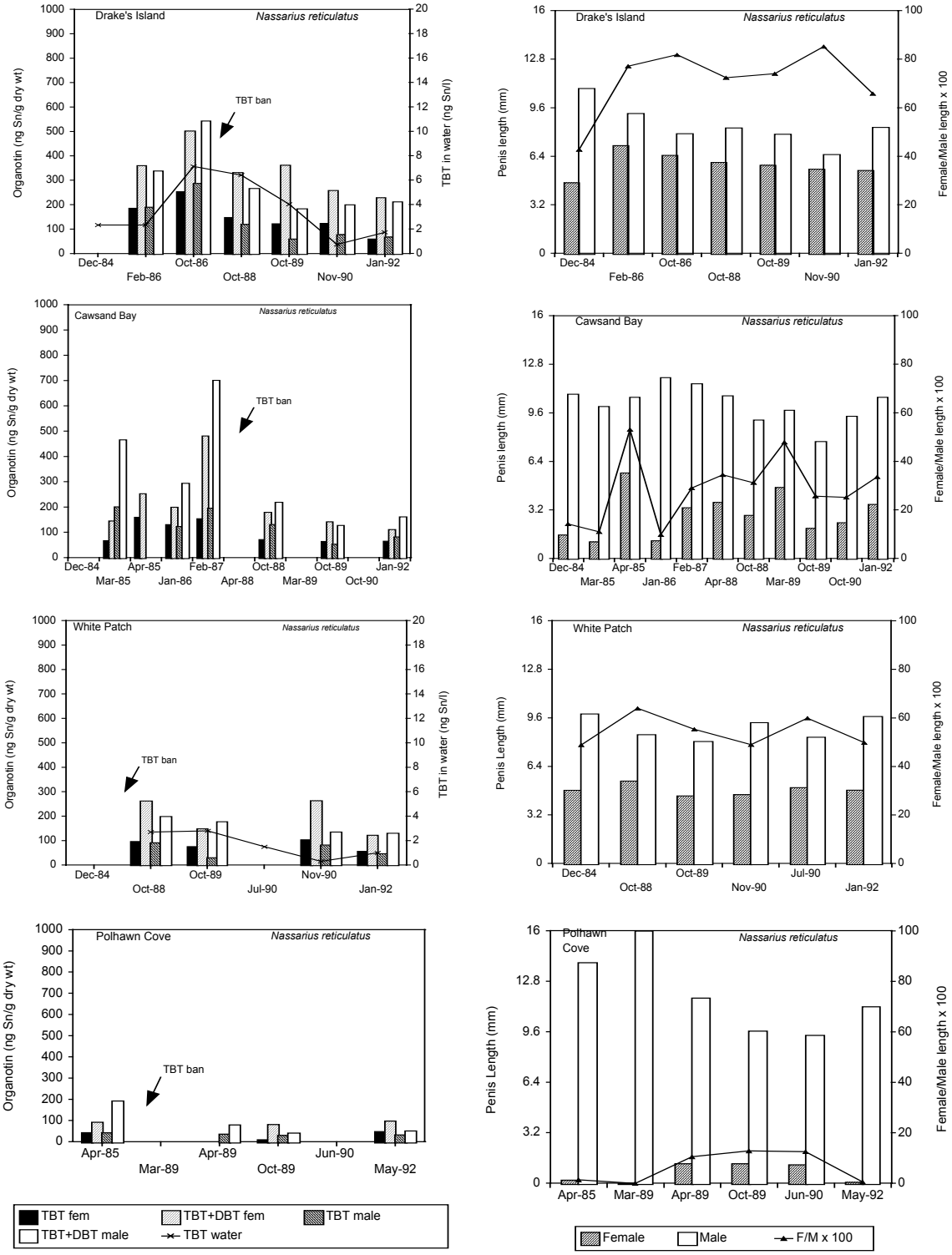



**Figure 19.** ***Nassarius (=Hinia) reticulatus*****: TBT and TBT+DBT data for both sexes compared with penis lengths and penis length ratios at sites in Plymouth Sound.**

*N. reticulatus* appears to be a useful alternative to *N. lapillus* as an imposex-based TBT indicator at contaminated sites in Plymouth Sound. Concentrations in water and tissues at some of the more polluted sites decreased by factors of 5 to 10 times between 1987 and 1992, following TBT restrictions. However, the intensity of imposex in *Nassarius* declined very slowly. This was attributed to the longevity of the snails, the limited reversibility of penis length and the limited recruitment of less-affected females.

Another alternative to *Nucella* and *Nassarius* in monitoring TBT impact is the European Sting winkle *Ocenebra erinacea.* Imposex was initially thought to be initiated at ~ 1 ng $l^{-1}$ TBT – similar to levels triggering effects in *Nucella* (Gibbs *et al* 1990). Observations made on populations in Plymouth Sound between 1986 and 1988 indicate the degree of impact (measured as RPSI) at between 36% (Edgcumbe) and 50% (Batten Bay). More recently it has been suggested that imposex in *Ocenebra* could be initiated by concentrations as low as 0.1 ng TBT (as Sn) $l^{-1}$ making it the most sensitive species known.

Apart from these few neogastropod species it is not known which other taxa have been affected by TBT in Plymouth Sound and its estuaries, though molluscs and possibly crustaceans would be anticipated to have been most at risk. Recovery of marine communities from TBT pollution has not been adequately studied though indications are that this may take at least a decade, even where TBT levels have returned to near zero. A limited 're-survey' of dog whelk populations in the south west was conducted by the Agency in 1998 (Geileskey, 2000), though not exactly at the same sites as used previously by MBA (Bryan *et al*., 1986). The more recent study indicated continued reductions in imposex levels at open coastal sites on the edge of Plymouth Sound (RPS at Wembury and Bovisand <1%). However in 1998, populations of *Nucella* were absent from Stonehouse and had been eliminated from Cremyll, at the mouth of the Tamar, where previously individuals (with high RPS scores) had been found (Bryan *et al*., 1986). This reinforces the concept that, despite general improvements in water quality, there may be a considerable delay factor before biota respond. Continuation of time-series surveys would be timely, now, to verify and assess the extent and timescales of improvement that have occurred as a result of existing legislation, and as baselines prior to the anticipated global ban in 2003.

*Current sources of antifoulants, including TBT*

Devonport Dockyard, Millbay Docks, Cattedown Wharves and assorted marinas around the SAC are intuitively seen as the major users of antifouling compounds, including, until recently TBT. It is thought that the Royal Navy no longer applies this type of paint though it may have to remove TBT coatings from previous treatments. Following the introduction of the EQS value of 2ng $l^{-1}$ TBT in 1987, MOD were involved in considerable efforts to control and monitor discharges from their dockyards (Allison and Sawyer, 1987). Containment of TBT pollution (in the Tamar), to an acceptable level, involves collection of washdown material in bowsers and transportation to the Chelson Meadow disposal site alongside the Plym Estuary. TBT levels in this material appear to be of the order of 210-880 µg $l^{-1}$ with typical production of 100,000 – 200,000 gallons (Collier 1992). If correct this represents

disposal of between 100 and 700g TBT for each washdown (between 5-10 times per year). This is filtered in gravel-based waste pits and the liquid waste diluted with ground water before collection in a leachate lagoon, for further settling, and subsequent discharge into the Plym Estuary.
Thus, Chelson Meadow disposal site was considered to be another potential source of TBT to the local marine environment and leachate from the tip and nearby estuarine sediments were the subject of a study by Devonport Management Limited almost a decade ago (Collier 1992). Dissolved TBT levels in leachate drains and lagoons were reported to be near or below the detection limit of 10ng $l^{-1}$ Sn (24ng $l^{-1}$ as TBT). Since this is an order of magnitude higher than the EQS, it is not possible to judge the associated risks from this source. Similarly, findings for the sediments were also judged 'inconclusive'. These data are now 10 years old and levels of TBT may well have declined (see section 7). Nevertheless, it would seem that a thorough independent study of contaminant pathways and concentrations in the Plym, and adjacent parts of the Plymouth Sound, is overdue.

Regarding other antifouling issues, studies have shown that sacrificial anodes can be an important localised source of zinc to marinas, harbours and estuaries. The local increase in concentrations of dissolved zinc near open marinas may be between 2 and 5µg $l^{-1}$, with levels in enclosed marinas being as high as 20µg $l^{-1}$. Increases in zinc concentrations in marina sediments of up to twice background levels (by up to 200µg $g^{-1}$) have been observed (Bird *et al*., 1996). Such sources are likely to be of potential significance in inshore parts of the Plymouth cSAC, particularly in the Hamoaze, lower Plym and perhaps the Yealm, and should be investigated further. The same applies to other toxicants and booster biocides including Zn pyrrithione, Cu, Irgarol and diuron .

### 5.1.3. Hydrocarbons (Oil, Petrochemicals, PAHs)

Although there is no evidence of significant current damage, oil pollution is a continual threat to all inshore marine habitats, and particularly pronounced in the cSAC due to the intensity of shipping traffic in Plymouth Sound and the adjacent English Channel. Risks include small leaks, spills and discharges as well as the possibility of a major accident. This threat was highlighted early in 2002 when two incidents involving large shipping occurred; the *MV Willy*, a petrol tanker, ran aground in Cawsand Bay in the west of the Sound, and a freighter, the Kodima ran aground in Whitsand Bay, Cornwall, just west of the cSAC boundary. Neither incident resulted in significant oil pollution although local and national contingency plans have been prepared to fully assess and minimise the impact from spills which may occur (MCA 2002).

Potentially there are a number of ways in which oil could impact on the interest features of the cSAC. Intertidal habitats are under greatest threat from the physical effects of oil pollution: the most vulnerable of these are the sheltered rocky coasts, intertidal sand and mudflats and saltmarshes of the enclosed inlets and bays (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. Sub-lethal changes could be manifested as increased bioaccumulation, induction of components of the mixed function oxidase (MFO) enzyme system, and higher order changes in productivity, fecundity and behaviour. Subtidal habitats (e.g.

reefs and sandbanks) and their associated biota may be threatened in the higher energy areas such as the more exposed outer Sound, where the likelihood of oil/water emulsions forming is greater. Any marine mammals would be endangered through the consumption of contaminated food, exposure to volatile fractions (eyes and lungs) and, for seals, smothering of intertidal haul-out sites. Birds would be affected by consumption of contaminated food and damage to plumage.

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 and 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

*Oil*

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, offshore oil production (e.g. drilling, transport, refining and burning of oil, and petrochemicals) and the atmosphere (PAHs).

There are few reports available in the literature regarding hydrocarbon oil in the cSAC. Readman *et al* (1986) analysed hydrocarbon mixtures isolated from three estuaries, the Dee, the Mersey and the Tamar (sediments collected near the road and rail bridges). HPLC chromatograms showed a dominance of unsubstituted parent PAHs indicative of a combustion origin in all three estuaries. The 'hump' on the chromatogram for unresolved complex mixture (UCM), which is a sign of degraded or chronic oil contamination, was particularly high in the Mersey sample, relatively minor for the Tamar and low for the Dee. Quantitative measurements are given in table 11 below for comparison. However, recent contamination from relatively undegraded oil in the Tamar was indicated by similar proportions of *n*-alkanes containing odd, and even numbers of carbon atoms, though the source of this oil contamination was not determined.

**Table 11. Concentrations of UCM (Unresolved Complex Mixture) in Tamar sediments (µg $g^{-1}$ dw)**

| | Mersey | Dee | Tamar |
|---|---|---|---|
| UCM | 104 | 10 | 42 |

From Readman *et al* (1986)

*PAHs*

PAHs are ubiquitous environmental contaminants. Although they can be formed naturally (e.g. forest fires) their predominant source is anthropogenic emissions, and the highest concentrations are generally found around urban centres (Cole *et al*., 1999). In the aquatic environment PAHs are generally highest in sediments, intermediate in biota and lowest in the water column (CCME 1992). They are of particular concern in the marine environment as the lower molecular weight PAHs are toxic to marine organisms and metabolites of higher molecular weight PAHs are carcinogenic (Law *et al*., 1997). PAH concentrations in the sediments have been linked to liver neoplasms and other abnormalities in fish (Malins *et al.,* 1988). In addition, some PAHs have been identified as endocrine disruptors (Anderson *et al*., 1996a,b; Kocan *et al.,* 1996). Total hydrocarbon concentrations in fish from Plymouth Sound and estuaries are reported to be elevated (45 mg $kg^{-1}$ ww) in comparison to fish from other UK estuaries (e.g. Chesil and the Fleet, 5.2 mg $kg^{-1}$ ww) (Allen *et al.,* 2000), however the nature of the hydrocarbons is not specified.

An MPMMG survey (1998) found total, and some individual, PAHs, to be low in waters just outside Plymouth Sound and in the Tamar Estuary. Similarly, earlier studies of PAHs in the Tamar Estuary have reported concentrations of individual PAHs in water to be <1 - 50ng $l^{-1}$ (Readman *et al.,* 1982; 1984). Highest concentrations occur at the turbidity maximum, with a secondary concentration maximum localised to the industrialised portion of the estuary (the Hamoaze) and associated with anthropogenic inputs. 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 ($\leq$200) PAHs (including naphthalene, phenanthrene and anthracene) have a low affinity for particulates and are subject to microbial degradation. Their solubility and vapour pressure is higher than group 2 PAHs and photo-oxidation and air-water exchange are important in the estuary. Consequently group 1 PAHs tend to have comparatively shorter residence times, and exhibit a complex distribution pattern. In contrast, *group 2* or high molecular weight ($\geq$200) homologues (including benzo(a)pyrene, fluoranthrene, pyrene and chrysene) are readily adsorbed onto suspended particulates. They are correlated with suspended solids along most of the estuary, the exception being in the vicinity of the dockyard/urban area, where high PAH inputs alter the relationship. Due to the high particulate affinity and microbial refractivity, the principal fate of group 2 PAHs in the Tamar estuary is sediment burial. Axial profiles of individual PAHs and a selection of environmental variables in the waters of the Tamar are shown in figure 20.

The distribution pattern of PAHs in sediments of the Tamar generally mirrors that of the waters. Concentrations in the riverine sediments have been reported to be generally low, <1 - 50ng $g^{-1}$ dw (Readman *et al.,* 1982, 1984). This was attributed to the relatively pristine environment of the catchment area, and removal of PAH rich particulates by fast flowing freshwater. However, in the upper estuary and turbidity maximum zone, where sedimentation and flocculation processes deposit riverine particulates, levels were higher (30 – 1500ng $g^{-1}$ dw).

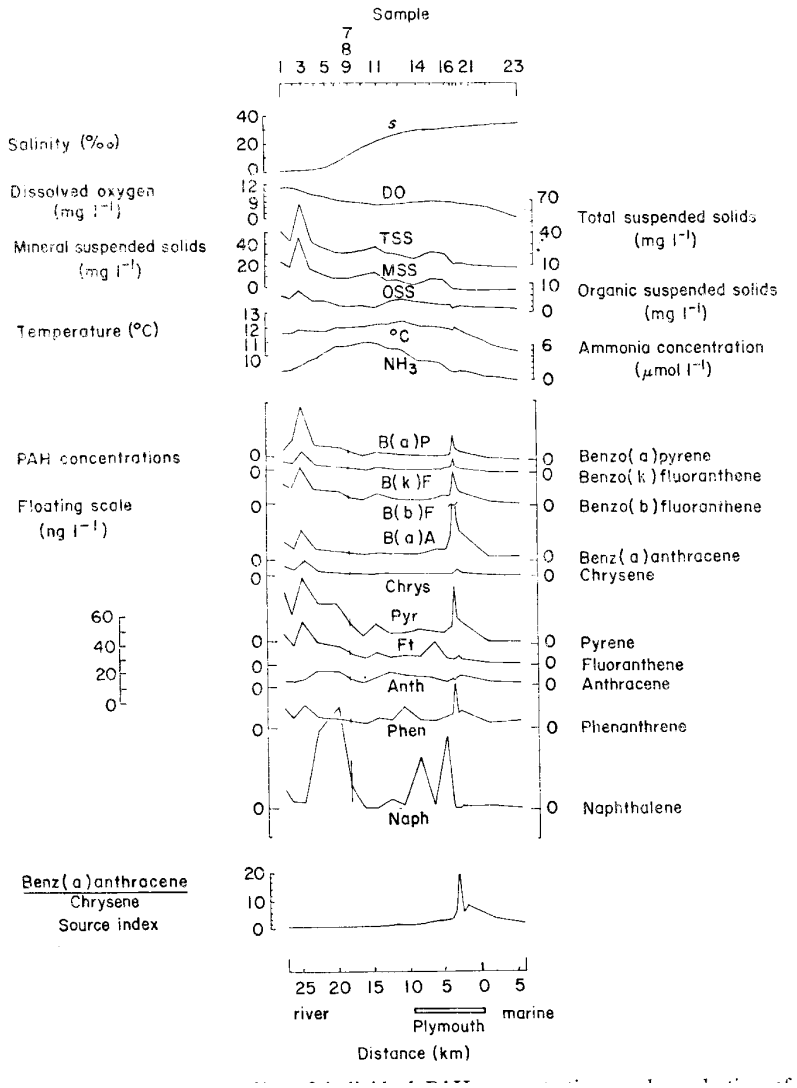



**Figure 20. Axial profiles of individual PAHs and a selection of environmental variables in waters of the Tamar estuary. Distances from the mouth of the estuary are shown at the bottom of the diagram and the position of Plymouth is indicated.** (From Readman *et al.,* 1982 with permission)

Highest concentrations were apparent in the region of Calstock. Toward the sea, concentrations of PAHs decrease, probably as a result of dilution and microbial degradation, although there is a secondary peak associated with the urbanised portion of the estuary (the Hamoaze).

Local sources include motor vehicle exhaust, road run-off, airborne particulates, street dust, sewage, domestic and industrial waste water, and coke oven emissions. In the Tamar River and upper estuary, away from urban areas, sources of PAHs are considered to be principally atmospheric deposition, although where the river runs close to major roads, polluted run-off is implicated. In the lower reaches of the estuary close to Plymouth the principal source, as indicated by PAH covariability with lead, and secondary peaks of PAHs in sediments near the Tamar road bridge, is thought to be road run-off (Readman *et al*. 1984).

Modelling dispersal of toxins in the Tamar, Harris *et al* (1984) simulated a dramatic seasonal change in the distribution of group 2 PAH, benzo(a)pyrene. In the summer B(a)P is retained upstream of the turbidity maximum due to its high affinity for particulates which at this time are continually resuspended and suffer a net upstream flux. The increased freshwater flow which occurs in the autumn and winter is predicted to be sufficient to overcome this and distribute B(a)P more evenly along the estuary. This is similar to the simulated behaviour of TBT described in section 5.1.2.

In a study of PAH transport and suspended matter, Fernandez *et al.,* (1999) compared several European systems including the Tamar. The rivers were all situated where economic activities were expected to be similar and therefore inputs comparable. Figure 21 shows mean total PAHs in water and sediments as a function of river flow/discharge. Findings indicate that PAH concentrations, per volume unit, are generally enhanced in high flow rivers (figure 21a). In contrast PAH concentrations (μg $g^{-1}$ suspended matter) tended to decrease in higher flow situations (figure 21b). The Tamar has relatively low flow in comparison to other European rivers, therefore is liable to transport particulates rich in PAHs, representing an immediate hazard to local fauna and flora.

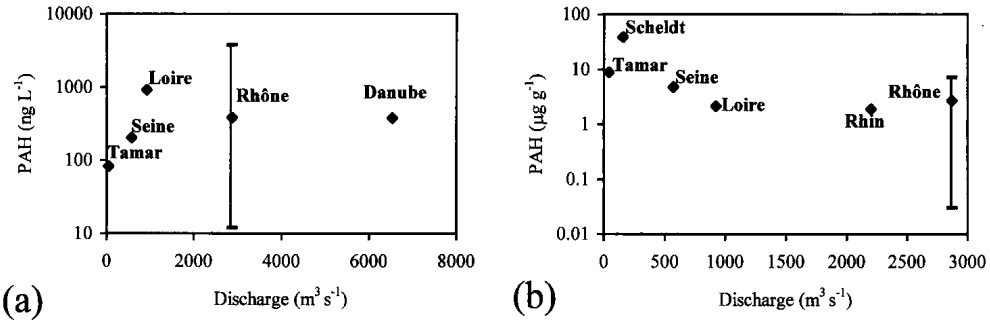



**Figure 21. Mean total PAH concentrations ng $l^{-1}$ (a) and PAH loads μg $g^{-1}$ (b) for several European rivers:** (From Fernandes *et al.,* 1999) with kind permission of Kluwer Academic Publishers) Seine and Rhone (Fernandez *et al.,* 1999), Loire (Tronczynski, 1985), Scheldt and Rhin (van Zoest and van Eck 1990), Tamar Readman *et al* 1982) and Danube (Klyuev 1993). Maximum and minimum for the Rhone are also shown.

Recently, MPMMG (1998) Woodhead *et al*, (1999) report ΣPAH concentrations of between 1000 and 10000μg $kg^{-1}$ dw in sediments of the Tamar and Plymouth Sound, and indicate that phenanthrene, pyrene and benzo(a)pyrene, comprise a significant proportion of the total. This represents a significant increase since the 1980s which could have consequences for interest features in the cSAC. A number of values in the Tamar are above interim threshold effects levels, and occasionally probable effects levels (Woodhead *et al*, 1999).

There is a paucity of up-to–date information in the literature regarding effects of PAHs in the Plymouth Sound and Estuaries cSAC. However, one recent bioindicator study indicates that the reported levels of PAH may not be significantly affecting fish; hepatic microsomal 7-ethoxyresorufin *O*-deethylase (EROD) activity, which is indicative of exposure to PAHs (and PCBs), was found to be low in eels (*Anguilla anguilla*) from the upper Tamar in comparison with eels from other UK estuaries

(Doyotte *et al.,* 2001). Nevertheless, further information on biomarker-type effects would be useful to confirm the status of biological responses.

Unpublished chemical information on specific hydrocarbons and PAHs in Plymouth Sound and Estuaries cSAC, extracted from the Agency database, is briefly reviewed in sections 7 and 8.

### 5.1.4. Pesticides, Herbicides And Endocrine Disruption

This section deals with pesticides in the Plymouth Sound cSAC and SPA, together with any evidence of their involvement in endocrine disruption. Other endocrine disruptors are described at the end of this section.

Pesticide concentrations measured in waters and sediments of the cSAC (1995-1999) are listed in table 12 compiled from a review by Allen *et al.,* 2000. Compounds which may be present in elevated concentrations are discussed in the text below, under the relevant sections[1].

**Table 12. Median concentrations of pesticides measured in water, sediments, fish and invertebrates of Plymouth Sound and Estuaries cSAC (1995-1999). (data from Allen *et al.*, 2000)**

| | Seawater ng $l^{-1}$ | n | Sediment mg $kg^{-1}$ dw | n | Fish mg $kg^{-1}$ ww | n | Invertebrates mg $kg^{-1}$ ww | n |
|---|---|---|---|---|---|---|---|---|
| Organophosphates (total) | 15000 | 64 | | | | | | |
| Atrazine | 30 | 8 | | | | | | |
| Simazine | 30000 * | 8 | | | | | | |
| Dieldrin | 0.6 | 8 | 0.0017 * | 2 | 0.019 | 3 | 0.001 | 11 |
| Aldrin | 0.5 | 8 | 0.0017 | 2 | | | | |
| Endrin | 1 | 8 | 0.0015 | 2 | | | | |
| Isodrin | 1 | 8 | | | | | | |
| DDD | | | 0.0022 * | 2 | 0.033 | 3 | 0.002 | 11 |
| DDE | | | 0.0023 * | 2 | 0.048 | 3 | 0.002 | 11 |
| DDT | 2.9 | 8 | 0.0047 * | 2 | 0.03 | 3 | 0.001 | 11 |
| Endosulfan | 1250* | 16 | | | | | | |
| HCB | 0.7 | 8 | 0.0017 | 2 | 0.007 | 3 | 0.0005 | 11 |
| Alpha-HCH | 0.3 | 8 | | | 0.0005 | 3 | 0.0005 | 11 |
| Beta-HCH | 2.1 | 8 | | | 0.0005 | 3 | 0.0005 | 9 |
| Gamma-HCH | 1.4 | 8 | | | 0.005 | 3 | 0.0005 | 11 |
| Trifluralin | 11400 | 8 | | | | | | |
| Nonylphenol | 0.059 | 8 | 0.035 | 4 | | | | |
| Octylphenol | 0.04 | 8 | 0.025 | 4 | | | | |

* Exceeding EQS or interim marine sediment quality guidelines (ISQGs)

*Organochlorine pesticides (OCs - chlorinated hydrocarbons)*

[1] It should be noted that levels of organophosphates, simazine, endosulphan and trifluralin in seawater seem unrealistically high and units may be wrongly labelled in the report of Allen *et al*, 2000 – perhaps these should be pg $l^{-1}$ rather than ng $l^{-1}$.

OCs of concern 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. Some organochlorine pesticides have been identified as endocrine disrupting substances (e.g dieldrin, aldrin, lindane, endosulfan, DDT and its metabolites).

Many OCs are toxic List 1 contaminants, and undesirable effects on environmental quality and animal health led to a ban and/or severe restriction on the production and use of many OCs in most developed countries during the 1970's and 1980's

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). Thus, Allen *et al*., (2000) report low DDT concentrations in waters of the cSAC (table 12), which appear to be well below EQS levels of 0.025µg $l^{-1}$ (annual average). However, median concentrations of DDT in sediments of the cSAC are reported as 4.7 µg $kg^{-1}$, higher than the interim marine sediment quality guidelines of 2.9µg $kg^{-1}$, and equal to 'probable effect' levels. Though also elevated in sediments of the cSAC, concentrations of DDD and DDE, were reported as lower than that of the parent compound (see table 12), which would suggest more recent inputs of DDT. This situation is also indicated by MPMMG (1998). Considering that DDT has been banned from use as a pesticide in the UK, further research into sources and current levels of DDT contamination are recommended.

*Dieldrin*

Another endocrine-disrupting OC pesticide which may be of concern in the cSAC is dieldrin; concentrations in sediments of the cSAC (1.7µg $kg^{-1}$, table 12) exceed the interim marine sediment quality guidelines of 0.71µg $kg^{-1}$. MPMMG (1998) also indicate that elevated levels of dieldrin were found in sediments of the cSAC at some sites. 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 '70s, when otters were restricted to a handful of upland tributaries on the cleanest rivers[1].

*Lindane*

Due to its toxicity and endocrine-disrupting effects, the use of gamma-HCH (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 the five pesticides listed as most frequently exceeding 0.1µg $l^{-1}$ in estuaries and coastal waters of the south west during 1993 (NRA 1995), and above limits of detection in 50% of water samples in taken from the Tamar in an MPMMG study (1998). The latter report median concentrations of lindane to be generally below the EQS of 20ng $l^{-1}$ in the Tamar although at individual sites, values exceeding the threshold were measured. Allen *et al* (2000) report median concentrations of lindane to be only 1.4 ng $l^{-1}$ in the seawater of the cSAC between 1995-1999.

*Endosulfan*

Endosulfan is a mixture of two isomers, endosulfan 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. Endosulfan 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). Allen *et al* (2000) report high levels in seawater of the cSAC (median 1.250µg $l^{-1}$, table 12), well in excess of the water quality standard for the protection of saltwater life[2]. No further information is available regarding endosulfan levels in the cSAC. Greve and Wit (1971) found that 75% of the endosulfan in the River Rhine was associated with particulate matter (mud and silt) therefore sediments levels in the cSAC may be important. However the ultimate fate in the marine environment, its metabolites and degradation products are not known, and further research into sources and impact of this toxic compound is strongly recommended.

[1] http://www.nfucountryside.org.uk/wildlife/home.htm 2002
[2] Note however the caveat concerning units at the start of section 5.1.4 (p 49)

*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 mean 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 affects 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, fenitrothion and dimethoate (Cole *et al.,* 1999).

Little information is available from the literature for levels of individual OPs in the cSAC. However, Allen *et al* (2000) report the median total organophosphate concentration in seawater of the cSAC (1995-1999) to be 15µg $l^{-1}$ (see table 12). This appears to be somewhat elevated in comparison to other UK estuaries[1], e.g. the Severn and the Dee (median OPs, 5ng $l^{-1}$) and in the light of WQS values: 0.01µg $l^{-1}$ for azinphos-methyl and fenitrothion, 0.02µg $l^{-1}$ for malathion, and 1.0µg $l^{-1}$ for dimethoate (annual averages). Maximum allowable concentrations are 0.04, 0.5 and 0.25µg $l^{-1}$ (azinphos-methyl, malathion and fenitrothion respectively).

The solubility, sorption, potential to bioaccumulate and extent of toxicity to aquatic life vary according to the individual OP. Jones *et al* (1996) reviewed the toxicity of azinphos-methyl to marine organisms and concluded that crustaceans were the most sensitive group with 48-hour LC50 values between 0.3 and 1µg $l^{-1}$ for pink and brown shrimps *Pandalus montagui* and *Crangon crangon*. Fish may be less susceptible to OPs, a maximum acceptable concentration for malathion of 6µg $l^{-1}$ has been reported for a full life cycle test with sheepshead minnows *Cyprinodon variegates* (Suter and Rosen 1988).

A recent biomarker study (Kirby *et al.,* 2000) investigated the occurrence and levels of neurotoxic contamination in 16 UK estuaries (including the Tamar) by

[1] Note, however, the caveat concerning units at the start of section 5.1.4 (p 49)

determination of cholinesterase (ChE) activity in the muscle of the flounder (*Platichthys flesus*). Reduced ChE activity in fish muscle is a specific indication of exposure to neurotoxins, particularly OPs and carbamates. In total, 12 out of the 16 sites, including the Tamar, showed significant depression of ChE activities compared to the Alde (control site). Activity in fish from Warren Point on the Tamar was 9717, and the Alde, 16573 mU $min^{-1}$ mg $protein^{-1}$ (figure 22). The same study analysed waters from each sampling point for OP and carbamate pesticides, and detected 26 ng $l^{-1}$ of the OP etrimfos in water from Tamar. Other pesticides were below detection limits, however, several of these compounds are relatively non-polar and may be associated with sediments or bioaccumulate in the dietary organisms of the flounder.

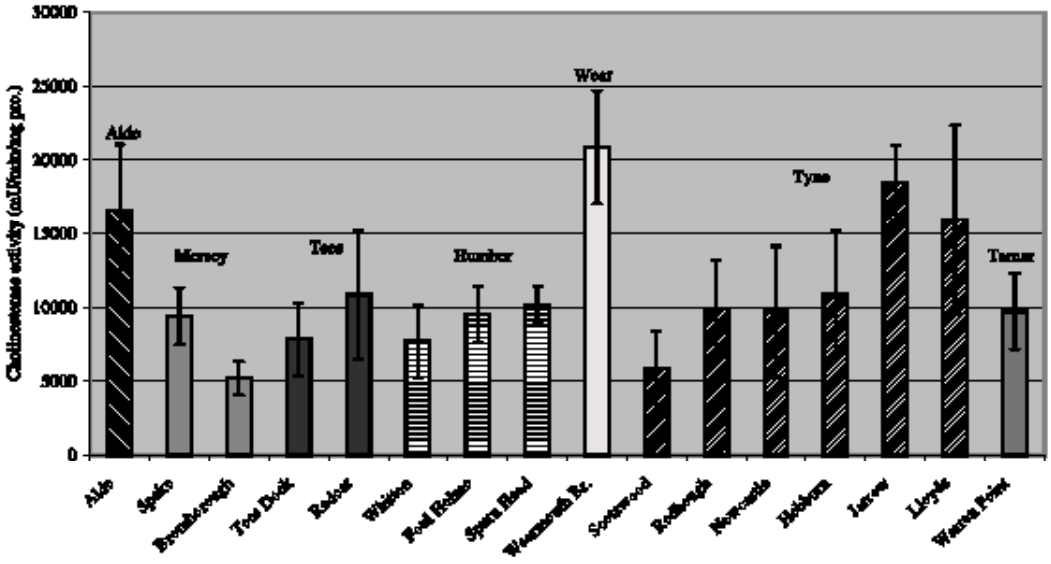



**Figure 22. Cholinesterase (ChE) activity in flounder muscle from English estuaries.** Error bars = 95% confidence limits (from Kirby *et al.,* 2000 with permission from Elsevier)

*Herbicides*

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 $l^{-1}$. They have also been identified as endocrine-disrupting substances (EA, 2000). Because of their major usage and high water solubility they 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 (NRA 1995). Elevated concentrations were reported by MPMMG (1998) for the Tamar, Thames and Mersey. Water samples collected from the Tamar and Tavy in 1991 contained 3.3 - 30.9ng $l^{-1}$ dissolved simazine (highest at Denham Bridge, in the FW Tavy) and 14 - 229ng $l^{-1}$ dissolved atrazine (Ahel *et al*., 1992). Despite being elevated, additive concentrations of these two compounds appear to fall below the EQS threshold in the estuarine waters of the cSAC.

However, a recent review of endocrine disruptors in marine sites (Allen *et al*., 2000) report median concentrations of 30ng $l^{-1}$ for atrazine, and 30,000 ng $l^{-1}$ for simazine (see table 12) in seawater of the cSAC (between 1995-1999). These and other findings (discussed elsewhere in this report) led Allen *et al* to suggest that the Plymouth Sound and estuaries site is a high priority for research into the presence and effects of these compounds. There is though, concern over the units used for simazine and several other pesticides in Allen *et al's* report, as indicated at the start of this section.

Triazine concentrations in Tamar sediments were below detection limits of 5ng $g^{-1}$ (Ahel *et al*., 1992). Partitioning on to sediments therefore appears to play only a minimal role in estuarine transport and typical axial profiles for the Tamar are dominated by soluble forms (figure 23). As with other contaminants, the position of the maximum is likely to be influenced by a combination of variable inputs, tidal state and river flow. Generally there is a decrease in concentrations down the water column although differences are relatively small in vertical profiles. Atrazine and simazine were the only triazines detected in water samples (Ahel *et al*., 1992).

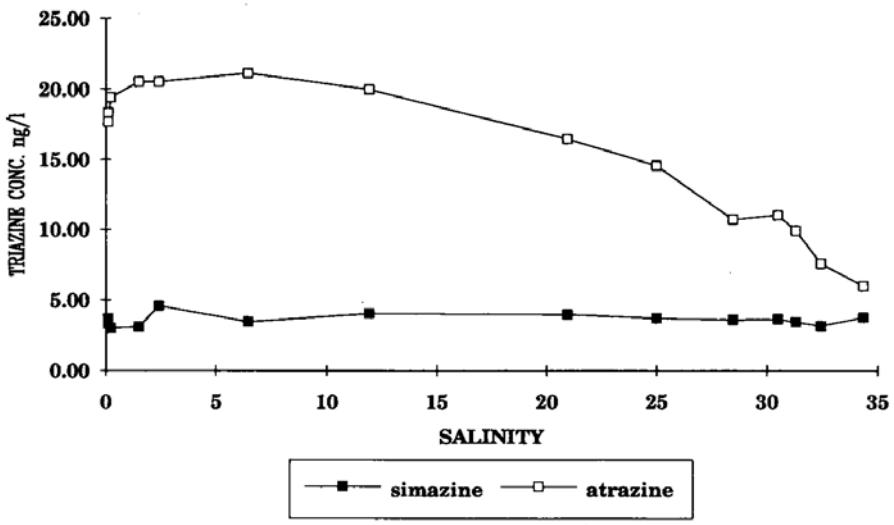



**Figure 23. Profiles of atrazine and simazine, Tamar Estuary (From Ahel *et al.*, 1992: reproduced with kind permission of Elsevier)**

In their 1998 report on water quality monitoring in the UK, MPMMG suggest that the ban on non-agricultural usage of triazines in the mid 1990s may have resulted in a general reduction in some of the peak values observed in earlier surveys. However, the timing of such surveys could effect recorded concentrations: peak values are likely to occur during periods of highest pesticide applications or in association with high run-off (Evans *et al.,* 1993). This may explain why some of the published findings appear somewhat contradictory.

Irgarol 1051

The use of the *s*-triazine herbicide Irgarol 1051 in antifouling paints rose over the last decade since the application of paints containing TBT was restricted to vessels over 25m (see section above on TBT). It is one of the so called "booster biocides" formulated with copper to prevent fouling, and produced in response to the full

International Maritime Organization ban on the use of TBT on all shipping which will come into force in 2003. Irgarol 1051 is a particularly effective algicide, reported to inhibit periphyton photosynthesis and significantly affect microalgal community structure at concentrations of 0.25µg $l^{-1}$ (Dahl and Blanck 1996).

Okamura *et al* (2000) assessed Irgarol 1501 and its breakdown product M1 by a battery of bioassays with marine and freshwater species. Both compounds affected aquatic plant species such as red macroalga *Porphyra yezoensis* conchospores, brown macroalga *Eisenia bicyclis* gametophytes, freshwater green microalga *Closterium ehrenbergii*, and floating macrophytes *Lemna* species at low concentrations. The toxicity of Irgarol 1051 was higher than that of M1 for all the aquatic plant species tested. 'No effect' concentrations (NOEC) of Irgarol and M1 for brown seaweed were respectively, 0.3 and 9.3µg $l^{-1}$ and the authors suggest the possibility that both Irgarol 1051 and M1 may influence the primary producer community in the aquatic environment.

In tropical waters, Owens *et al.,* (2002) found substantial reduction in zooxanthellae photosynthesis after six to eight hours of exposure to environmentally relevant concentration. Zooxanthellae are the symbiotic algae essential to the health of corals and which give them their colour. Using coral respirometry techniques, reduction in coral photosynthesis occurred well within the concentration range of Irgarol 1051 reported for Bermuda and the Florida Keys. In some more heavily contaminated areas such as Singapore, and at concentrations considerably lower than those reported for tropical waters, there was no net photosynthesis, suggesting complete shutdown of the photosynthetic apparatus.

It is clear that Irgarol 1051 is a potent inhibitor of coral photosynthesis at environmentally relevant concentrations. The effects of chronic exposure to this herbicide, and potential interactions of other contaminants and stressors such as temperature are not yet known.

Irgarol 1051 is widely distributed in European estuarine and coastal waters and sediments (*Zhou et al*., Tolasa *et al*., 1996). Scarlett *et al* (1997) detected Irgarol 1501 in water from all (7) sites sampled within the Plymouth Sound and Estuaries cSAC (table 13). Highest levels were found in close proximity to harbour and marina sites, where boat density was greatest and water flow restricted. The same study investigated toxicity of Irgarol 1051 to a key reproductive stage (zoospores) of the green alga *Enteromorpha intestinalis* in the laboratory. Findings indicated a NOEC concentration of 22ng $l^{-1}$. Growth inhibition occurred at concentrations of 50ng $l^{-1}$, and followed a logarithmic curve with increasing concentrations. Some effects close to marinas might therefore be anticipated from concentrations measured in table 13. Photosynthetic efficiency in adult fronds of *E. intestinalis* was inhibited in the laboratory by 2.5µg $l^{-1}$ (72hour - EC50), which is above current environmental levels.

**Table 13. Irgarol 1051 concentrations within Plymouth Sound cSAC during July and August 1995** Data from Scarlett *et al* (1997)

| Sample location | Irgarol 1051 (ng $l^{-1}$) |
|---|---|
| Drakes Island (east of pier) | 9 - 24 |
| Queen Anne's Battery Marina | 28 – 43 |
| Sutton Harbour Marina | |
| - near lock gates | 37 – 78 |
| - marina | 48 – 127 |
| - channel | 26- 52 |
| River Yealm (ferry jetty) | 1 |
| Wembury Beach | <1 |

Subsequently, Scarlett *et al.,* (1999) investigated the risks posed by Irgarol 1051 to the seagrass *Zostera marina* in the cSAC. Laboratory exposures indicated rapid uptake of the herbicide by *Zostera* leaves; tissue concentrations (dry weight basis) in excess of 300 times the water concentration were found within 2 days of exposure. Photosynthetic activity was significantly reduced at 0.18µg $l^{-1}$ (0.4µg $g^{-1}$ dw leaf tissue), close to the levels encountered at the more contaminated sites in Plymouth Sound (table 13).

Elsewhere, Irgarol 1501 concentrations in SW estuaries (Salcombe and the Yealm) were low: typically <0.003µg $l^{-1}$, with the highest, 0.01µg $l^{-1}$ in the Yealm (January 1998). However, concentration factors (CF = concentration in tissue (µg $g^{-1}$) ÷ concentration in water (µg $ml^{-1}$) in *Zostera* plants from the Yealm and Salcombe estuaries were up to 25000 (Scarlett *et al.,* 1999).

Proof of adverse effects in the cSAC has not yet emerged from the few studies carried out to date, but the increase in use of herbicide, coupled with relatively high levels of boating activity in the estuaries and approaches to the Tamar, may pose a threat to marine life, including any remaining *Zostera* at Cawsand Bay and near Drakes Island. The Yealm in particular, where International Coatings have three testing rafts for (anti-fouling) marine paints, (Misery Point, Warren Point and opposite Madge Point) in addition to trade discharges to the estuary, there is a potential for impact upon *Zostera* beds situated at Cellars beach. Regular monitoring of Irgarol 1501 levels in waters of the cSAC, and further research to establish the effects of the herbicide on *Zostera* and other non-target species is therefore recommended[1].

## Trifluralin

Trifluralin is a list II, selective, pre-emergence herbicide used commercially and in some domestic applications to control annual grasses and broadleaf weeds. It is highly toxic to fish and other aquatic organisms: the 96-hour LC50 is 0.02 to 0.06mg $l^{-1}$ for rainbow trout, although variables such as temperature, pH, life stage, or size may affect the toxicity of the compound (Johnson and Finley, 1980). Chronic

[1] Concerns regarding the effects of Irgarol 1051 have led recent UK legislation: antifoulings containing Irgarol 1051 (and also the commonly used antifouling herbicide diuron) were banned from sale at UK chandlers after November 2001, and a total ban on application to boats less than 25 metres overall will come into effect in November 2002 (for diuron the ban applies to all boats). However this is not a Europe-wide ban, therefore leaching from visiting, and larger vessels in the cSAC will still occur

exposure to trifluralin can also cause spinal deformities in fish (Wells and Cowan, 1982) and reduce the viability of eggs and larvae of the Dungeness crab *Cancer magister* (Caldwell *et al.,* 1979). Trifluralin has also been identified as an endocrine disruptor (Cole *et al.,* 1999).

Concentrations of trifluralin in waters of the cSAC are reported in Allen *et al.,* 2000 as 11.4µg $l^{-1}$ (table 12; though note again reservations over units), well in excess of EQS, (0.1µg $l^{-1}$) and liable to be also elevated in the sediments: in the aquatic environment trifluralin is readily degraded by photolysis and adsorbed onto sediments Cole *et al.,* 1999). High bioaccumulation factors (>1000 for algae and fish) and slow depuration have been reported for freshwater organisms, therefore there is a potential for bioaccumulation in marine organisms. Again, there is a distinct lack of information regarding the sources and impact of this toxic substance in this, and other marine sites.

*Other Endocrine disruptors*.

Alkylphenol polyethoxylate (APE) surfactants

Concentrations of the weakly oestrogenic degradation products of alkylphenol polyethoxylate (APE) surfactants (nonylphenol, octylphenol, nonylphenol monoethoxylate and nonylphenol diethoxylate) were measured in water and sediments from British rivers and estuaries collected during 1994 and 1995, including the Tamar (Blackburn *et al.,* 1999). Concentrations in all samples from the Tamar were below the limits of detection and water concentrations did not exceed the 'no observed effect' concentration for the induction of vitellogenesis[1] in caged trout (5-20 µg $l^{-1}$ total extractable alkylphenols). More recent measurements of surfactants are also low, Allen *et al* (2000) report median levels of nonylphenol and octylphenol in waters of the cSAC (1995-1999) to be 0.06 and 0.04ng $l^{-1}$ respectively, and for sediments, 0.04 and 0.03mg $kg^{-1}$ dw (table 12). Therefore oestrogenic effects on Tamar fish populations seem unlikely. This assumption is borne out by a study of oestrogenic endocrine disruption in flounder *Platichthys flesus* from UK estuarine and marine waters (Matthiesson *et al.,* 1998) which reports lower VTG expression in male flounder collected in the Tamar, than in fish from other UK estuaries including the control site (The Alde). It therefore seems unlikely that the Tamar receives significant concentrations of APE from the various trade waters and sewage treatment works (STW) which discharge.

Phthalates

'Phthalates' is the generic name given to esters of 1,2-benzenedicarboxylic acid. Phthalate esters are manufactured worldwide on a large scale, being mainly produced for use as plasticisers in resins and polymers, especially in food packaging and as a softener in PVC (87% of the total production of phthalates is used for this purpose).

[1] Exposure of fish to oestrogenic material can be detected by the presence of vitellogenin (VTG) in the blood plasma of male fish. VTG is the protein precursor of yolk and is synthesised by the liver in females specifically in response to oestrogens produced by the ovaries. Male fish contain almost no natural oestradiol therefore the presence of VTG in males is a definite marker of exposure to exogenous oestrogenic material

Although some 27 phthalate esters are manufactured, only a limited number are produced in large quantities. A review by Lewis *et al* (1998) identified a number of phthalates of particular interest in terms of their environmental fate and behaviour or because they were on the High Production Volume Chemicals List from the EC:

- dimethyl phthalate (DMP)
- diethyl phthalate (DEP)
- two isomers of dibutyl phthalate (DBPs); di-iso-butyl phthalate (D*i*BP) and di-*n*-butyl phthalate (D*n*BP)
- butylbenzyl phthalate (BBP)
- dicyclohexyl phthalate (DCHP)
- three isomers of dioctyl phthalate (DOP); di-*n*-octyl phthalate (D*n*OP), di-iso-octyl phthalate (DIOP) and di-2-ethylhexyl phthalate (DEHP)

DEHP is the most widely used phthalate ester (Sheahan *et al*., 2000). DEHP, DBP, DMP, DEP, and BBP are some of the most commonly detected phthalates in the aquatic environment (Bedding *et al*., 1982; Lewis *et al.,* 1998). For marine water samples DEHP was measured at concentrations >0.05µg $l^{-1}$ in 37 of 38 samples collected from UK estuaries and coastal sites (Law *et al*., 1991). The highest concentration of DEHP measured in this survey was 8.4µg $l^{-1}$ from just off the Hoe, within Plymouth Sound. Concentrations of other phthalates detected within the cSAC in this study are given in table 14.

**Table 14. Concentrations (ng $l^{-1}$) of phthalates in sub-surface (unfiltered) water samples from Plymouth Sound cSAC. (**Data from Law *et al.,* 1991)

| Site | D*i*BP | | D*n*BP | | DEHP | | DEP | |
|---|---|---|---|---|---|---|---|---|
| | 1988 | 1989 | 1988 | 1989 | 1988 | 1989 | 1988 | 1989 |
| Hamoaze | 15 | 20 | 50 | 53 | 99 | 680 | | <1 |
| Western King Pt | 16 | 31 | 42 | 200 | 110 | 3300 | | <1 |
| Plymouth Hoe | | 49 | | 150 | | 8400 | | 18 |
| SE Drakes Island | | <10 | | <50 | | 70 | | <1 |

Potential sources of phthalates in the aquatic environment are: wastewater discharges from production and processing activities (resin and plasticiser compounding, fabrication of PVC and during the production of adhesives and coatings) together with release following use and disposal of materials containing phthalate esters (including losses of plasticiser during the lifetime of products or during incineration or refuse and other waste landfill) (Cole *et al.,* (1999).

Some phthalate esters can be regarded as having low propensity for bioaccumulation, DBPs have intermediate tendency, whilst DOPs, including DEHP, have a high affinity for sediments or for partitioning to biota. Tissue levels for DEHP in different fish species from U.K. waters have been measured and range from 13 - 51µg $kg^{-1}$ wet weight (Waldock, 1983). For molluscs a higher range of 9.2 - 214µg $kg^{-1}$ was reported.

The toxicity of a range of phthalate esters to aquatic microorganisms, algae, invertebrates and fish has been reviewed by Staples *et al*., (1997) and Lewis *et al.,* (1998). The low molecular weight phthalates (which includes all those mentioned above) consistently 'exerted acute and chronic effects at concentrations below the limit of solubility across all test types and species'. EC50s ranged from 0.003mg $l^{-1}$ to 537 mg $l^{-1}$, depending on the test species and endpoint. Matthiessen *et al.,* (1993) attempted to assess the environmental hazard posed by phthalate esters in the marine environment and estimated 'safe' levels for chronic exposure, or 'no effect' levels (table 15).

**Table 15. Chronic exposure levels of phthalates estimated to be 'safe' for aquatic life) from Matthiesson *et al* (1993)**

| Chemical | Estimated 'safe' level µg $l^{-1}$ * |
|---|---|
| Dimethy phthalate | 300 - 500 |
| Diethyl phthalate | 80 - 300 |
| Di-iso-butyl phthalate | 10 - 30 |
| Di-n-butyl phthalates | 6 - 20 |
| Diethylhexyl phthalate | 1 - 35 |

- Chronic safe levels were estimated by applying arbitrary safety factors of x100 for acute fish and invertebrate data and x10 for chronic data.

Later, Lewis *et al.,* (1998) proposed environmental quality standards (EQS) for a range of phthalate esters in saline waters which appear to be higher. These were derived from toxicity, and bioavailability studies (table 16). No current accepted or proposed standards for phthalates in sediments can be found.

**Table 16. Proposed EQS for the protection of saltwater life for phthalates (µg $l^{-1}$) from Lewis *et al* (1998).**

| Chemical | Annual average | Maximum allowable concentration | Notes |
|---|---|---|---|
| Dimethy phthalate (DMP) | 800 | 4000 | 1 |
| Diethyl phthalate (DEP) | 200 | 1000 | 1 |
| Di-butyl phthalates (DBPs) | 8 | 40 | 1,2 |
| Butylbenzyl phthalate (BBP) | 20 | 100 | 1 |
| Di-octyl phthalate (DOPs) | 20 | 40 | 1,3 |
| Dicyclohexyl phthalate (DCHP) | - | - | 4 |

1) Tentative Standard; 2) Total DBPs (D*i*BP, D*n*BP); 3) DOPs (DEHP, DIOP, DNOP); 4) Insufficient data to derive standard

DEHP, DBP and BBP have been shown to be weakly oestrogenic in vitro (human breast cancer cell lines and trout oestrogen receptor; Jobling *et al*., 1995). Similar results have been demonstrated by Knudsen and Pottinger (1999) for three major teleost steroid-binding sites.

Endpoints measured in toxicity studies are not chosen specifically to determine endocrine disruption, however the restricted number of endocrine disruption studies in aquatic species indicate that such effects are likely to be limited in the aquatic

environment. The greatest potential for either toxic or endocrine disrupting effects is likely to arise in molluscs associated with contaminated sediments (e.g. dredge spoil sites) since many of the phthalates concentrate in the sediments and molluscs metabolise phthalates more slowly (Sheahan *et al*., 2000).

Implications for biota in the cSAC due to elevated levels of phthalates are therefore not clear. Further research is required to determine chronic effects of phthalate esters on marine organisms, e.g. on growth and reproduction and subtle effects on endocrine systems.

Polychlorinated biphenyls - PCB's

PCBs have low water solubility and a high affinity for suspended solids, especially those with high organic carbon content, therefore in the aquatic environment they are usually found in much higher concentration in sediments, where they are amongst the most persistent of environmental contaminants.

There are few records of levels of PCB contamination in Plymouth Sound and estuaries. MPMMG (1998) found concentrations of the individual congener, PCB 153, in sediments of the Tamar to be relatively low (<2.5µg $kg^{-1}$ dw). PCB 153 is relatively abundant therefore may be used to give an overall impression of PCB contamination. However, the authors acknowledged that there were limitations in their survey, notably that detection limits were inadequate, also that many of the samples were sandy sediments (coarse, with low organic carbon content) therefore may not be representative. In contrast, a CEFAS report gives median concentrations of total PCB's in sediments of the cSAC (1995-1999) to be 0.197mg $kg^{-1}$ dw (Allen *et al.,* 2000).

The sediment quality guideline value for PCBs in sediments is 0.0215 mg $kg^{-1}$ dw, and the probable effect level (PEL) is 0.189 mg $kg^{-1}$ dw (CCME 1999).

Like the majority of organochlorine substances, PCBs are lipophilic, dissolving more readily in fats than in water, therefore tend to accumulate in the fatty tissues of living organisms. Sediment dwelling organisms are obviously the most vulnerable of estuarine biota, and PCB's accumulated in the tissues of invertebrates can be transferred and magnified along the food chain resulting in very high concentrations in upper trophic levels such as fish species, birds and marine mammals. Allen *et al.,* (2000) report median total PCB concentrations in invertebrates of the cSAC to be 0.027mg $kg^{-1}$ ww, in comparison to 0.004mg $kg^{-1}$ ww in invertebrates from the relatively uncontaminated Wash and North Norfolk coast. Median PCB concentrations in fish from Plymouth cSAC were 0.708mg $kg^{-1}$ ww. MPMMG (1998) report concentrations of approximately 0.02mg $kg^{-1}$ ww PCB 153 in the liver of fish from the Tamar. A discussion of the most recent EA data on PCBs in mussels and flounder is provided in a later section but generally conform to the published data described here.

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), 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.

Thus, in higher organisms such as marine mammals some organic EDs are linked with immune system suppression and also population decline though it is difficult to establish cause-effect relationships (Allen *et al.,* 2000). In local terms, further study would be needed to evaluate the presence and possible current risk to higher organisms from substances such as, PCBs, DDE and TBT; in general terms however UK seal populations are regarded at potentially at risk based on measured residues of PCBs and DDE in their fish diet (CSL, 2000). Food items of various sorts will also be the most likely route of exposure to sea birds and waders, many of which are extremely sensitive to ED substances such as DDE, lindane, PCBs and dioxins, as has long been known. Studies of effects of these and other chemicals such as PAHs and metals (e.g. on egg shell thinning; abnormal reproductive behaviour and development) are 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, might represent additional, but as yet unquantified, risks (Allen *et al.,* 2000, CSL, 2000).

Metals and organometals

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 non-receptor-mediated 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 nature: the effects of long-term exposure to levels such as those found in the Plym and parts of the Tamar, for example, is not known. 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 (see section 5.1.1) is not available (Allen *et al.,* 2000). Experimental studies on freshwater crayfish have nevertheless suggested that Cd and Hg at a 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). In view of enhanced bioaccumulation of these and other metals at a number of sites (tables 3 - 8) similar reactions in marine crustaeans and other organisms from the SAC 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; as yet however it is not known whether metal exposure in the Tamar results in similar chronic effects.

Among organometallic compounds the androgenic impact of TBT on neogastropods is most widely documented. The impact of this compound in dogwhelk and mud snail populations in Plymouth Sound is detailed in a separate section (5.1.2). In vivo tests on guppies have also indicated that methyl mercury may impair steroidogenesis (Wester, 1991) though as yet there have been no tests on the occurrence and impact of this compound in the Plymouth Sound and Estuaries cSAC.

Thus, information on endocrine disruption in the cSAC is patchy. A recent report by CEFAS on Endocrine Disruptors in European Marine Sites in England, commissioned by EN, has identified the Plymouth Sound and Estuaries SAC as a high priority for future research in this area, based on a combination of discharge volume and elevated concentrations of contaminants (Allen *et al.,* 2000). The combined pressure caused by a cocktail of chemicals could contribute to the exhaustion of the general cortisol stress response (see below) in some species. As for direct evidence: Endocrine disruption from TBT is well established, as reported in section 5.1.2 of the current report, and the figures for dissolved TBT in recent years (median 28ng $l^{-1}$) reported by Allen *et al.,* 2000 would indicate this may be an ongoing problem. However, there appears to be a question mark over current TBT levels in the system (our earlier investigations indicate lower TBT concentrations) and therefore further survey of TBT contamination and imposex are warranted.

As for effects caused by other EDs, the conclusions drawn by Allen *et al*. seem somewhat equivocal. On page 106 of their report, Allen *et al.,* 2000 (citing results of their earlier work) imply that male flounder examined in 1997 revealed no significant feminising effects (indeed the paper by Allen *et al.,* 1999, indicates vitellogenin levels in male fish from the Tamar are equivalent to baseline levels). Subsequently, on page 124, Plymouth Sound is listed among sites where oestrogen exposure 'is undoubtedly feminising male fish'. It is acknowledged, however, that only a few fish have been sampled to date and further sampling is needed to clarify the issue.

### 5.1.5 Radionuclides

Devonport Royal Dockyards Ltd is authorised to discharge radioactivity into the SAC and surrounding area, largely in relation to its submarine refit programme. The form of this activity includes tritium ($^{3}H$), Carbon-14, Argon–41, Cobalt-60 and small quantities of other radionuclides.

Routine surveillance of environmental radioactivity (e.g $^{3}H$, $^{54}Mn$, $^{58}Co$ $^{60}Co$, $^{90}Sr$, $^{95}Nb$, $^{124}Sb$, $^{131}I$, $^{137}Cs$, $^{155}Eu$, $^{241}Am$) and estimated maximum dose rates resulting

from authorised discharges of liquid radioactive waste into the Tamar are now reported by the Food Standards Agency/SEPA. Results of the available monitoring data from the 2000 monitoring programme (RIFE, 2001) indicates that the radiological significance of environmental radionuclides continues to be low. A small amount of tritium (48 Bq $kg^{-1}$ wet wt.) was determined in *Carcinus maenas* from the Lynher and traces of $^{137}Cs$ were found in mud and seaweed *Fucus vesiculosus* from Kinterbury (4.5 and 0.12 Bq $kg^{-1}$, ww, respectively) and in mussels from Mayflower Marina (0.14 Bq $kg^{-1}$). These compare with values of 130 Bq $kg^{-1}$ of tritium in crabs and 510, 6.7 and 2.6 Bq $kg^{-1}$ $^{137}Cs$ in mud, seaweed and mussels, respectively, from the Cumbrian coast near Sellafield. $^{99}Tc$ was detectable at low levels in the Kinterbury *Fucus* sample. Other fission and activation products also tend to be in trace quantities: levels of radioactivity in the majority of bioindicator samples taken from the Tamar/Lynher (crabs, oysters, mussels) were, in fact, cited as 'less than' values (RIFE, 2001). The same applies to crabs from Plymouth Sound.

A small number of $^{60}Co$ measurements in sediment cores have been reported by Lindsay and Bell (1997) for samples taken in the upper estuary in 1991. These indicate very low levels (<0.13 Bq $kg^{-1}$ dw) at depths below 20cm, but increase by approximately two-fold in the top third of the core (max 0.32 Bq $kg^{-1}$). These compare with an upper value of 55 Bq $kg^{-1}$ in mud from the Ravenglass Estuary, Cumbria (RIFE, 2001). However, it should be noted that although $^{3}H$ will increase due to the recent authorisation, $^{58}Co$ will be reduced.

The projected combined dose from all sources in 2000, to the most exposed groups of humans affected by Devonport discharges (taking into account consumption of fish and shellfish and exposure to sediments), was 0.009mSv. This is <1% of the maximum allowable dose limit of 1 mSv from discharges. (By contrast the critical group in the Sellafield area receives 0.15 mSv). It compares with an annual background dose to residents in Cornwall of about 7.5 mSv, and to residents in Devon of 4.9 mSv, arising from geological sources, building materials, radon gas and cosmic radiation (RIFE, 2001).

Discharges of tritium from the Devonport Dockyard are expected to rise sharply as a result of a recent substantial increase in the consent (to accommodate refit of the nuclear submarine fleet). Possible routes of transfer will include the atmosphere, direct discharges to the Hamoaze (dispersal by water, some deposition in sediments) and via discharges to the sewers. Potentially the most significantly exposed groups would be sewage workers and farming families involved with disposal of sewage to land. Overall the increases are not expected by DML or EA to raise dose rates significantly (radiotoxicity of tritium is not regarded as being particularly high). Nevertheless, it has recently been established from different sites around the UK that bioaccumulation of tritium does occur (RIFE, 2001). It would seem advisable to conduct a series of baseline studies on key species, and processes, with a view to monitoring the effects of this significant change in limits. Genotoxicity screening of marine organisms, to look for DNA damage, should be included.

Remobilisation of radionuclides locked in sediments can arise as a result of dredging and any application to undergo such an operation must first be subjected to an appraisal of impact. Such an appraisal was made with reference to the Tamar in 2000,

with a view to dredging and spoil disposal options. Mean values in surface sediments near Devonport (in Bq $kg^{-1}$ d.wt) were $^{40}K$ 652; $^{137}Cs$ 4.8; $^{212}Pb$ 35; $^{214}Bi$ 25; $^{226}Ra$ 27; $^{228}Ac$ 29; $^{234}Th$ 55.

The results of the assessment, according to RIFE (2001) indicate that risks to humans are minimal (of the order of 0.01mSv). However, potential impact of radionuclide remobilisation arising from dredging, on marine biota, are not discussed in the report and appear to be an important area for research.

## 5.2 Non-Toxic Contaminants

This section deals with non-toxic contamination in Plymouth Sound and Estuaries cSAC. 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).

### 5.2.1 Organic enrichment

Natural sources of organic carbon, or organic matter, include river-borne phytoplankton and organic detritus, run-off from the land and marginal vegetation. These inputs are supplemented considerably in urbanised estuaries by anthropogenic point sources such as sewage effluent, some industrial effluents and fish and shellfish installations. The addition of large amounts of organic matter from anthropogenic sources can exceed the capacity of parts of the marine environment to process it, resulting in accumulation, usually in the sediments.

Organic matter occurs in natural waters in dissolved (dissolved organic matter DOM) and particulate (particulate organic matter POM) forms. Much of the biological DOM is metabolised by heterotrophic bacteria, while most of the DOM with geological origins (e.g.humic substances) is resistant to microbial breakdown. Some other animals can use biological DOM but are largely outcompeted by bacteria. Concentrations of POM depend significantly upon discharge and on concentrations of suspended particulate matter. During summer months, the 'living organic carbon' of algae accounts for much of the POM in all but the most polluted rivers (Tipping *et al.,* 1997).

Organic carbon is readily assimilated into the tissues of marine organisms, and can be transformed from particulate to dissolved and lost to the atmosphere as $CO_2$ by respiration. Organic matter can exert a controlling influence on the oxygen mass balance of aquatic systems: by stimulating the biological productivity both in the water column (increasing biological oxygen demand - BOD), and in the sediment (increasing sediment oxygen demand - SOD) (Tipping *et al.,* 1997). SOD is related to the settlement of suspended solids with a high organic content (as is the case for suspended solids discharged in STW effluent). Thus, a relationship exists between

water column dissolved oxygen status and organic enrichment, which might, in part, be responsible for the low dissolved oxygen concentrations in the upper Tamar Estuary observed during summer low river flow conditions (see below).

In addition to its relationship with oxygen status of rivers and estuaries, dissolved organic carbon (DOC) is intimately involved in a range of important biogeochemical processes; potential toxicity of industrial and urban effluents is ameliorated through complexation of trace metals (Suffet and McCarthy 1989) and partitioning of organic pollutants such as PAHs and PCBs (Chiou *et al* 1986). DOC adsorbed onto particles causes the alteration of their physico-chemical properties and can modify bioavailability in various ways (Bryan and Langston 1992 : Keil *et al.,* 1994).

Miller (1999) investigated the dynamics of organic carbon in the waters of the Tamar estuary (Gunnislake Weir down to Devils Point) by looking at axial profiles. The range of DOC concentrations (April to December, 1991) in the estuary was 478 – 110µM, which is consistent with other published data for riverine and coastal sea waters respectively. Non-conservative mixing behaviour in the estuary was found; DOC concentrations were uncoupled from salinity and inversely related to turbidity, whilst POC and turbidity were significantly correlated.

A major input of DOC was indicated in the low salinity region approximately 10km from the weir. This occurred downstream of the turbidity maximum and peaks for chlorophyll *a* and POC, but coincided with the position of a (primary treatment[1]) sewage effluent outfall near Bere Alston. The influence of other large-scale sewage inputs was also noted by Miller (1999); a distinct peak in DOC at 24km from the Weir corresponded to the Saltash outfall[2], and further peaks coincided with Camels Head (26km) and Ernesettle (21.5km). It had previously been concluded that such localised inputs were quantitatively insignificant compared to the estuarine DOC flux (Mantoura and Woodward 1983).

Concentrations of organic material in sediments were not reported Miller (1999), however axial profiles of POC show peaks in the vicinity of the turbidity maxima consistent with a sedimentary source. It was concluded that tidally-induced resuspension of bottom sediments is an important control mechanism for organic carbon in the estuary.

Watson *et al* (1993) analysed sediments from four sites in the Tamar estuary and found a declining gradient of organic carbon content from the medium silt sediments of upper estuarine and creek (head of St Johns Lake) sites (2.5 and 2.3%), to the coarse sediment of the mid estuary (1.5%) and fine sands of the lower estuary (1.06%).

[1] Effluent treatment is secondary since 1991 (EA pers comm.)
[2] Now ceased and flows transferred to Ernesettle (EA pers comm.)

### 5.2.2 Nutrients

Water quality with regard to nutrients is primarily assessed in terms of the trophic status, or degree of nutrient enrichment of estuaries and near shore waters. 'Nutrient enrichment' generally refers to nitrogen and phosphorus species that 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.

Table 17 shows estimated nutrient budgets for three Welsh estuaries (based on Parr *et al.,* 1999) and although many Welsh coast estuaries are oligotrophic, and different estuaries will vary according to the geology and urbanisation of the catchment area, these figures may be considered typical for many estuaries.

**Table 17. Estimated source of estuarine nutrients (based on Parr *et al.*, 1999)**

| Source | Nitrogen % | Phosphorus % |
|---|---|---|
| Agricultural sources (livestock waste and inorganic fertiliser run-off) | 25 - 49 | 3 - 49 |
| Sewage Treatment Works | 3 - 13 | 26 - 62 |
| Atmospheric deposition | 2 - 6 | 1.5 - 1.8 |
| Nitrogen fixation | <5 | - |
| Background | 13 - 15 | 10 - 19 |

Using models to estimate nutrient inputs, Fraser *et al.,* (2000) compared the relative contributions of diffuse and point sources inputs to the Tamar Estuaries complex in 1931 and 1991 (table 18). The figures are the result of an integrated approach taking into account a wide range of physical characteristics and parameters such as the local geology and sediment type, land use, volume, dilution and flushing rate, rainfall, vertical mixing, and wave exposure, all of which influence the nutrient status of environmental waters. These variables are almost unique to individual catchments and confound attempts to make accurate predictions without taking them into consideration.

**Table 18. Proportion of nitrogen and phosphorus exported from diffuse and point sources in the Tamar catchment (data from Fraser *et al.*, 2000)**

| | Source | Nitrogen % | | Phosphorus % | |
|---|---|---|---|---|---|
| Year | | 1931 | 1991 | 1931 | 1991 |
| | Diffuse | 95.3 | 97.7 | 85.3 | 89.7 |
| | Point | 4.7 | 2.3 | 14.7 | 10.3 |

The model estimates suggest that the relative proportion of nitrogen inputs from diffuse sources in the Tamar catchment has increased by 2.4% over the 60-year period covered, and diffuse inputs of phosphorus have increased by 4.4%.

During this period, it is estimated that the total N loading delivered to the Tamar Estuary rose from 13.4 kg $ha^{-1}$ in 1931 to 39.3 kg $ha^{-1}$ in 1991, representing a 194% increase in N loading. The total P loading delivered to the Tamar Estuary rose from 0.75 kg $ha^{-1}$ in 1931, to 1.57 kg $ha^{-1}$ in 1991, representing a 52% increase in P loading on the estuary over the 60 years.

**Table 19. Total nitrogen and phosphorus loading delivered to the Tamar Estuary (Data from Fraser *et al.*, 2000)**

| | Nitrogen | | Phosphorus | |
|---|---|---|---|---|
| Year | 1931 | 1991 | 1931 | 1991 |
| Loading (kg $ha^{-1}$) | 13.4 | 39.3 | 0.75 | 1.57 |
| Total (kg) | 1236896 | 3630600 | 69542 | 145451 |

According to this model, N export to the Tamar Estuary has increased at a more rapid rate than P export. The authors suggest that the increased differential is driven by a number of factors: the conversion of unfertilised moorland and rough grazing to intensively fertilised agricultural grazing land, changes in fertiliser application rates to crops and grass, and predominantly by increasing stocking densities of cattle and particularly sheep on grazing land. N and P export from human sewage is predicted, from the model, to play an insignificant role in the delivery of nutrients from this catchment to the Tamar Estuary whilst average flows are observed. It could be argued, therefore, that point sources should not be the primary focus in the development of eutrophication control action plans for this catchment. In the tidal estuary, however, point source inputs may be more important, locally. This is placed in context by recent calculations of relative loadings of nitrogen species from fresh water and STW inputs, for various sub-estuaries feeding into the cSAC (annexes 8 and 9 respectively, provided by P.Jonas, EA). It should also be noted that whilst STW inputs, generally, are an order of magnitude lower than freshwater loadings, this is not the case in the Plym where both sources appear to be roughly equivalent in size.

Nevertheless, these calculations confirm that numerically, Total Inorganic Nitrogen inputs to the cSAC are dominated by the Tamar River.

Ultimately, the potential for nutrient enrichment and localised effects will be determined by physico-chemical and biological characteristics of the site such as flow, seasonal variability, flushing, tidal regime, primary production and reactivity with sediments 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 - reflected by an increase in chlorophyll $\alpha$ concentrations. Dissolved oxygen levels in the water column fluctuate during the growth phase of a 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.

Some of these changes are quantifiable and, in addition to nitrogen, phosphorus and ammonia, a range of other parameters can be measured for determination of 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, although the principal inorganic form is orthophosphate and is measured as dissolved orthophosphate (soluble reactive phosphate SRP), or as total reactive phosphate (TRP) by measuring phosphate in unfiltered samples.

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 $l^{-1}$. Freshwater entering estuaries usually has a N:P ratio of >10, therefore the water column, particularly at the freshwater end of the estuary is more likely to be P- than N-limited, although saltmarshes are usually N-limited (Cole *et al* 1999).

Published information on nutrients and related water quality data in the Plymouth Sound and Estuaries cSAC mostly relates to the Tamar, although this generally includes the lower reaches (the Hamoaze) as far as Devils Point. An early study of major nutrients in the waters of the Tamar Estuary (Mommearts, 1969) found higher phosphate content at Plymouth City level and suggesting localised pollution. Similarly, Morris *et al* (1981) report a pronounced localized maxima for phosphate in the lower 10km of the estuary, indicative of significant inputs to this region. The authors found that anthropogenic discharges had a major influence on the distribution of phosphate throughout the estuary but only minor localized effects on the distributions of nitrate and silicate which both showed essentially conservative mixing behaviour in the estuary. Nutrient concentrations reported in this study were up to 3.05, 3.85 and 0.034mg $l^{-1}$ for N, Si and P (respectively) in the upper (freshwater)

estuary, and 1.0, 1.3 and 0.06mg $l^{-1}$ for N, Si and P (respectively) in the lower 10km of the estuary.

Knox *et al* (1986) carried out a total of 11 axial surveys of nutrients in the Tamar between January 1975 and June 1977 and also found, almost without exception, conservative mixing behaviour for nitrate in the estuary (highest concentration in freshwater with progressive linear dilution to low N in seawater). The nitrate profile differed on one occasion (July 1976) during this period when unusual conditions triggered an intensive diatom bloom (see below). During the bloom, there was evidence of significant nitrate removal taking place within the estuary. Under normal conditions there were no indications for significant sources or sinks for nitrate within the estuary, and the large amount of nitrate entering in freshwater effectively swamped the influence of smaller fluxes present.

Concentrations of nitrite and ammonium within the estuary were generally correlated and axial profiles of both exhibited estuarine maxima indicating production in the upper reaches of the estuary (Knox *et al.,* 1986). This was attributed to production in the sediment augmented by water column nitrification in the region of the freshwater/brackish water interface. A previous study of ammonium in the estuary had also indicated that ammonium profiles were dominated by sediment input and no significant effects from localised sewage inputs could be inferred (Knox *et al*., 1981). However, Morris *et al* (1985) suggested that net inputs of ammonia and nitrite arising from anthropogenic sources prevailed in the lower estuary and probably exceeded the sum of riverine and upper estuarine sources. Readman *et al* (1986) reported coprostanol concentrations of 1.6µg $g^{-1}$ (dw) in sediment samples taken from adjacent to the road and rail bridges of the Tamar. Coprostanol is one of the principal sterols of human and animal faeces (Martin *et al* 1973) and its presence provides evidence of sewage contamination (Hatcher and McGillivary, 1979).

Morris *et al* (1985) also found an ammonia maximum in the middle to upper estuary and attributed this to releases from the sediment facilitated by tidal sediment disturbance. In this study, nitrite distributions reflected conservative mixing of riverine inputs during the winter months but internal inputs within the low salinity, turbidity maximum zone became increasingly significant from spring to late summer (with a concomitant degree of local oxygen depletion – see below).

MPMMG (1998) reported concentrations of nitrogen species (ammonia, nitrite and nitrate), phosphate and silicate for National Monitoring Programme sites in estuaries and coastal waters throughout the UK. For all nutrients (winter and summer) 50% of results for the Tamar were above detection limits, but not particularly elevated in comparison to other UK sites such as the Humber, Tees and Mersey which receive large inputs of sewage and industrial effluent, the main sources of ammonia.

There is very little specific information on sensitivity of estuarine macrofauna, or on the rare species and special interest features within the cSAC, to nutrient enrichment. For example there have been no specific studies of nutrient impact on *Zostera* communities. Elsewhere, local increases in nutrient levels (e.g. from sewage, agricultural runoff or aquaculture) are reported by some to have favourable consequences for eelgrass beds, usually where *Zostera* growth is limited by available nitrate (Fonseca *et al*., 1987). Eutrophication is more often a cause of the decline, or the lack of recovery of, *Zostera* beds (Borum, 1985; Wetzel and Neckles, 1986; den

Hartog and Polderman, 1975; Kikuchi, 1974). A variety of different harmful effects have been identified: Metabolic imbalance caused by high nitrate concentrations (Burkholder *et al*., 1992); Increased growth of epiphytic and blanketing algae (e.g. Deegan *et al.,* 1997; Borum, 1985; Burkholder *et al.*, 1992; Wetzel and Neckles, 1986; den Hartog, 1987); phytoplankton blooms which can increase turbidity and reduce biomass production (Dennison, 1987); and increased vulnerability to wasting disease (Buchsbaum *et al.,* 1990). Indirectly, therefore, the secondary productivity of benthos will almost certainly be linked to nutrient status through effects on sediment and epibenthic flora, including phytoplankton.

The available published literature does not suggest a major nutrient enrichment problem in the cSAC, however there is a distinct lack of up-to-date information. Studies indicate that sewage discharges in the lower Tamar estuary may have had a significant effect on water quality during the latter part of the 20th century and evidence of sewage contamination in Tamar sediments was reported by Readman *et al.,* (1986).

SWW have made significant investments to improve the wastewater treatment facilities at STWs affecting the cSAC, and predict considerable improvements to water quality[1]: Saltash sewage (primary) treatment works on the Tamar Estuary was closed at the end of 2001 and the flows transferred to Ernesettle, Plymouth. Ernesettle sewage treatment works has been upgraded by adding secondary treatment and UV disinfection. Other (unspecified) estuary improvements planned by SWW between 2000-2005 are at: Calstock and St Dominick (upper Tamar), St Germans, Wilcove and Cremyll (Lynher and Hamoaze) and the Plymouth Central area.
Sewerage from Kingsand and Cawsand has been redirected to Millbrook for secondary treatment. Wastewater from the two villages was discharged without treatment to the streams which flow across the associated beaches prior to 1998, when the adjacent beaches were designated as bathing waters (see section 7.2.7). On the Yealm, storm overflows in Brixton and Newton Ferrers were improved in 2001 and Elburton storm discharge will be improved in the near future. Sanitary standards have been set for the discharge from Newton Ferrers STW and UV disinfection is planned at Brixton STW by 2004 (for summary of water company improvements see annex 7). However, these improvements will have little effect on the nutrient content of discharges (EA pers comm. – see section 10)

OFWAT Regulator has given approval to SWW to make changes to the volume of water abstracted at Lopwell to ensure that the River Tavy is protected from over abstraction although this may not happen until 2005 (EA pers. comm.). This may increase the freshwater flow in the estuary and help to alleviate the problems arising during low flow conditions (see sections on turbidity and siltation, chlorophyll *a* and phytoplankton). Changes are also proposed to the fish pass at Lopwell to improve access for fish over this structure.

[1] http://www.swwater.co.uk/index.cfm?articleid=214

### 5.2.3 Chlorophyll *a*

Chlorophyll *a* concentrations in excess of 10µg $l^{-1}$ are considered indicative of phytoplankton blooms, though not necessarily eutrophication (Anon, 1993). Results for the Tamar Estuary from the NMP programme conducted between 1992 and 1995 indicated maximum values in excess of 30µg $l^{-1}$, among the top ten sites in the UK (MPMMG, 1998). None of the estuaries included in the NMP have been designated as eutrophic waters under the EC Urban Waste Water Treatment Directive because 'there is no evidence of problems caused by the phytoplankton'. It would seem however that more extensive seasonal and spatial coverage may be needed before conclusions are drawn, since distributions are likely to be influenced in estuaries by a complex array of factors.

Knox *et al* (1986) noted an intense bloom of *Cyclotella atomus* in the upper estuary area (salinity ~10ppt) during a nutrient survey of the Tamar in July 1976. Freshwater flow into the estuary was extremely sluggish due to lack of rain, and water temperature was unusually high (23.6°C). The water in the upper estuary was said to be stained yellow-brown by the bloom with a cell count of ~3 x $10^8$ cells $l^{-1}$ and chlorophyll levels of ~$10^3$µg $l^{-1}$.

Investigating seasonal patterns in the Tamar in 1991, Miller (1999) observed the highest chlorophyll *a* concentrations (>50µg $l^{-1}$) during May and June, centred on the upper reaches of the estuary, 7.5 – 17.5km downstream from Gunnislake Weir. In July, the distribution pattern changed and became more evenly spread along the estuary. From August to October the chlorophyll *a* maxima was situated in the mid-estuary. The distribution of chlorophyll *a* concentrations in the Tamar Estuary appear to show broad seasonality and can be over two orders of magnitude higher during the spring blooms of May and June compared to other months (Miller, 1999; see also Section 6 and Section 7.2.5 for other observations on phytoplankton seasonal succession and blooms.)

### 5.2.4 Turbidity and siltation.

We have already described the importance of suspendable sediment behaviour on contaminant (especially metal) distributions in the Tamar Estuary (e.g. see section 5.1.1. 5.1.2, 5.1.3). The reactivity of these contaminants is a function of the highly dynamic and cyclical nature of the suspendable sediment transport system (Ackroyd *et al.,* 1986). Studies of seasonal sediment migration and fluxes of suspended solids indicate that under normal flow conditions a net transport of material towards the head of the estuary by tidal pumping (Bale *et al.,* 1985; Uncles *et al*., 1985). There is a tendency therefore for resuspendable sediment to be continuously accumulated in the turbidity maximum zone in the upper estuary, at the expense of mid-estuarine material. During periods of high river flow, predominantly in winter, there is a tendency for the turbidity maximum to be shifted seaward (notably in extreme events when considerable of erosion of surface layers can occur). This cyclical process allows the mid-estuarine region to be recharged with a fresh supply of particles.

Darbyshire (1996) illustrates some typical turbidity values encountered, under low flow conditions, in the upper estuary over spring and neap tidal cycles. At Calstock, turbidity values range from 29 FTU at the surface at high water to 558 FTU near the bed at low water (spring tide). Over the ebb the increase was gradual but at mid ebb

there was a sharp increase over the whole water column and particularly near bed. Little reduction occurred over LW and again, close to the bed a sharp increase took place in the early flood before declining to wards HW. (Generally turbidity values tend to be higher on the flood tide due to tidal asymmetry: shorter faster flood compared to longer slower ebb). At neap tide a similar pattern occurs but with much lower values (~13 – 128 FTU). Depth-averaged values for Calstock during spring and neap tidal cycles are shown in figure 24 (replotted from data presented by Darbyshire, 1996)

Suspended solids concentrations follow a similar pattern to turbidity (ranges from 10 mg $l^{-1}$ close to the surface to ~500 mg $l^{-1}$ near the bed at Calstock). Upstream levels can be higher, occasionally exceeding 1000 mg $l^{-1}$ at Morwellham. Even higher values may be encountered during periods of high run-off following periods of prolonged rainfall. Further detailed descriptions of longitudinal dispersion characteristics for suspended solids in the Tamar Estuary can be found in West *et al* 1990 and Uncles *et al* 1994. The contribution to the suspended particulate matter made by phytoplankton is sometimes highly significant in the upper estuary as discussed by Jackson et al. (1987).

### 5.2.5 Dissolved oxygen (DO)

There have been observations indicating low dissolved oxygen concentrations in the upper Tamar Estuary during summer low river-flow conditions, with greatest depletions – occasionally as low as 3% DO – usually occurring towards the end of summer (Darbyshire 1996; Harris, 1988, 1992). Historically, these sags have been associated with large numbers of salmonid deaths. For example during the summer and autumn 1989 an estimated 100-200 mortalities were estimated in the upper estuary (Harris, 1992; Darbyshire (1996).

In an attempt to explain the mechanisms for this, the EA Cornwall Area Investigations Team collected samples for various water quality parameters (DO, BOD, suspended solids, $NH_4^+$ and total oxidised nitrogen) over spring and neap tidal cycles, during periods of low river flow, at two sites, Morwellham and Calstock (Darbyshire, 1996). Conclusions were that, at Calstock, during neap tides, extreme salinity stratification occurs throughout the whole tidal cycle resulting in depletion of DO close to the bed (minimum 62% DO -up to 30% lower than surface waters). This suggests an oxygen demand associated with the sediments. During spring tides, transient periods of stratification occurred (over high water and early ebb) creating a similar, if less pronounced phenomenon. The large amounts of particulates brought into suspension sometimes coincides with sags in DO concentrations (further indication of an oxygen demand associated with sediment), however, overall, there appears to be no clear correlation between DO and turbidity. Depth-averaged values (% DO) for Calstock, during spring and neap tidal cycles, and relationships to turbidity are shown in figure 24 (replotted from data presented by Darbyshire, 1996).

It is perhaps not the entire picture however, since the DO sags are predominantly summer events, suggesting a biological component, whereas tidal resuspension occurs year-round. Evidence for this biotic influence arises from observations that the DO sag coincides with peaks in dissolved organic carbon (DOC) and a minimum of chlorophyll fluorescence. Perhaps, as first proposed by Morris *et al*., (1978),

freshwater algae are unable to withstand the osmotic shock of seawater and their deaths lead to the release of DOC which is degraded by oxygen-utilising bacteria. The section on phytoplankton below continues this debate as to the cause of oxygen depletion.

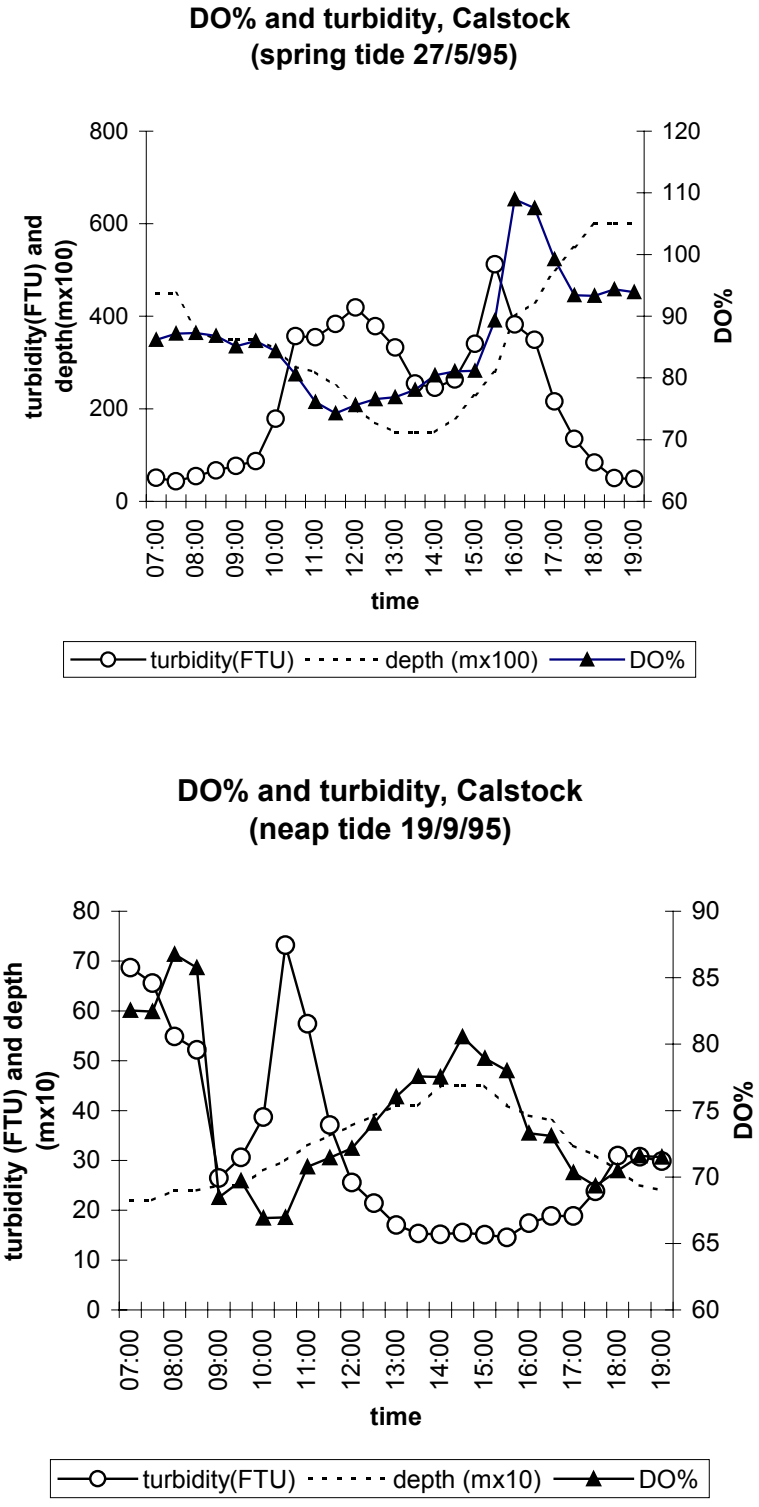



**Figure 24. Profiles for dissolved oxygen (%) and turbidity (FTU) over spring (upper) and neap (lower) tidal cycles at Calstock, Tamar Estuary. Depth profile indicates stage in tidal cycle (redrawn from data in Darbyshire, 1996).**

It is likely that various factors contributed to the salmon mortalities in 1989. These include lengthy drought conditions and relatively high water temperatures (promoting algal growth and microbiological activity), followed by a short period of heavy rain which introduced additional riverine detritus. In addition to lowering DO levels, the resultant conditions may have produced relatively low pH's and high suspended solids (trapped in the upper estuary following spring tides), coupled with associated contaminants. Poor water quality arising from this combination would undoubtedly add to the physiological stress that migrating fish normally encounter during the transition from sea water to fresh water (significant runs take place during spring, summer and autumn in the Tamar; Harris 1992).

It is possible that water abstraction at Gunnislake and Roadford further reduce low river flows. Lowered energy in the estuary may sustain stratification and associated poor water quality (EA pers comm).

The presence of the STW at discharge at Calstock, and other unidentified discharges, is cited as a possible contributory factor (Harris, 1992). Although it served only 1800 people in 1989, the Calstock outfall is sited in a critical position within the estuarine mixing zone and could have imposed an additional reduction in water quality which the salmonids were unable to tolerate. Various recommendations were made at the time to mitigate the effects of low DO on fish, including improvement to water quality. It is not known whether these were implemented by the NRA/EA.

## 6. STUDIES ON BIOLOGICAL COMMUNITIES

The Plymouth Sound and Estuaries Marine Conservation Review (Reay, 1998) provides useful background information on the SAC, whist the Plymouth Marine Fauna (MBA, 1957), compiled from the records of the Marine Biological Association, is a comprehensive species-by-species guide to the distribution of organisms.

Further information on studies relating to key organisms, or groups of organisms are reviewed below.

*Phytoplankton:* The phytoplankton communities of the brackish water region of the Tamar have been studied by Jackson *et al* (1987). During the study period (1982-1983), particularly in summer months, composition in the upper estuary was dominated, sometimes almost exclusively, by 'freshwater'[1] diatoms *Cyclotella atomus* (and to a lesser extent *C.striatica*) - up to a salinity of 8‰. This represents the most productive section of the estuarine water column and algal productivity can be directly related to DO saturation. Originally it was speculated that the salinity-induced death of these algae could be responsible for the DO sags in the upper estuary. However, the study by Jackson and co-workers establishes that significant *C. atomus* mortalities only occurred at salinities greater than 8‰ and did not coincide

[1] Although Jackson *et al* ., (1987) nominally describe *C.atomus* as a freshwater diatom, it appears to thrive in salinities between 0-4‰ in the Tamar and its presence in brackish water is described by other authors. Belcher and Swale (1978) consider it as primarily a freshwater species with halophilic tendencies.

with the region of oxygen depletion. The latter event may be due, in part, to decreased photosynthesis as a result of the low light availability at the turbidity maximum coupled with oxidative degradation of trapped organic matter (Morris *et al* 1982; Jackson *et al*., 1987, see previous section on DO and turbidity).

On occasions the phytoplankton community in the upper estuary was dominated by other species, including the marine diatom *Rhizosolenia delicatula,* though viability of this species diminishes at salinities below 4‰. In addition to the diatoms *C. atomus* and *C.striatica,* other freshwater species included the green alga *Nannochloris* sp. Dinoflagellates including *Heterocapsa triquetra* and an *Amphidinium* sp generally dominated marine communities, though these tended to contribute little to the biomass (Jackson *et al.,* 1987).

Biomass of algae may reach 8mg $l^{-1}$ in prolonged periods of low flow in summer but are rapidly depleted as algae are flushed out during high run-off events. Tidal cycling in itself does not appear to affect overall productivity to such an extent.

An earlier description of the nature and succession of phytoplankton populations in relation to different salinity zones in the Tamar Estuary (from Plymouth Sound to Pentillie Quay, and also some nearshore sites in the Channel off Plymouth) was given by Mommaerts (1969). Comparisons with the study of Jackson *et al* (1987), illustrate the temporal variability in community data. Over the sampling period between March and September, Mommaerts produced an inventory consisting of 135 different types, of which, 94 were typically marine, 10 were brackish water and 7 were freshwater species. A further 24 species were littoral/benthic species presumably mixed into the water column through resuspension events. Clearly some of the marine species entering the estuary from the sea are entirely allochthonous, transported on the flood tide from Plymouth Sound. Nevertheless, some species having euryhaline characteristics (e.g. *Skeletonema costatum, Procentrum micans, Nitzchia closterium*) are able to find suitable conditions and develop as autochthonous populations, albeit temporary.

During an April survey, species with optimum concentrations in the euhaline region (salinity always above 30‰ – generally seaward of Devonport Dockyard) were *Thalassiosira decipiens*, *Skeletonema costatum* and *Gymnodinium spp.* Dominant species in the mesohaline section (salinity between 5.5 and 18 ‰ – upstream limit Pentillie) were *Katodinium rotundatum, Nitzchia closterium, Cryptomonas spp* and flagellates (Chrysophyta). Again, the principal characteristic was the continuous decrease in diversity upstream, due to the progressive loss of marine species. A dip in diversity was also observed close to the confluence with the Tavy, as a result of the lowered salinity.

Key successional observations of Mommaerts were that from March to April *Nitzchia closterium* was abundant and was succeeded by *Thalassiosira decipiens* (April-September). From June-late summer *Gonyaulax tamarensis* and *Peridinium trochoideum* populations developed. At the end of July a dense population of *Gyrodinium* sp developed in the Tamar and was also abundant off Plymouth. *Skeletonema costatum, Cryptomonas spp, Gymnodinium spp Katodinium rotundatum*

were amongst some of the more obvious species or groups of species that persisted throughout the entire season (Mommaerts, 1969). Overall, the abundance of organisms in Tamar Estuary was interpreted as demonstrating the high productivity of the estuary, sustained by the nutrient inputs from river flows and enriched by urban inputs towards the mouth (*see* 'nutrients').

Further observations on seasonal and yearly changes in phytoplankton off Plymouth over a period of 24 years have been described by Maddock *et al.,* 1989. A high species diversity was recorded throughout the year, together with a strong seasonal cycle. A total of 104 species was divided into eight groups showing different seasonal and year-to-year occurrence. The seasonal pattern of species changed in a fairly systematic way and there were two periods (1968-70 and 1983-85) when the changes were most marked. These patterns could be related to changes in the weather patterns, and were similar to those found by other workers in other groups of organisms and in other areas.

Phytoplankton studies also include investigations of blooms in the Plymouth area and their consequences for other organisms. In the late 1970s and early 1980s a number of dinoflagellate blooms occurred in the western English Channel, composed mainly of *Gyrodinium aureolum* (Boalch, 1983). Toxic effects on both vertebrates (apparent suffocation of fish) and invertebrates (moribund infauna on sediment surface) were manifested when cell densities were > four million $l^{-1}$. Production of toxins which attack respiratory cell membranes, rather than deoxygenation, were the suspected mechanism of toxicity. Red tides caused by *Noctiluca* also coincided with trends in fish numbers, though there was little evidence of any direct toxic effect. At the time of these events it was not known whether dinoflagellate blooms were becoming more frequent, or merely attracting more attention.

*Macroalgae*: In 1973, transects across Blackstone Reef, Wembury, were made (Boalch *et al*., 1974), repeating surveys originally carried out in 1930. The main change in the intervening period appears to have been a decrease in fucoid cover of the reefs. The authors suggest this may have been due to trampling at this frequently visited site. *Ascophyllum nodosum* appears to be particularly susceptible because of its slow growth rate. It was also suggested at the time that increasing numbers of visitors to the site may cause further deterioration to the reef though the creation of the Wembury Voluntary Marine Conservation Area, in 1981, has hopefully helped to halt this trend.

The first occurrence of the invasive seaweed *Sargassum muticum* was recorded in the nearby River Yealm in August 1976. This was the furthest record West since it was first discovered on the Isle of Wight in Feb 1973. Since then, *S. muticum* has spread along the south coast to the Isles of Scilly and along the north Cornish coast to Lundy. Because of its rapid growth and reproductive capacity it competes with native species such as *Zostera* and is considered a nuisance in harbours, beaches and shallow waters.

Conditions between Drakes Island, the Hamoaze and the mouth of the River Plym - classified as outer estuarine - can be very turbid and surface salinity may fall below 30‰. The littoral and shallow sublittoral areas are colonised with a high proportion of open coast species including the kelps *Laminaria digitata, L. hyperborea* and *L.*

*ochroleucha*. The average abundance and ratio of these three Laminarian species are an indication of favourable condition for kelp forest communities in large shallow inlets and bays. *L. ochroleucha* is a south-western species and any changes in the relative proportion of this species may therefore be indicative of long-term changes in water temperature, clarity or wave exposure (EN, 2000).

*Macrofauna:* Probably the most comprehensive record of the distribution and composition of the fauna in Plymouth Sound and Estuaries cSAC is the Plymouth Marine Fauna, first published by the MBA in 1904, revised in 1931 and most recently in 1957. This compilation attempts to describe the make-up of marine fauna in the South West and includes large areas of the Tamar Estuary, Plymouth Sound, the Yealm Estuary (including Wembury) and the Plym Estuary. However, the authors recognised that it was doubtful whether a complete, up-to-date account of the distribution and comparative abundance of all species in an area would ever be possible because of the logistics involved in such a study; this is almost certainly still true today. For a more recent summary of the biota and detailed site description, the reader should refer to the review prepared for the JNCC by Moore *et al*., (1999), as part of their marine nature conservation review (MNCR).

It is probably not useful to reiterate the long lists of species recorded. However, it is interesting that preliminary remarks in the 1957 Plymouth Marine Fauna noted the disappearance of much of the *Zostera* beds in the early 1930s. This, in turn, had brought about considerable changes in the fauna of, among other places, Cawsand Bay (from which seagrass had gone completely at that time) and the Yealm Estuary (whose faunal assemblages had been 'much reduced in abundance and in stature').

There are sporadic reports of seahorse (*Hippocampus*) species in, or close to, the marine site - associated with areas of seagrass, their normal habitat. Occasional specimens of *Hippocampus ramulosus* have been recorded west of Plymouth on the south coast of Cornwall, often in warmer years[1], and one juvenile male short-snouted seahorse *Hippocampus hippocampus* was caught in the Plymouth area in 1998. This was the first definite record of this species from mainland Britain[2]. Little is known about the extent of seahorse populations nationally, there is an ongoing survey initiated by the MCS to establish their conservation status.

Table 20 (Allen *et al.,* 2000) shows interest features of the cSAC and some of the important fauna now associated with those habitats. This is not a definitive list and a brief description of additional notable macrofauna and key studies follows:

[1] http://www.wildlifetrust.org.uk/cornwall/wow/audit2/act_r1.htm
[2] http://ourworld.compuserve.com/homepages/BMLSS/NMA.htm

**Table 20. Macrofaunal organisms of importance associated with interest features of Plymouth Sound and estuaries cSAC. (adapted from Allen *et al.*, 2000)**

| Marine Habitats of Interest | Subfeatures | Important Organisms Present at the Site | | | | | |
|---|---|---|---|---|---|---|---|
| | | Fish | Molluscs | Crustaceans | Annelids | Sponges | Miscellaneous |
| Large shallow inlets and bays | Intertidal Rock and Boulder Shore | | *Hiatella arctica* | | *Myxicola aesthetica*<br>*Polydora spp* | | *Dendrodoa grossularia* (sea squirt) |
| | Subtidal rocky reef | | *Okenia elegans* (Sea slug) | | | sponges | *Aiptasia mutabilis* (anemone)<br>soft corals<br>*Eunicella verrucosa* (sea fan)<br>hydroids<br>bryozoans<br>*Ophiopsila arenea* (brittle star)<br>*Alcyonum digitatum* (dead mans fingers)<br>*Amphianthus dohrnii* (anenome) |
| | Kelp forest communities | Important nursery area for crabs and lobsters | | | | | |

**Table 20 (cont)**

| Marine Habitats of Interest | Subfeatures | Important Organisms Present at the Site | | | | | |
|---|---|---|---|---|---|---|---|
| | | **Fish** | **Molluscs** | **Crustaceans** | **Annelids** | **Sponges** | **Miscellaneous** |
| Large shallow inlets and bays (cont.) | Subtidal mud communities | | *Philine aperta* | *Goneplax rhomboides* (angular crab)<br>*Calianassa subterranea* (burrowing shrimp)<br>*Upogebia delturna*<br>*Upogebia stellata* | | | *Edwardsia claparedii* (anenome)<br>*Ophiura spp* (brittle star)<br>*Virgulaira mirabilis* (sea pen) |
| Estuaries | Subtidal mud communities | feeding grounds for juvenile fish, eg. Solea solea | | | | | |
| | Intertidal mixed muddy sediment communities | | *Cerastoderma edule* (cockle)<br>*Ostrea edulis* (native oyster) | | | | |
| | Subtidal mixed muddy sediment communities | | | | | | *Hartlaubella gelatinosa* (rare hydroid) |
| | Estuarine bedrock, boulder and cobble communities | | | *Balanus crenatus* (acorn barnacle)<br>*Carcinus maenas* (shore crab) | *Sabella pavonia* (peacock worm) | *Hymeniacidon perleve* (orange peel sponge) | *Cordylophora caspia* (hydroid) |

**Table 20 (cont)**

| Marine Habitats of Interest | Subfeatures | Important Organisms Present at the Site | | | | | |
|---|---|---|---|---|---|---|---|
| | | **Fish** | **Molluscs** | **Crustaceans** | **Annelids** | **Sponges** | **Miscellaneous** |
| Estuaries (cont.) | Saltmarsh and reedbed communities | nursery areas for juvenile bass and other fish species | | | | | |
| Sandbanks which are slightly covered by seawater all the time | Eelgrass bed communities | seahorses | cuttlefish | swimming crabs | | | anemones |
| | | | | hermit crabs | | | *Echinocardium cordatum* |
| | | | | Shore crabs | | | brittle stars |
| | Gravel and sand communities | | *Spisula elliptica* | | *Pisione remota* | | *Echinocardium cordatum* |
| | | | *Dosinia lupinus* | | *Polygordius lacteus* | | |
| | | | *Gari tellinella* | | | | |
| | | | *Glycera lapidum* | | | | |
| | Muddy sand communities | | *Abra alba* | | *Melinna palmata* | | |
| | | | *Chamelea gallina* | | | | |
| | | | *Thyasira flexuosa* | | | | |

Pipefish S*ygnathus acus,* the rare sea slug *Stiliger bellulus* and the nationally rare hydroid *Laomeda angulata* are found in the *Zostera marina* bed in the entrance to the Yealm (Cellars Beach). In a series of transects across part of the seagrass bed, Webster *et al* (1998) found 83 associated species, representing 6 phyla, 9 classes and over 50 families of macro-invertebrates. Dominant species were polychaetes (35spp), bivalves (20spp) and amphipods, (13spp).

Sea anemone *Sargatiogeton undatus* and the sea squirt *Morchellium argus* have also been recorded at Cellars Beach but are not normally found in this type of habitat. Other species of interest in the Yealm are the tentacled lagoon worm *Alkmaria rominji* which has statutory protection under the revised list of species (Wildlife and

Countryside Act 1981) and *Hartlaubella gelatinosa,* an unusual estuarine hydroid found on bedrock in the upper reaches of the estuary (Mears, 1997).

The abundance of the common intertidal barnacles, *Chthamalus montagui, Chthamalus stellatus*, *Semibalanus balanoides* and *Elminius modestus* has been monitored since 1951 at a site near Cellars Beach, in the Yealm Estuary (Southward, 1991). The two chthamalids are of warm-water distribution while *S. balanoides* is a boreo-arctic species; thus, changes in the abundance of these species are linked to environmental temperature. The fourth barnacle, *E. modestus*, is an Australasian immigrant that reached south Devon in 1948. It increased during the 1950s on the transect but has since stabilized at a low level of abundance that shows large interannual variations not directly related to temperature.

Between 1951 and 1975 coinciding with a secular decline in sea temperature, there was a long-term trend toward reduction of *Chthamalus* and increase in *S. balanoides*: a trend which has since reversed. Superimposed on the long-term trend was an approximate 10 year cycle in the ratio of barnacle species which had been linked to the 10-11 year solar (sunspot) cycle (Southward *et al.,* 1975), however biological data have since diverged from this pattern and now show less correlation with sea temperature. The TBT-induced disappearance of the dog-whelk *Nucella lapillus* at the site (see section 5.1.2) coincided with changes in the proportions of barnacle species. *Nucella* was present at the site in large numbers in the 1950s and 1960s but numbers gradually dwindled to zero by 1985. Southward (1995) hypothesised that *N. lapillus* (which preys on barnacles and mussels) could act as a structuring factor on the barnacle zone, increasing the rate of barnacle turnover in its presence and reducing the amplitude of change in its absence. This hypothesis cannot now be tested by exclusion experiments due to the overall low population density of *Nucella.* Changing weather patterns and other effects of global climate shift may also be involved, and Southward concludes that, based on the available data, it is difficult to separate the effects of these factors and determine the causes of the changed relationships after 1975.

Continuation of barnacle observations within the SAC should be encouraged and could help to distinguish the other biotic and abiotic factors which control the relative proportions of the species in relation to temperature and climate. Ultimately it may provide an early warning system for the biological effects of global change in climate, which is relevant to all SACs and marine systems.

*Crepidula fornicata*, the non-native slipper limpet is present on the hard substrata of the lower shore at Warren Point in the Yealm, although numbers of this invasive species are not reported (Moore *et al,* 1999). *C. fornicata* is known to have been introduced to Essex between 1887 and 1890 from North America, in association with the American oyster *Crassostrea gigas* (Crouch 1894, 1895; Orton 1912; Fretter & Graham 1981) and showed fairly rapid spread (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.

High densities of *C. fornicata* may 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 (the pseudofaeces of *C. fornicata* smother other bivalves and render the substratum unsuitable for larval settlement) (Fretter & Graham, 1981; Blanchard, 1997). In this way, *C. fornicata* has become a serious pest on oyster beds and has caused many traditional oyster fisheries to be abandoned (e.g. in the Norman Gulf, France) (Blanchard, 1997). However, De Montaudouin *et al*. (1999) showed that *Crepidula* had no major influence on the local density or diversity of smaller coexisting macroinvertebrates and did not affect the growth of 18 month old oysters. At present, there are no indications that the slipper limpet is present in large numbers in the cSAC, but the trend of rising temperatures may precede its spread; Minchin *et al.,* (1995) indicate that temperatures may be an important limiting factor in its ability to develop extensive populations.

The Yealm Estuary opens into Wembury Bay on the open coast feature of the cSAC, where Wembury Voluntary Marine Conservation Area (VMCA) was created in 1981 in recognition of the important and diverse marine life of the area. Wembury VMCA covers the four miles of coast from Gara Point to Fort Bovisand. The nationally-scarce anemone *Cataphellia brodricii* or latticed corklet is found on the lower shore. A rare sponge *Axinella damicornis* is found on the bedrock of reefs, south of the breakwater and the coarse shell substrata off Bovisand Bay is the only site within the cSAC which supports bivalves *Spisula elliptica, Dosinia lupinus, Gari tellinella, Glycera lapidum,* and polychaetes *Pisione remota* and *Polygordius lacteus.*

The central part of Plymouth Sound, between the breakwater and Drakes Island is said to be affected by increased turbidity and occasional reduced salinity (Moore *et al,.* 1999) which are a result of the outflow of rivers into the Sound. Pools and overhangs here are colonised by organisms which are normally sublittoral including the jewel anemone *Corynactis viridis.* This area includes Cawsand Bay, where the rare sea slug *Stiliger bellulus* is present in small beds of *Zostera marina* (Moore *et al.,* 1999).

Further north, off Picklecombe Point, in the sublittoral hard substratum, communities are poorly developed and diversity is reduced (e.g. the common urchin *Echinus esculentus* is absent), and a long slate ridge stretching across to Drakes Island is sparsely colonised (Moore *et al.,* 1999). To the west of Cawsand Bay, scoured kelp communities are found with unusually large numbers of the anemone *Urticina felina* and ascidian *Distomus variolosus* on the stipes. The average abundance of *Distomus* is a measure of favourable condition for kelp forest communities in large shallow inlets and bays as it is sensitive to deviations in salinity and siltation (EN 2000).
Intertidal communities on the limestone bedrock shores of this inner Sound area are dominated by limpets *Patella vulgata,* whilst barnacles *Chthamalus montagui* are less dense than on shores of the open coast. The limestone slopes steeply into the sublittoral and down to form the sides of a deep channel at the mouth of the Hamoaze. Interesting communities of rock-boring bivalves and worms colonise the limestone, typically the piddock *Hiatella arctica*, polychaetes M*yxicola aesthetica* and *spionid Polydora sp.* Similar communities occur off Eastern King Point, with the addition of abundant *D. variolosus*is.

*Polychaete* populations were studied in the region of Stonehouse Creek in the late 1960's by P.E. Gibbs and species listings are archived at the MBA. These may prove a useful reference set to assess ecological changes in this relatively impacted site in the lower Tamar Estuary.

Fish

Probably one of the best accounts of fish populations in the Tamar and Lynher is that of Hartley (1939) who undertook approximately one hundred hauls between November 1935 and December 1937 and consequently was able to give valuable insights into diet, growth and general ecology of commonly occurring and rarer species. These are listed in table 21.

**Table 21. Fish species in the Tamar and Lynher Estuaries with original nomenclature recorded by Hartley (1939).**

| Major species | Occasional species |
|---|---|
| *Pleuronectes flesus* –flounder | *Raia clavata* – thornback ray |
| *Pleuronectes limanda* –dab | *Raia maculata* – spotted ray |
| *Pleuronectes platessa* – plaice | *Clupea alosa*- allis shad |
| *Rhombus laevis*- brill | *Centronotus gunnellus* – butterfish |
| *Solea vulgaris* – sole | *Trachinus vipera* – lesser weaver |
| *Solea lascaris* – sand sole | *Arnoglossus laterna* – Scald fish |
| *Clupea harengus* – herring | *Trigla gurnardus* – grey gurnard |
| *Clupea sprattus* – sprat | *Trigla hirundo* –tub fish |
| *Clupea pilchardus* – pilchard | *Trigla cuculus* – red gurnard |
| *Salmo trutta* – sea trout | *Cottus bubalis* - long-spined sea scorpion |
| *Salmo salar* –salmon | *Labrus bergylta* – bergylt |
| *Anguilla vulgaris* – eel | *Crenilabrus melops* – gilt-head |
| *Sygnathusacus* – pipe fish | *Ctenolabrus rupestris* – goldsinney |
| *Atherina presbyter* –sand smelt | *Zeus faber* – John Dory |
| *Mugil chelo* and *M. auratus* –grey mullets | *Mullus surmulletus* –red mullet |
| gadidae –cod, pout, whiting, pollack | *Spinachia vulgaris* –sea stickleback |
| *Callionymus lyra* – dragonet | |
| Gobiidae –gobies | |
| *Agonus cataphractus* –the pogge | |
| *Caranx trachurus* –horse mackerel | |
| *Morone labrax*- bass | |
| *Scomber scombrus* -mackerel | |

The list is far from comprehensive and there are numerous additions of occasional visitors to the Sound. In particular there has been a progressive spread of southern marine species, northwards, which may be linked to the effect of climate change. Off Plymouth, a gradual trend in demersal species, towards colder water types, was reversed in the 1970s, possibly signifying a switch in climate (Southward and Boalch, 1994). Nevertheless, the list below is probably still fairly representative of the types found in current day seine hauls.

Several species are of obvious commercial and conservation significance of which salmonids and bass are prime candidates. The potential problems faced by the

salmonid population has been discussed in section 5.2.5. Presumably similar stresses may challenge bass, though this has not been reported.

The Plymouth area and Tamar Estuary is a significant spawning and nursery ground for bass, *Dicentrarchus (=Morone) labrax* (Dando and Demir, 1985). Eggs have been found at sea 28 km or more offshore, indicating that spawning may take place relatively close to shore (March/April) though the precise location is not known. The post-larvae are found closer to the shore as they migrate towards the Tamar Estuary. Initially these larvae appear to concentrate at the head of the estuary, perhaps just ahead of the salt wedge, apparently feeding on the copepod *Eurytemora affinis*. Larvae are present in the estuary from May to August and gradually descend seaward as they develop as juveniles. The shallow creeks of the Tamar are void of bass during winter months as the fish move to offshore wintering areas. However fish return in the following spring and may be as old as four before they depart the nursery, finally, for the open sea.

Abundance, growth and first year survival of fish in the Tamar nursery have been followed throughout most of the 1980s and 1990s and show considerable variations between years (Kelley, 2002). Growth appears to be faster, and numbers higher, than in the smaller, but cooler, Camel Estuary in Cornwall. There are no obvious links to water quality, however. Temperature appears most critical: sustained cold spells in 1963 and early 1996 appear to have eliminated most of the previous year classes from the Tamar. In contrast, the hot summers of 1959 and 1976 produced exceptionally strong year classes. Flooding, if it occurs in late summer and autumn is not a problem for the young fish but could be damaging earlier in the year immediately following their arrival as post-larvae (Kelley, 2002). Successful conditions for spawning in recent years appear to have counteracted potentially damaging effects of over-fishing.

The Tamar Estuary is also an important nursery ground for juvenile sole *Solea solea* which usually appear as 10mm larvae in April-May and remain until the end of their second year. Their distribution and movement within the estuary are described by Coggan and Dando (1988).

Allis shad *Alosa alosa* are rare in the UK, although formerly known to spawn in several British river systems, the only recently confirmed spawning site is in the Tamar Estuary. *A alosa* is rare and declining throughout its range on the western coasts of Europe. Relatively little information is available on the habitat requirements of allis shad in freshwater. It grows in coastal waters and estuaries but migrates into rivers to spawn, swimming up to 800km upstream in continental Europe. However, allis shad do not readily traverse obstacles to migration such as dams or weirs, and this has been a major cause of their decline. Adults spawn at night and the eggs are released into the current where they settle among gaps in gravely substrates. Spawning sites tend to be used year after year, and relatively shallow gravely areas adjacent to deep pools are thought to represent optimal spawning habitat. Almost all adults die after spawning.

Population declines in many parts of Europe have been attributed to the effects of pollution, overfishing and river obstructions to migration[1].

No specific studies regarding *A. alosa* in the Tamar are available, although a recent report on the status of shad in the Severn Estuary gives some information on the life cycle and indicates environmental factors which may affect this species (Bird 2002).

*Zostera*

There are reported to be several seagrass beds within the cSAC although the bed in the mouth of the River Yealm is believed to be the most extensive. A study by Webster *et al* (1998) showed a roughly triangular area of *Zostera marina* approximately 20000m$^2$ in Cellars Cove. The shoot density in the seagrass bed was patchy and relatively low compared to other sites (table 22), although this may be due to environmental conditions. Abundance of macrofauna also appears to be lower than that observed in other studies of seagrass beds; however, direct comparisons can be misleading due to several factors, including contrasting sampling techniques and efficiencies, and environmental regimes (Lewis and Stoner, 1981). Webster *et al* (1998) found that in patches of higher shoot density within the *Zostera* bed, there was a corresponding increase in the mean leaf number per shoot, representing an increase in above-ground structural complexity. No significant differences in abundance of macroinvertebrates were found between areas of differing shoot density; however, univariate analysis revealed that faunal diversity increased significantly with shoot density.

**Table 22. Comparison of macro-invertebrate abundance and shoot density found in studies of fauna associated with *Zostera marina* (from Webster *et al.*, (1998).**

| Location | Abundance (macro inverts/ m$^2$) | Shoot density (shoots/ m$^2$) | Reference |
|---|---|---|---|
| Roscoff (English Channel) | 1094 – 27350 | 500 – 800 | Jacobs (1980) |
| Eo Estuary (NW Spain) | 13850 - 17835 | 100 – 253 | Currás *et al* (1993) |
| Åland Archipelago (Baltic Sea) | 24994 – 52682 | 50 – 500 | Boström and Bonsdorff (1997) |
| Yealm Estuary (Plymouth Sound & Estuaries cSAC) | 1911 - 12229 | 12 - 144 | Webster *et al* (1998) |

The sheltered bay area of the central Sound includes Cawsand Bay, where small beds of *Z. marina* and its associated fauna are present (Moore *et al.,* 1999). *Zostera* has presumably recolonised this area since its reported disappearance in the mid 20$^{th}$ Century (MBA, 1957), although there are no precise records of its density or extent available. *Zostera* beds were also reported on the lower shores west of the pier on

[1] JNCC.gov.uk

Drakes Island (MBA 1957) although no recent references to seagrass in this area have been found.

The lower Tamar Estuary from Devils Point to the entrance of the Lynher is known as the Hamoaze. The embayment of St Johns Lake, to the southwest of this zone has areas of saltmarsh around its shores and *Zostera spp.* were reported to grow over large stretches (Spooner and Moore, 1940). Beds of *Zostera hornemanniana (*or *Z. angustifolia* as it now known*)* and associated seagrass fauna were also recorded by MBA (1957), however, with the exception of a reference to loose traces of the dwarf seagrass *Z. noltii* in St Johns Lake (Cornwall Wildlife Trust[1]) there are no recent records of seagrass in this area.

The sparse evidence suggests that seagrass beds in the cSAC are relatively impoverished or declining, and 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 (EN 2000) and it is important to identify possible stressors in the vicinity of seagrass beds. Its decline nationally may have serious consequences for the associated rich and diverse fauna, including seahorse populations which are often associated with beds of *Zostera* and fine algae. 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 23 summarises natural events and human activities which may be contributing factors.

**Table 23. 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.<br>• 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 in conditions 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.<br>• Widlfowl 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.<br>• 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. |

[1] http://www.wildlifetrust.org.uk/cornwall/wow/audit2/act_r1.htm

**Table 23 (cont.). Natural events and human activities which may be contributing factors to the decline of *Zostera spp.* (adapted from Davison and Hughes (1998)**

| **Human activities**<br>- 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, epiphtyic 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 24 summarises the key factors which may limit or facilitate seagrass bed recovery in marine SACs and elsewhere.

**Table 24. 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<br>Unusual increases in wildfowl grazing pressure | Healthy and stable epiphyte grazer populations<br>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 |

*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 are declining at a rate of greater than 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 the one Evaluated Species in the Tamar Estuaries complex SPA, namely the Avocet (Armitage *et al* 2002).

No alerts were triggered for Avocet. In fact the population on this site rose by over 25% over the 5 and 25 year periods considered (prior to 2000) and was stable over the 10 year period. Possible adverse factors reported at the site, including changes in water quality resultant from improvements to waste water discharges and recreational disturbance (Armitage *et al* 2002), are therefore not considered sufficiently important to trigger additional investigations into bird populations ('Level 2' assessment).

**Statutory Biological Monitoring.**
Various organisations have undertaken statutory biological monitoring in the Plymouth SAC in recent years. Some of these, and their purpose, are listed below:

South West Water Services Ltd have conducted environmental monitoring surveys of Plymouth sewage sludge disposal grounds in 1990 and 1995 (to comply with the 1974 Dumping at Sea Act and the 1985 Food and Environment Protection Act, FEPA). This comprises 32 grab samples over a 16km$^2$ area, 10km south of the Plymouth Sound Breakwater. In the 1995 survey 179 species were identified.

Devon Wildlife Trust Marine Survey, and Cornwall and the Isles of Scilly Marine Life Records, provide ongoing littoral and sublittoral survey of Devon, Dorset and Cornwall coasts. Results are processed by the Joint Nature Conservation Committee as part of the Marine Nature Conservation Review.

The biological and compliance monitoring programme, to determine whether the conservation objectives for the European Marine Site are being met, now falls under the remit of the Tamar Estuaries Consultative Forum and is one of the principal components of their Management Plan (see Tamar Estuaries Consultative Forum, 2001, for full list of responsibilities). Collation of biological data to allow judgement on the condition of each feature within the site will be primarily the responsibility of EN. Targets for the monitoring programme are detailed in EN's Regulation 33 package (summarised in Table 1 of this report). Specifically ENs responsibilities are to monitor:

- The extent of all intertidal Annex I habitats
- The extent and species composition of saltmarsh communities
- The extent and distribution of inter-tidal biotope communities
- The distribution of characteristic rocky shore communities
- The composition of low-shore boulder and rockpool communities
- The occurrence of non-native inter-tidal species
- The extent of sub-tidal habitats
- The distribution and species composition of sub-tidal rocky reef communities
- Algal species within kelp forests
- The extent and sediment character of sub-tidal sandbanks
- The species composition of sub-tidal sandbanks
- The extent and distribution of sub-tidal mixed muddy sediments, bedrock, boulder & cobble communities
- The extent and composition of eelgrass bed communities

Annex I bird populations, and their location, are to be monitored by the Wetland Bird Survey (usually based on counts undertaken once per month outside of the breeding season *see above*).

# 7. WATER STATUS AND QUALITY STANDARDS

In this section we examine unpublished data, mainly supplied by EA, of key determinands which may influence the Plymouth Sound and Estuaries cSAC. Summary statistics have been drawn up by the EA (mainly based on the last 15 years in EA listings), and raw data analysed in an attempt to establish further evidence as to whether or not existing water (or sediment) quality is causing impact. Where relevant, temporal trends are discussed otherwise only the most recent data are shown.

It should be noted that much of the data from monitoring surveys 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 it allows at least a crude assessment of water quality issues. With this caveat in mind we have scrutinised summary statistics supplied by the EA of a number of determinands, including dissolved metals. These statistics are broken down in to:

1) effluent streams – to gauge the importance of specific point sources
2) harmonised monitoring points; freshwater site immediately above the tidal limit (to characterise riverine input)
3) tidal waters – a site by site review of data within the cSAC itself.

In the absence of extensive site-specific biological effects information, comparison of water-monitoring results with Environmental Quality Standards (EQS) are used in order to gain a first-order approximation of possible impact on biota. Descriptions of 'risk' to the site, for 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, discussed more extensively in section 10, this is an uncertain supposition. Though acute biological and ecological effects are unlikely below the EQS, subtle sub-lethal effects are possible. EQS compliance is are used here merely help to prioritise those sites and conditions in need of closer investigation and does not necessarily assure Favourable Condition.

## 7.1 Toxic contaminants

### 7.1.1 Metals

Results from the NMP surveys conducted between 1992 and 1995 revealed no evidence that EQS standards (see annexes 1 & 2) for Cd, Cu, Ni, Pb and Zn were exceeded in the Plymouth cSAC though concentrations did increase from offshore, through intermediate, to inshore sites. As indicated in the previous sections this is due to the proximity to inputs as well as natural processes and can give rise to potential water quality issues at estuarine sites, particularly in low salinity regions. These are discussed here on a metal by metal basis.

Copper

Riverine sources to the cSAC have been assessed by comparison of monitoring data for harmonised monitoring points (HMP[1]), or their equivalent, in the various catchments.

The EA database confirms that a number of streams and adits in the Tamar catchment contain elevated Cu (e.g. upto 4400µg $l^{-1}$ in runoff from the Clitters mine, Gunnislake). Though diluted by the main river the net effect on water feeding the estuary at Gunnislake is a degree of enrichment higher than that found in other catchments (figure 25). Median dissolved Cu levels at Gunnislake have been reasonable constant since 1990 (annual median values 9.8 - 16µg $l^{-1}$). Minimum and maximum concentrations over the same period were 5 - 20µg $l^{-1}$.

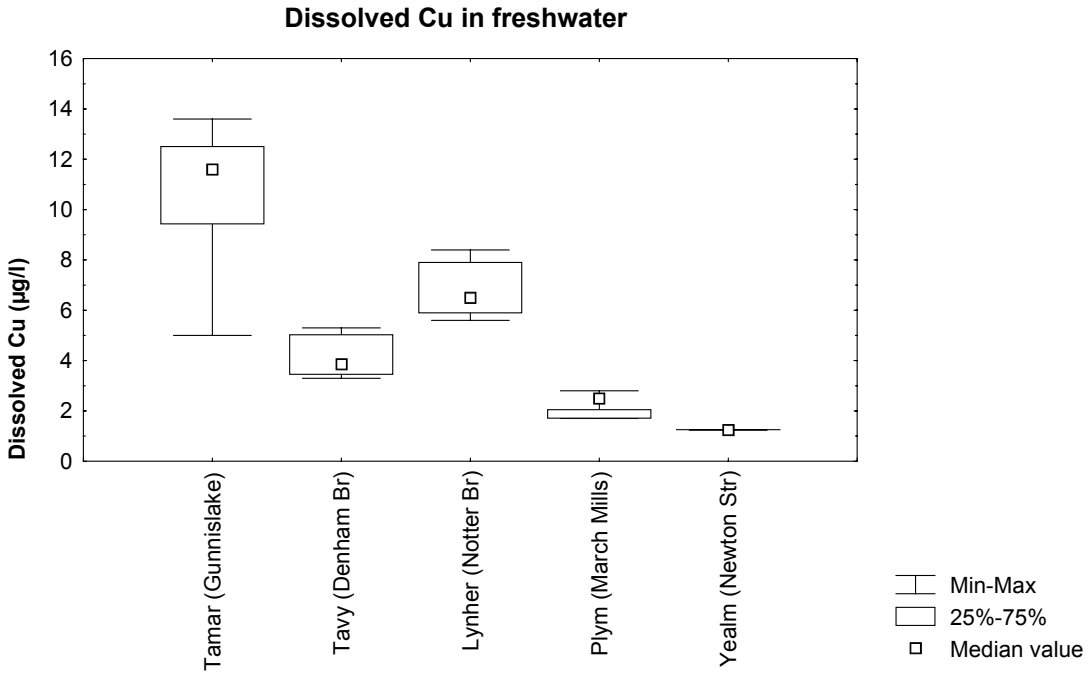



**Figure 25. Concentrations of dissolved Cu at harmonised monitoring points (or similar) in freshwater catchments feeding Plymouth Sound Estuaries. Data are for 2001 except Newton Stream (1998). Data source EA**

In contrast, the Tavy/Walkham catchment is subject to less substantial enrichment than the Tamar (individual sources up to 16µg $l^{-1}$) as reflected in lower annual values at the Denham bridge HMP (figure 25). There are occasional high values in the Tiddy/Lynher Catchment (e.g. up to 265µg $l^{-1}$ in the Marke Valley Stream at Upton

[1] Harmonised monitoring point is usually the freshwater site immediately upstream of the tidal limit used to guage riverine inputs to the estuary. If no HMP data available nearest equivalent site has been taken.

Cross) though the overall effect at the HMP at Notter Bridge implies only marginal enrichment of tidal waters from riverine sources (figure 25).

Net influence of inputs to the Plym catchment, as reflected in monitoring data from Tory Brook, at Marsh Mills indicates a small degree of enhancement (annual median value 4.4-7µg $l^{-1}$ between 1994 and 2002). Discharges from Plympton sewage works seem to contribute relatively little. Trade discharges could be more significant to overall riverine loadings (e.g. Imerys Marsh Mills Dryers - 150µg $l^{-1}$ in 1998). Trade discharges from Chelson Meadows tip may also contribute to localised sources in the estuary and have been increasing in recent years as indicated in figure 26.

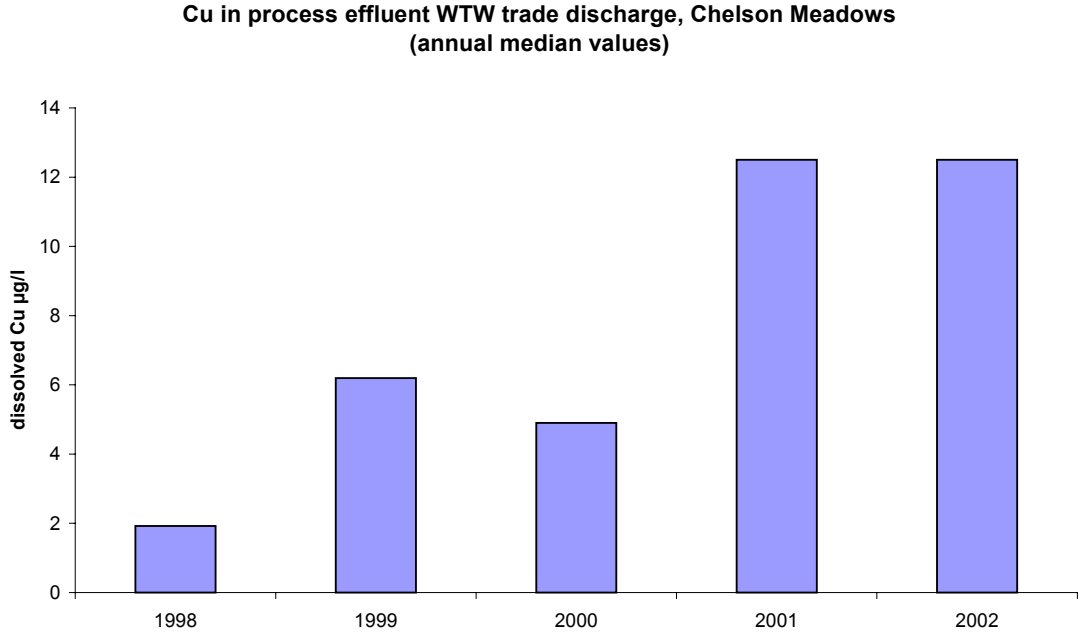



**Figure 26. Cu in process water from WTW discharge, Chelson Meadows showing gradual increase since 1998**

Monitoring data for the Cu inputs to the Yealm catchment are few in number and restricted to Newton Stream at the head of Newton Creek. Meaningful trends are difficult to discern. Some evidence of enhancement here was indicated for 1997 samples (9.1µg $l^{-1}$) but not 1998 (1.25µg $l^{-1}$). Indications from EA monitoring of trade effluents suggests a possible source of localised enhancement from the International Paints Laboratory effluent (annual median values 50 and 12.5µg $l^{-1}$ Cu in 1996 and 1998, respectively; corresponding maxima of 140 and 31µg $l^{-1}$). However from monitoring of tidal waters it seems unlikely that these have a significant effect on estuarine water quality (see below).

Summary statistics for dissolved Cu in tidal waters of Plymouth Sound and estuaries are shown in figure 27 and to a large extent reflect catchment trends i.e generally highest in the Tamar, Tavy and Lynher estuaries and lowest median values in the Yealm and Plymouth Sound. There is little evidence to suggest that individual

discharges are impacting the system. Annual median values throughout the SAC are below the EQS of 5µg $l^{-1}$. Only occasionally do values approach or exceed this threshold.

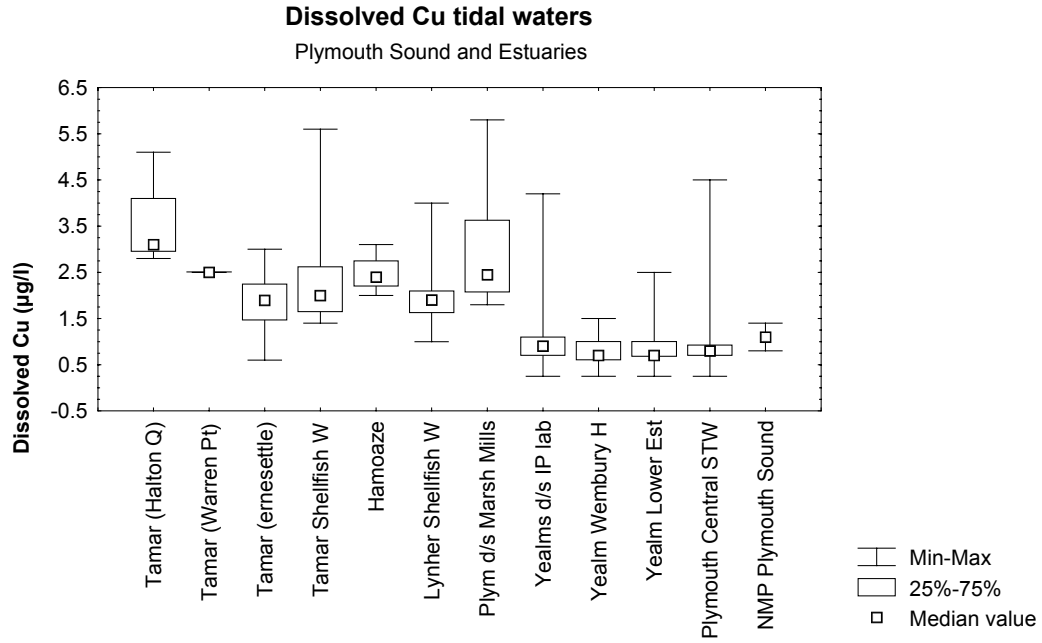



**Figure 27. Concentrations of dissolved Cu in tidal waters, Plymouth Sound and Estuaries. Data are for 2001 except Halton Quay, Warren Pt and Hamoaze (1997) and the NMP site (1994-97). Data source EA.**

Arsenic

In common with Cu there are elevated levels of dissolved As (upto 115µg $l^{-1}$) in the freshwater streams and adits of the Tamar catchment particularly in the Gunnislake area. Effects in the Tamar at Gunnislake are to raise concentrations by approximately 2-3 fold above background (figure 28). A similar level of enrichment is seen in the Lynher catchment (Notter Bridge, figure 28). A slightly higher enhancement is seen in the Tavy (reflected in the HMP data for Denham Bridge). Limited sewage discharge data (Tavistock, Crowndale) indicate a small additional input in augmenting catchment sources in the Tavy (eg Cholwell Brook, Mary Tavy).

The annual median value for the Plym at Marsh Mills is the lowest of all the catchments and suggests little impact from sewage or trade discharges to the Plym. There is little available data for the freshwater Yealm, though the estuarine concentrations suggest virtually little enhancement relative to background (figure 29). Arsenic concentrations in other estuaries display similar trends to their catchments suggesting that these are the dominant sources with little influence from discharges. The low value recorded at the NMP site in Plymouth Sound can be considered a background for seawater.

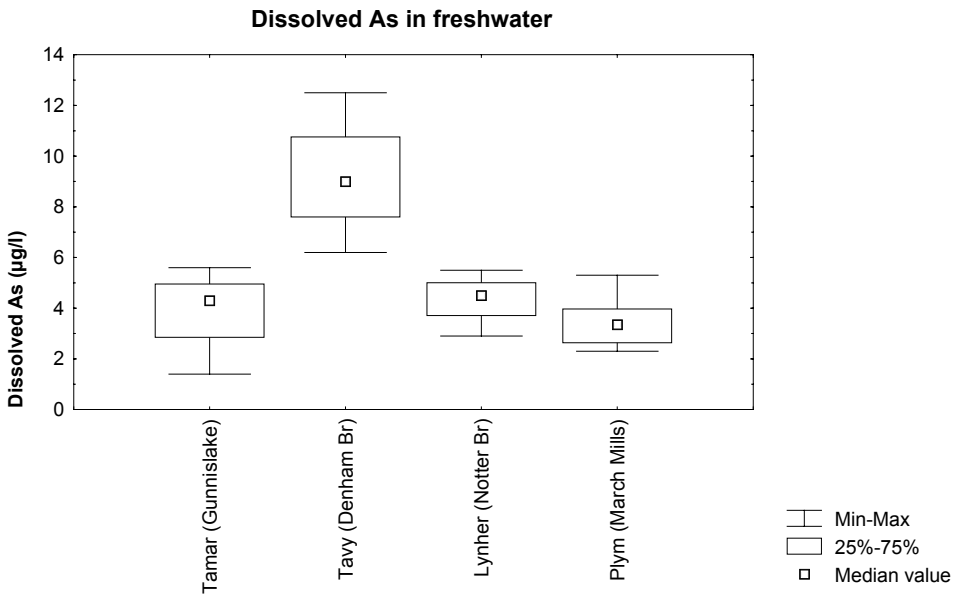



**Figure 28. Concentrations of dissolved As at harmonised monitoring points (or similar) in freshwater catchments feeding Plymouth Sound Estuaries. Data are for 2001. Data source EA.**

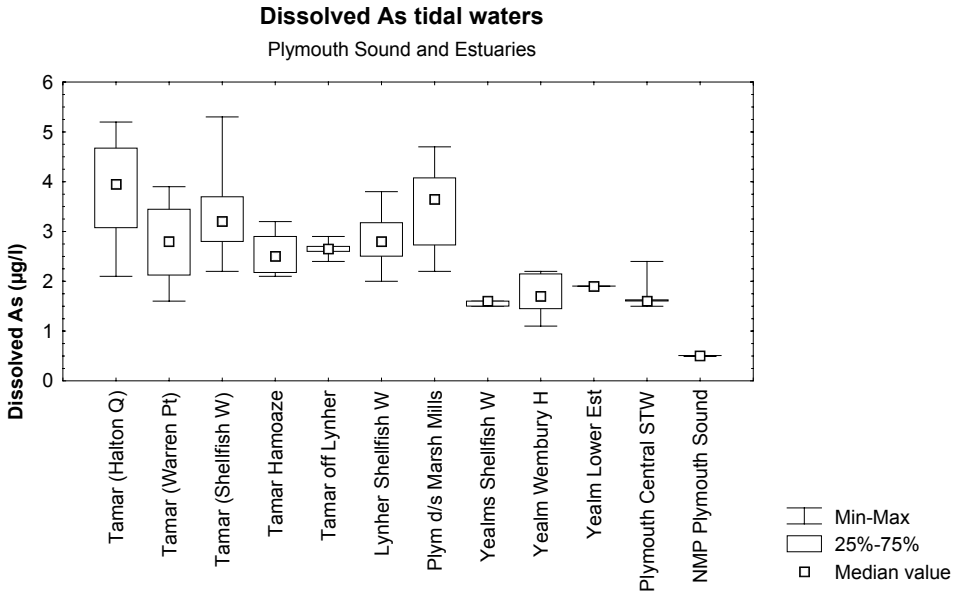



**Figure 29. Concentrations of dissolved As in tidal waters, Plymouth Sound and Estuaries. Data are for 2001 except Halton Quay, Warren Pt, Hamoaze, Plymouth Central and Sound (1997), Yealm shellfish site, Tamar off Lynher (1993), Yealm Lower (2001). Data source EA.**

## Zinc

Data for Zn in freshwater feeding into the Plymouth Estuaries again indicate enrichment in most cases (figure 30). Highest Zn concentrations are found in some of the streams in the Gunnislake and Callington area (upto 1674 µg $l^{-1}$ at Blanchdown) however in terms of the major rivers, concentrations are highest in the Lynher (figure

30). Data for river inputs to the Yealm were not available: trade discharges contain relatively high concentrations of Zn, sometimes exceeding 100µg $l^{-1}$, though, as with Cu, effects on estuarine water quality are probably not widespread (figure 31).

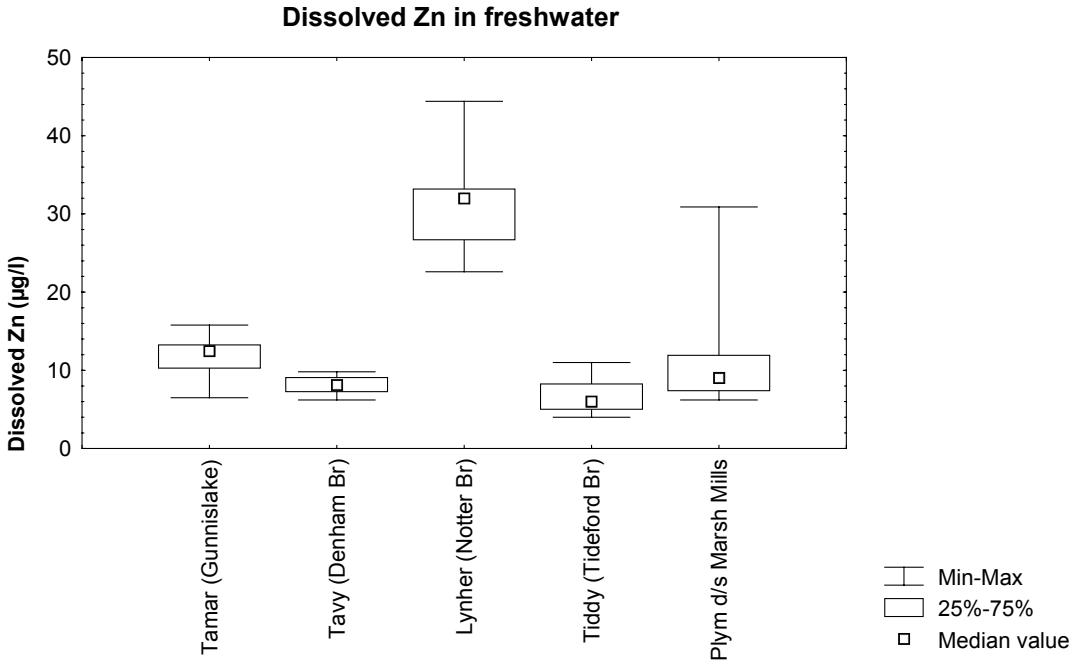



**Figure 30. Concentrations of dissolved Zn at harmonised monitoring points (or similar) in freshwater catchments feeding Plymouth Sound Estuaries. Data are for 2001 except Tiddy (1994). Data source EA.**

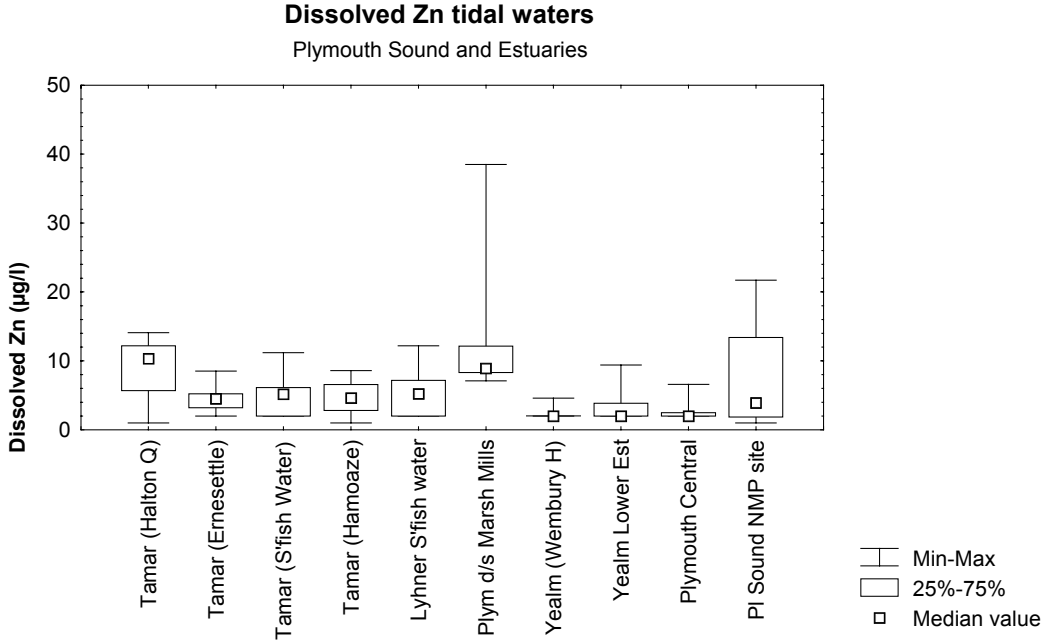



**Figure 31. Concentrations of dissolved Zn in tidal waters, Plymouth Sound and Estuaries. Data are for 2001 except Halton Quay and Hamoaze (1997) and the NMP site in Plymouth Sound (one sample in each of years between 1994 – 1997, which may account for apparent variability) .**

Annual median values for tidal waters are shown in figure 31. Though enhancement is evident for the upper Tamar and Plym, medians are well below the current EQS for Zn of 40µg $l^{-1}$. Proposals[1] to reduce this to 10µg $l^{-1}$ would bring these sites close to the threshold. It is not inconceivable that STW could have a localised impact on water quality. Table 25 shows summary statistics for effluent and surface boil samples influencing the Hamoaze.

**Table 25. Dissolved Zinc in STW effluent and surface boil samples, Hamoaze, 2001.**

| | Zn µg/l | | |
|---|---|---|---|
| | minimum | maximum | median |
| PLYMOUTH (ERNESETTLE) S T W - EFFLUENT | 9.52 | 79.8 | 16.7 |
| PLYMOUTH (CAMELS HEAD) S T W - SURFACE BOIL | 5.3 | 29.1 | 9.95 |
| TORPOINT TREVOL OUTFALL - SURFACE BOIL | 6.2 | 31.3 | 14.3 |
| DEVONPORT DOCKYARD OUTFALL NO.5 - SURFACE BOIL | 2 | 9.3 | 3.05 |

Cadmium

Dissolved Cd in riverine water entering the SAC (Tamar, Tavy, Lynher and Plym) are well below the freshwater EQS of 1µg $l^{-1}$ (figure 32). The somewhat elevated average values for the Lyhner and Plym are probably largely artifactual: most data for these sites are expressed as the detection limit or below. Enrichment in streams and adit drainage in the Gunnislake area (upto 6µg $l^{-1}$) and to a lesser extent the Tavy and Lynher catchment is again evident, but does not appear to have a major impact on estuarine water quality.

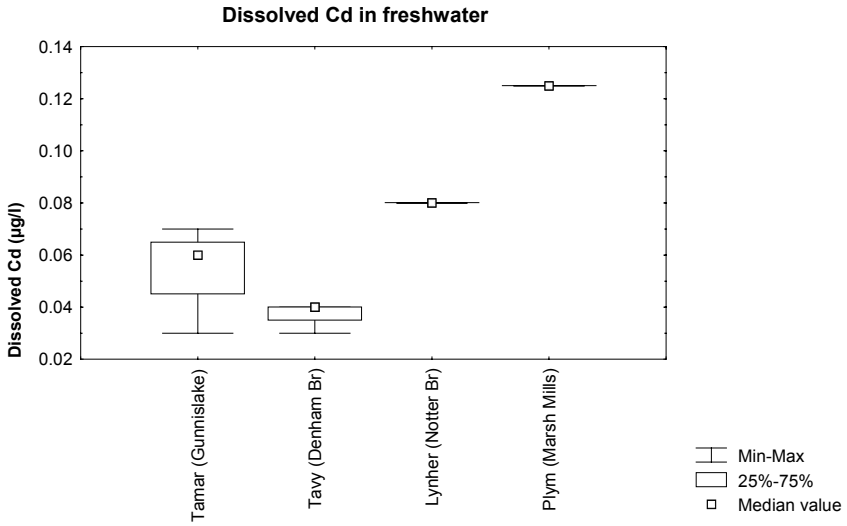



**Figure 32. Concentrations of dissolved Cd at harmonised monitoring points (or similar) in freshwater catchments feeding Plymouth Sound Estuaries. Data are for 2001. Data source EA.**

[1] Following a review of more recent toxicity data, Hunt and Hedgecott (1992) proposed a more stringent EQS to DoE of 10 µg $l^{-1}$, based on the lowest, most reliable NOECs (7 – 20µg $l^{-1}$) though this has yet to be adopted.

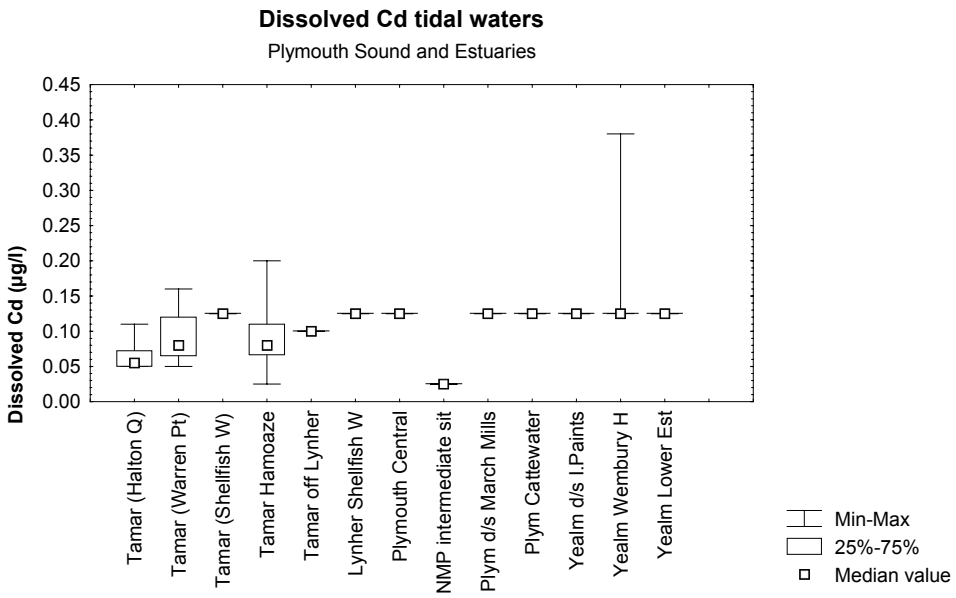



**Figure 33. Concentrations of dissolved Cd in tidal waters, Plymouth Sound and Estuaries. Data are for 2001 except Halton Quay, Warren Pt., Hamoaze and the NMP site in Plymouth Sound (1997); and Tamar off Lynher (1993).**

For many of the tidal sites medians and ranges appear identical as they are at the limits of detection (figure 33). The majority of dissolved Cd values in tidal waters of the SAC are well below estuarine / salt water EQS values (2.5 – 5µg $l^{-1}$). Hardly any of the consents examined have substantial Cd enrichment.

Chromium

Dissolved Cr in freshwater entering the SAC from most of the principal rivers (Tamar, Tavy, Lynher and Plym) are at or close to the detection limits in the EA data base (0.25 - 0.5µg $l^{-1}$). Minor enrichment in mineralised parts of the Tamar, Tavy and Lynher catchment is evident.

A similar picture applies to tidal waters: most values are at or below detection limits (maximum 0.8µg $l^{-1}$) – well below the salt water EQS of 15µg $l^{-1}$. Regarding consents to the tidal waters, highest dissolved Cr concentrations were at the Thanckes oil depot at Torpoint; Chelson Meadows disposal site and, for latest available data in 1998, International Paints (max ~15µg $l^{-1}$ at each of these sites). Clearly however these do not appear to have a major impact on water quality, although this does not rule out the need to consider localised effects such as sediment contamination..

Nickel

Elevated concentrations occur in the Tamar catchment associated with mineralised zones in the Gunnislake area (e.g. Blanchdown stream 67µg $l^{-1}$ annual median value in 1994 –compared to EQS of 50-200µg $l^{-1}$). However concentrations of dissolved Ni in freshwater entering the SAC from most of the principal rivers (Tamar, Tavy, Lynher and Plym) are at or close to the detection limits in the EA database (range 1.5-3.6µg $l^{-1}$).

Dissolved Ni concentrations in all components of the tidal waters of the SAC were correspondingly low (annual averages between 0.9 and 1.5µg $l^{-1}$) – substantially below the EQS of 30µg $l^{-1}$. Several consents to the tidal waters indicated a possible source; notably Chelson Meadows disposal site and, for latest available data in 1998, International Paints (annual average ~25µg $l^{-1}$ at each of these sites). Clearly however these sources do not appear to have a major impact on water quality in tidal waters, although this does not rule out the need to consider localised effects such as sediment contamination.

Iron

There are elevated concentrations of Fe in many of the streams in the Tamar catchment and to a lesser extent the Tavy and Lynher, this is reflected in the riverine concentrations entering the SAC (figure 34). However none of these exceeds the EQS for Fe of 1000µg $l^{-1}$). The most recent available data for the Plym (1996) are also shown in figure 35 and dissolved Fe appears somewhat lower than the other rivers: however there is insufficient data for the Plym to confirm this pattern.

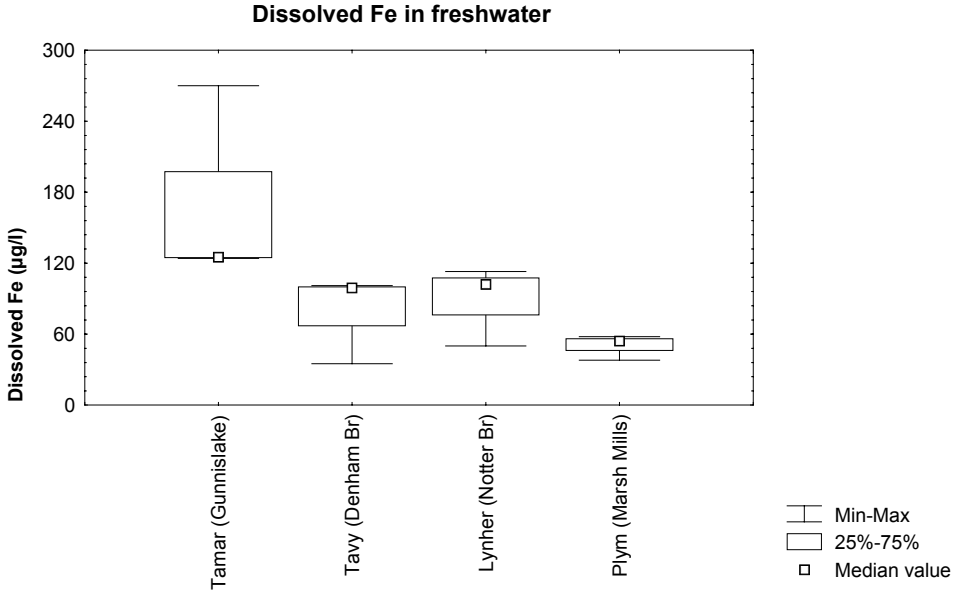



**Figure 34. Concentrations of dissolved Fe at harmonised monitoring points (or similar) in freshwater catchments feeding Plymouth Sound Estuaries. Data are for 2001 except Plym (1996). Data source EA.**

Data for concentrations of dissolved Fe across tidal waters of the SAC are less abundant and less consistent, temporally, than for most other metals. As indicated in figure 35, median values usually fall well below the EQS of 1000µg $l^{-1.}$ There are indications from figure 35 however, that the STW effluents can locally influence levels of dissolved Fe, albeit temporarily. This may be due to the presence of colloidal, rather than truly dissolved Fe (the latter is only sparingly soluble in saline waters).

The highly variable nature and occasionally high levels of 'dissolved' Fe in several consented discharges to the tidal waters and surface boil samples is exemplified in

figure 36. Although annual median values generally fall below 100µg $l^{-1}$, discharges from several sites (Chelson Meadows, Thanckes Oil Depot Torpoint, Ernesettle STW can give rise to dissolved Fe concentrations in excess of 1000µg $l^{-1}$). It is likely that these point sources have only a transient and localised impact on tidal water quality.

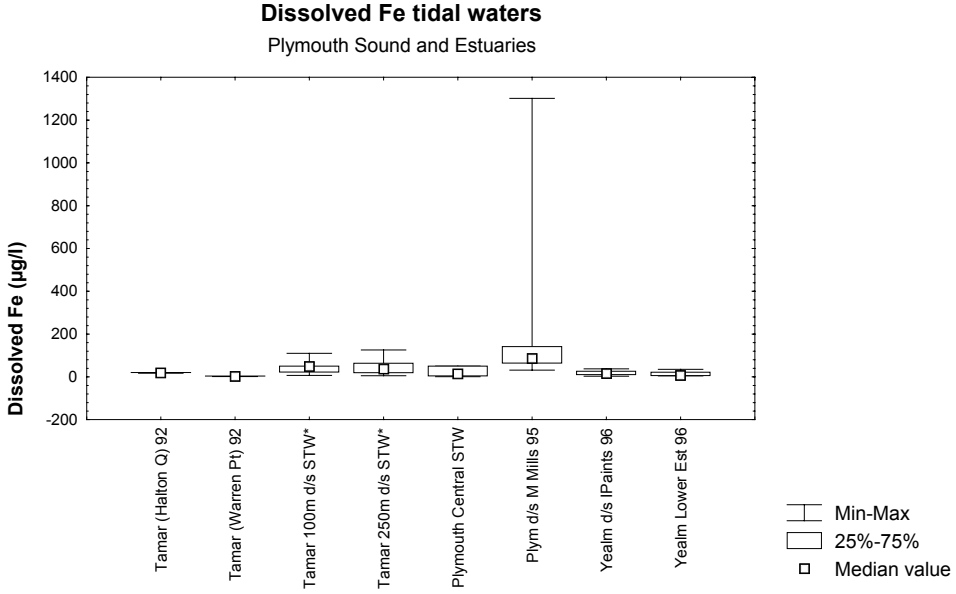



**Figure 35. Concentrations of dissolved Fe in tidal waters, Plymouth Sound and Estuaries. (Data are for 2000 if not specified in labels). * Plymouth Ernesettle STW.**

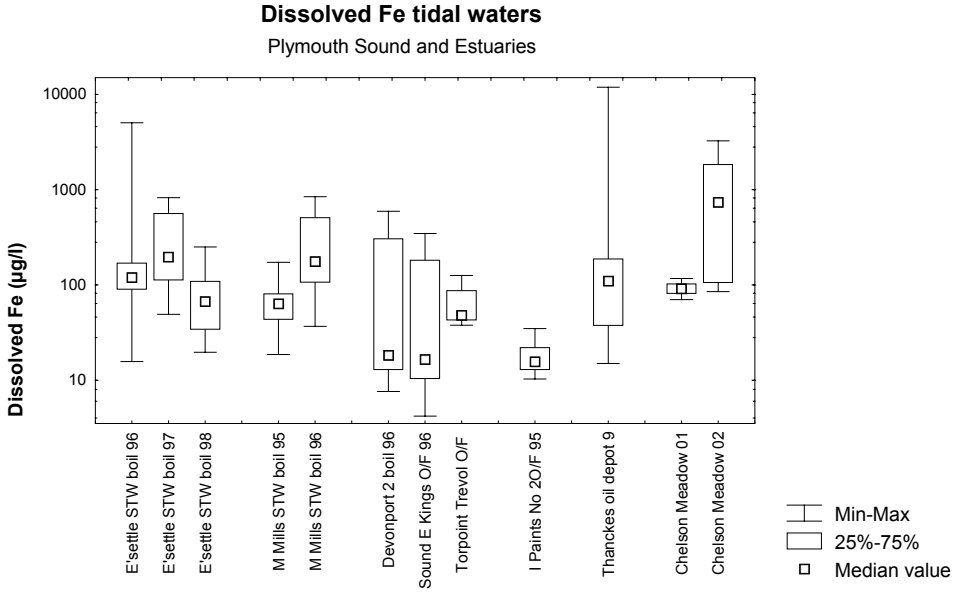



**Figure 36. Examples of elevated concentrations of dissolved Fe in discharges and surface boil samples, Plymouth Sound and Estuaries. (dates are specified in labels). Note logarithmic scale.**

Lead

Lead enrichment occurs in streams in the Tamar catchment (up to a maximum of 20µg $l^{-1}$, and an annual median of 5µg $l^{-1}$) and also the Tavy (up to a maximum of 58µg $l^{-1}$, and an annual median of 8.5µg $l^{-1}$). Riverine inputs to the estuaries are difficult to distinguish as many reported values are close to detection limits (which can differ between sites and times). All are below the EQS (4-400µg $l^{-1}$ depending on hardness). Median values (2001) for the Tamar, Tavy and Lyhner (HMP) sites range between 0.1 and 0.3µg $l^{-1}$, whilst that for the Plym is apparently higher (1.25µg $l^{-1}$), though possibly artifactually so -due to a higher detection limit.

For similar reasons it is difficult to discern trends in the reported data for dissolved Pb in tidal waters, though as indicated in table 26 all values are below the EQS of 25µg $l^{-1}$ for salt water

**Table 26. Annual median values for dissolved Pb ad Hg (µg $l^{-1}$) in tidal waters from Plymouth Sound and estuaries.**

| Site | year | Pb median | Hg median |
|---|---|---|---|
| TAMAR ESTUARY - HALTON QUAY | 1997 | 0.25 | 0.005 |
| TAMAR ESTUARY - WARREN POINT | 1997 | 0.25 | 0.005 |
| TAMAR ESTUARY - 100M DOWNSTREAM OF PLYMOUTH (ERNESETTLE) STW | 2001 | 0.83 | ns |
| TAMAR ESTUARY - 250M DOWNSTREAM OF PLYMOUTH (ERNESETTLE) STW | 2001 | 0.3155 | ns |
| TAMAR SHELL FISH WATER | 2001 | 1.25 | 0.005 |
| TAMAR ESTUARY - OFF LYHNER - NON DESIGNATED SHELLFISHERY | 1993 | 0.25 | 0.01 |
| LYNHER SHELLFISH WATER | 2001 | 1.25 | 0.005 |
| TAMAR ESTUARY - HAMOAZE | 1997 | 0.25 | 0.005 |
| NMP PLYMOUTH SOUND - NEW INTERMEDIATE SITE | 1997 | 0.25 | 0.005 |
| PLYMOUTH SOUND (PLYMOUTH SURVEY) | 1994 | 0.42 | 0.01 |
| PLYM ESTUARY - 100M DOWNSTREAM OF MARSH MILL STW | 2001 | 1.25 | 0.01* |
| YEALM ESTUARY - WEMBURY HOUSE | 2001 | 1.25 | 0.005 |
| YEALM ESTUARY - LOWER ESTUARY | 2001 | 1.25 | ns |

ns -no sample; *1993

STW surface boil and mixing zone samples occasionally show evidence of enrichment (upto ~50µg $l^{-1}$ Pb) as do trade effluent discharges such as Chelson Meadows and International Paint (up to 120 and 10µg $l^{-1}$, respectively). These appear to have only localised influences on dissolved Pb levels, perhaps because lead is rapidly scavenged by particulates.

Mercury

Data on dissolved Hg are limited compared to other metals and most of the reported values for freshwater and tidal waters (table 27) are at, or close to, detection limits (based on half detection limits these are of the order of 0.005-0.01µg $l^{-1}$). Therefore it is not possible to compare trends between different areas. All are below the EQS of 0.3µg $l^{-1}$ for marine waters. Of the small number of discharge samples taken the maximum reported (0.12µg $l^{-1}$) is also below the EQS value.

### 7.1.2 Organotins

Water quality standards for organotins (ng $l^{-1}$) are shown below (table 27).

**Table 27. Water Quality Standards for organotins**

| | |
|---|---|
| Tributyltin TBT | 2 ng $l^{-1}$ MT |
| Triphenyltin TPT (and its derivatives) | 8 ng $l^{-1}$ MT |

M= Maximum T= Total concentration (ie without filtration)

*Tributyltin (TBT).* The EQS for TBT of 2ng $l^{-1}$ is often exceeded, particularly in the estuarine parts of the Plymouth Sound SAC. Acute effects in a range of species such as algae, molluscs, crustaceans and fish are reported to occur at dissolved concentrations of the order of 1µg $l^{-1}$, which is above the range usually encountered. However chronic effects are known to occur in several species down to 1ng $l^{-1}$ and are clearly likely to be of significance in the Tamar cSAC.

It is difficult to produce an accurate synthesis of trends in the EA data due to highly variable detection limits. For example, detection limits for the Hamoaze samples alone range from <2 to <920 ng $l^{-1}$. In contrast some trade effluent data are displayed as > values (e.g. >2069, >7700 ng $l^{-1}$) For the purposes of this brief summary, tidal waters, STW surface mixing zones and effluent concentrations are considered separately. However it has to be stressed that little confidence can be placed on accuracy of the data. It is recommended that in the near future a more systematic surveillance of TBT in the SAC is carried out to establish trends.

Currently, indications are that little TBT enters the system from freshwater: concentrations at the HMP points on the Tamar, Tavy and Lynher all had median annual concentrations of 2 ng $l^{-1}$ TBT in 2001 (i.e at the limit of detection). There is an indication of an overall downward temporal trend in the reported Tamar data at Gunnislake (notably for maximum concentrations which included an exceptionally high value of 180ng $l^{-1}$ in 1997). The same applies to the Tavy at Denham Bridge and the Lynher at Notter Bridge. No freshwater data are available for the Plym or Yealm.

Tidal waters in the upper Tamar also display apparent downward trends though there has to be a question mark regarding some of the maximum values recorded for Halton Quay, and Hamoaze sites the mid 1990s (Halton up to 222ng $l^{-1}$ and Hamoaze up to 500ng $l^{-1}$ in 1997). The most recent information indicates much lower values throughout the system (figure 37). Even so the EQS appears to be breached in several locations in the Lower Tamar and in the Yealm.

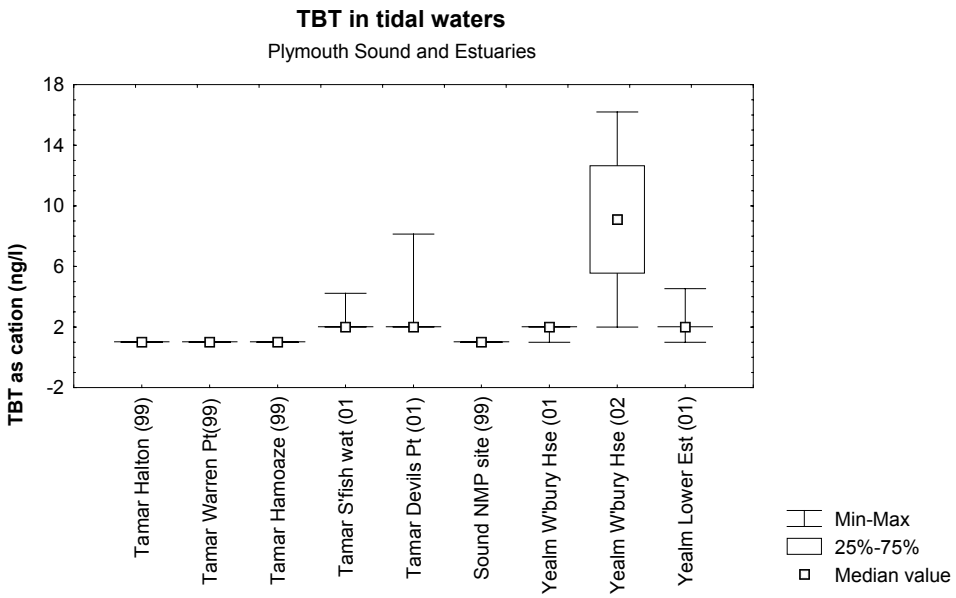



**Figure 37. TBT in tidal waters (ng $l^{-1}$ as cation) Plymouth Sound and Estuaries. (Years specified in labels).**

Surface boil samples (figure 38) indicate that STWs represent a source of TBT, or at least have done until recently: Data for Radford STW shows an apparent downward trend in annual median value since the mid-90's. Again, however this may be artifactual due to changing detection limits.

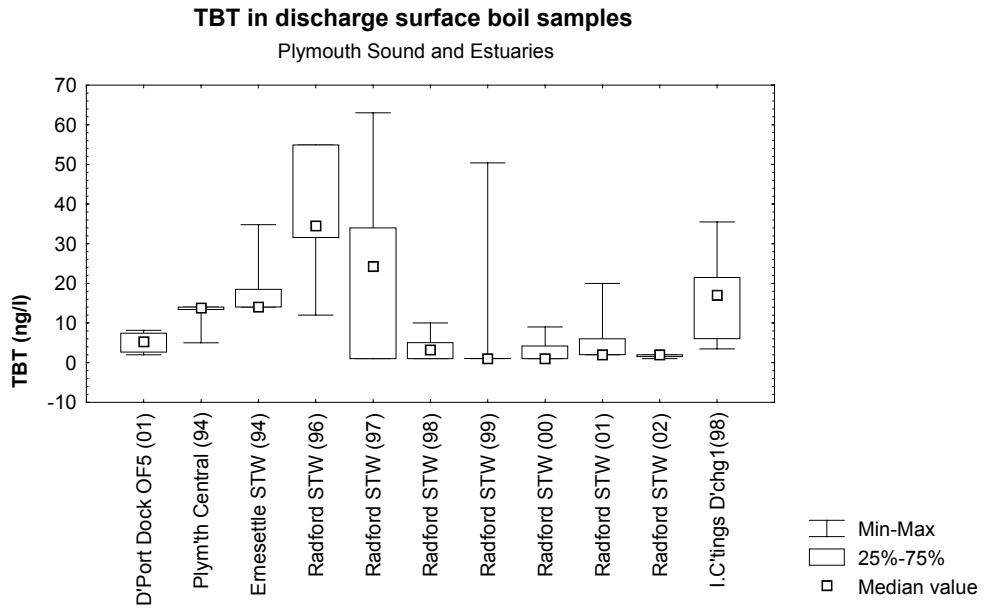



**Figure 38. TBT in Surface Boil samples from STW and other trade effluents. All values are ng $l^{-1}$ reported as TBT cation in EA database except Plymouth central and Ernesettle which are reported as tributyl tin**

Surface boil samples from International Coatings laboratory on the Yealm also show significant enrichment (figure 38). (Discharge no 2 surface boil samples had an even higher maximum of 500ng $l^{-1}$ but a comparable median value). Concentrations of TBT measured in this trade effluent clearly indicate significant enrichment and a possible source to the Yealm, particularly in during the 1990s years. However temporal data shown in figure 39 suggest that concentrations are significantly lower now, compared to the mid 1990s. Nevertheless the 2001 value of 155ng $l^{-1}$ is still cause for concern.

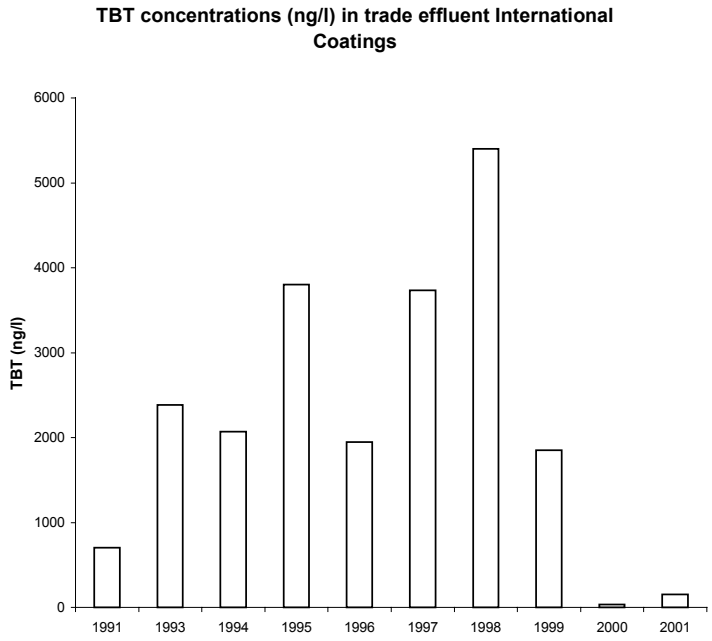



**Figure 39. Temporal trend in TBT concentrations (annual averages) in trade effluent from International Coatings Laboratory on the Yealm.**

By comparison to the IC discharges, TBT concentrations in other trade effluents including Chelson Meadows (max 20ng $l^{-1}$ in 2001) appear comparatively low. Data for STW effluents are also (with the possible exception of Saltash) low in comparison (figure 40) shows latest available values, note most are from the 1990s). Nevertheless, all probably continue to contribute to the chronic TBT loading in the SAC. Further well-designed surveillance is recommended together with an attempt compare loadings from different sources and to draw up a TBT budget for the region.

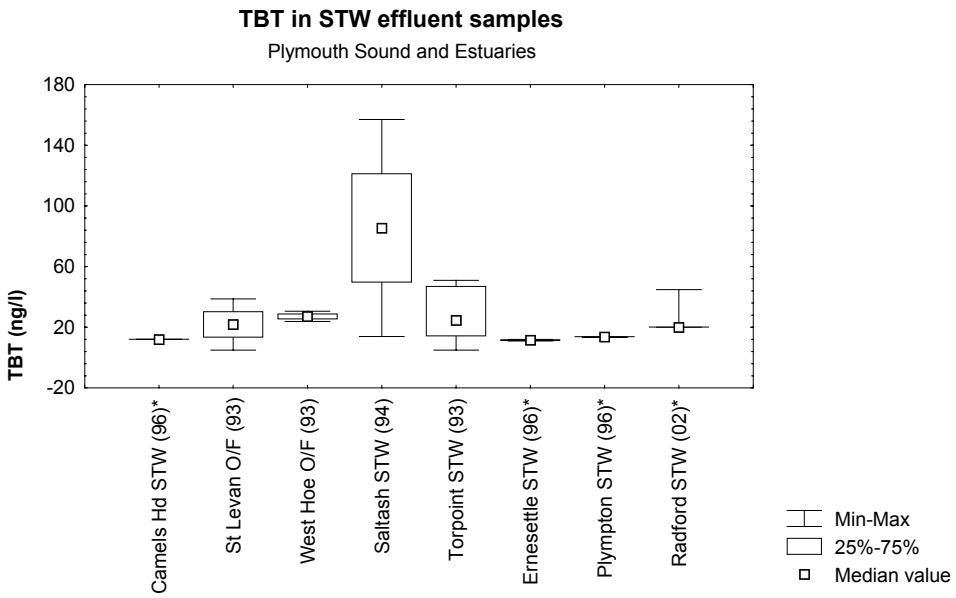



**Figure 40. TBT (expressed at tributyl tin or *tributyltin cation) in STW effluent samples .**

*Triphenyltin (TPT).* The EQS for TPT is 8ng $l^{-1}$. It is even more difficult to produce an accurate synthesis of trends in the EA data due to the fact that most of the data are reported as below (variable) detection limits. For example, the 75 measurements in the Gunnislake region of the freshwater Tamar are below detection limits which range from <12 - <138ng $l^{-1}$ –all above the EQS. A similar picture holds for the Lynher and Tavy catchments apart from a single value of 18ng $l^{-1}$ at Denham Bridge during 1994.

In fact out of a total of some 526 observations in the Tamar/Tavy/Plym/Yealm databases only the 14 samples shown in table 28 are above reported detection limits. Based on this limited evidence some TPT in sewage and trade discharges represent a possible source to the SAC and may be reflected in estuarine water samples close to discharges (demonstrated in table 28 for the Yealm). It is recommended that in the near future a more systematic surveillance of TPT in the SAC is carried out alongside TBT to establish trends in organotins.

**Table 28. Triphenyltin in effluent and estuarine water samples ( EA data set)**

| SAMPLING_POINT_NAME | SAMPLE_DATE | SAMPLE_MATERIAL | TPT ng/l |
|---|---|---|---|
| PLYMOUTH (ERNESETTLE) STW FE | 06/07/93 | FINAL SEWAGE EFFLUENT | 31.7 |
| PLYMOUTH (ERNESETTLE) STW FE | 04/10/93 | FINAL SEWAGE EFFLUENT | 47.84 |
| PLYMOUTH (ST.LEVAN ROAD) OUTFALL | 06/07/93 | CRUDE SEWAGE | 20.5 |
| DEVONPORT DOCKYARD NORTH YARD 5 O/F | 06/07/93 | CRUDE SEWAGE | 57.1 |
| TORPOINT (TREVOL) STW FE | 22/08/94 | FINAL SEWAGE EFFLUENT | 20 |
| DEVONPORT DOCKYARD NORTH YARD 2 OUTFALL | 28/07/94 | CRUDE SEWAGE | 13 |
| INTERNATIONAL PAINTS TRADE EFF. 2 | 10/04/96 | ANY TRADE EFFLUENT | 25 |
| INTERNATIONAL COATINGS MARINE LABORATORY | 21/01/94 | ANY TRADE EFFLUENT | 31.9 |
| INTERNATIONAL COATINGS MARINE LABORATORY | 28/02/97 | ANY TRADE EFFLUENT | 143 |
| INTERNATIONAL COATINGS MARINE LABORATORY | 26/03/97 | ANY TRADE EFFLUENT | 146 |
| INTERNATIONAL COATINGS MARINE LABORATORY | 20/04/94 | ESTUARINE WATER | 20.53 |
| RIVER YEALM - INT. PAINTS SURFACE BOIL 2 | 02/10/96 | ESTUARINE WATER | 18 |
| RIVER YEALM - INT. PAINTS SURFACE BOIL 1 | 02/10/96 | ESTUARINE WATER | 20 |
| RIVER YEALM 100M D/S INTERNATIONAL PAINT | 21/01/94 | ESTUARINE WATER | 17.3 |

### 7.1.3 Pesticides and Herbicides

Data for pesticides and herbicides in tidal waters of the cSAC are generally for the period 1990 – 1997. Up to date values are available for several of these substances in discharge waters, HMPs and designated shellfish sites. Where they occur, (half) detection limits have been used in the derivation of summary statistics.

HCH (total); Gamma-HCH (lindane)

There are few results in the EA database for total hexachlorocyclohexanes (HCH), the majority of results are for gamma-HCH (lindane) used in insecticides. For freshwater and tidal waters detection limits used are generally well below the EQS.

Concentrations of lindane in the rivers Tamar, Tavy and Lynher entering the SAC, expressed as annual median values, have been between 1-2.5ng $l^{-1}$ – below the EQS of 20ng $l^{-1}$ - at all sampling sites. Individual values up to 30ng $l^{-1}$ were observed in the Tamar up to 1997 but since then no individual value has exceeded the EQS.
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 imported from other counties results in lindane residues in sewage effluent. Hence, individual results above the EQS have usually been restricted to the vicinity of known sewage discharges.

Examples of lindane concentrations in effluent samples, many almost almost 10 years old are shown in figure 41. Lindane in sewage effluent and 'surface boil' estuarine waters, have sometimes relatively been relatively high in the past but there is broad evidence of decreasing usage.

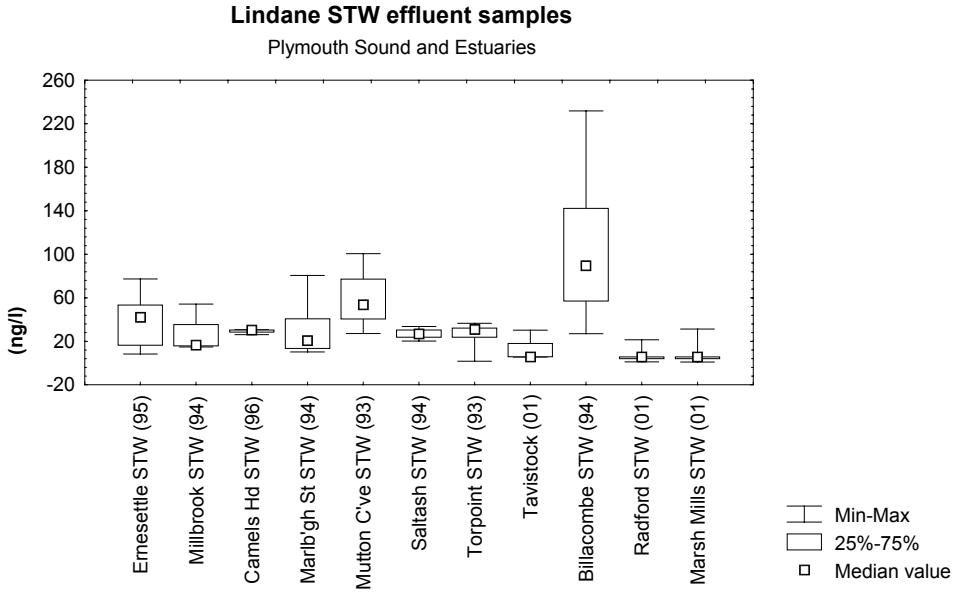



**Figure 41. Lindane (γ-HCH) in STW discharges. Data source EA**

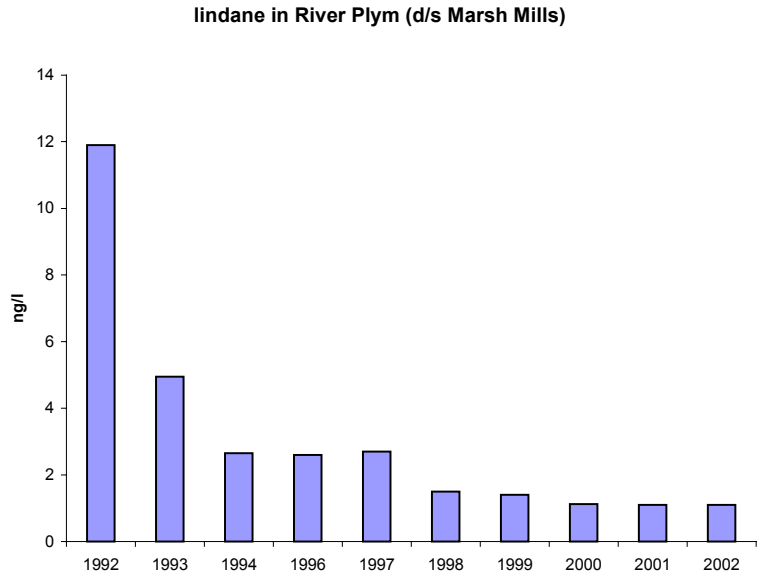



**Figure 42. Temporal trends in concentrations of lindane (annual median, ng $l^{-1}$) in the Plym Estuary below Marsh Mills STW**

Data for the Plym (freshwater samples) downstream of Marsh Mills STW illustrate the reductions of lindane that have occurred during the last decade. Annual averages have decreased tenfold (figure 42) and maximum individual values of up to 70ng $l^{-1}$ recorded in 1993 have been reduced by a similar order

Trade discharges from the Chelson Meadows disposal site introduce some lindane to the system (annual average 5.5ng $l^{-1}$, maximum 11ng $l^{-1}$ in 2001) but do not appear to threaten compliance with the EQS for waters.

Overall impact on sites in tidal waters is shown in figure 43. Highest values were in fact data from almost 10 years ago. All the most recent values are close to the detection limits of around 1ng $l^{-1}$ – well below the EQS.

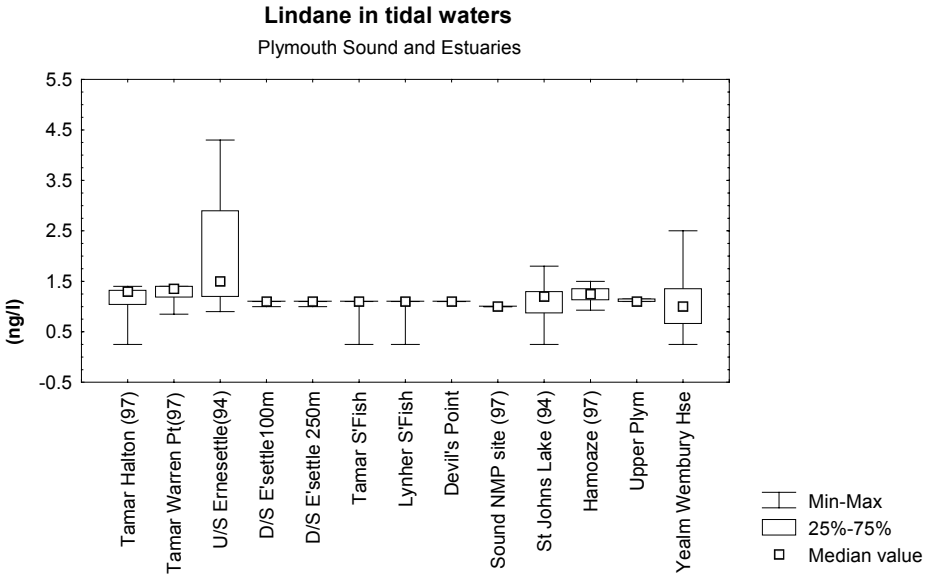



**Figure 43. Lindane (γ-HCH) in tidal waters. (Data for 2001 unless specified)**

DDT

There are no available data for total DDT in waters of the cSAC. Data for para, para-DDT (ppDDT) which is also a list 1 substance, shows that ppDDT in freshwaters entering the SAC at HMPs or equivalent 1990-2001 have been between 0.003 – 0.01µg $l^{-1}$ (expressed as annual average values) and are equal to, or below the EQS of 0.01µg $l^{-1}$ at all sampling sites.

For tidal waters, detection limits used (0.003 - 0.005µg $l^{-1}$) are well below the EQS. Annual average values have been between 0.0002 – 0.01µg $l^{-1}$ with highest values in the vicinity of STWs. No annual average values have exceeded or equalled the EQS 1990 - 1997.

Data for trade and sewage discharges show that individual values up to 0.18µg $l^{-1}$ were observed in discharges from STWs to the Hamoaze prior to 1997, although no individual value has exceeded 0.01µg $l^{-1}$ since then, however detection limits for ppDDT in discharges are set higher (up to 0.3µg $l^{-1}$ in some instances) and may not reveal exceedences.

Dieldrin

There have been occasional exceedences of the EQS for dieldrin (0.01µg $l^{-1}$) in freshwaters at HMPs although since the early 1990's annual average values have been much lower (<0.002µg $l^{-1}$). For tidal waters, elevated concentrations of dieldrin have been recorded in and around the vicinity of discharges, e.g Marsh Mills 0.38µg $l^{-1}$ in 1991, and more recently (2001) Chelson Meadow 0.013µg $l^{-1}$, although values for dieldrin in tidal waters away from these sources were generally around the limit of detection (0.001 - 0.005µg $l^{-1}$).

Aldrin

Similarly, for aldrin the EQS for estuarine waters is 0.01µg $l^{-1}$ and apart from occasional exceedences at HMPs in the early 1990s, annual average concentrations in fresh and tidal waters have been <0.005µg $l^{-1}$. Values for Aldrin were elevated in STW discharges (up to 0.18µg $l^{-1}$ for West Hoe and Billacombe 1992) but between 1993 – 2002 values have been <0.002µg $l^{-1}$, well below the EQS.

Atrazine and Simazine

Atrazine and Simazine are *s*-triazine herbicides and are on the UK red list of toxic compounds with a combined EQS of 2µg $l^{-1}$ (annual average). There are no statistics for the total sum of the two in the EA dataset, but annual averages for each are low (max 0.34 and 0.43µg $l^{-1}$, atrazine and simazine respectively) making exceedences of the EQS very unlikely. Maximum individual values for both simazine and atrazine have occurred primarily in and around STW discharges (up to 3.7µg $l^{-1}$). Away from these sources maximum concentrations of simazine in the cSAC have been recorded

in the Tavy at Denham Bridge and Lopwell Dam (up to 0.16µg $l^{-1}$ in 1999) and probably originate in cropsprays.

Irgarol 1051

There are few values in the EA statistics for the algicide Irgarol 1051 in waters of the cSAC. The available information is limited to 1998 –1999 in discharges from International Coatings, in the Yealm, and associated estuarine waters (surface boil nos 1 & 2). Elevated concentrations in discharges from the laboratory were recorded during 1998, mean and max 1196 and 2063ng $l^{-1}$, and up to 127ng $l^{-1}$ in the surface boil (no 1). For 1999 there is only one value for each of the surface boils during the year and all statistics are recorded as 4 ng $l^{-1}$. Raw data show values for 1999 to be <8ng $l^{-1}$. There is no information for Irgarol 1051 in sediments.

Elevated concentrations of Irgarol 1051 have been reported in and around marinas in the cSAC (see section 5.1.4.), therefore further, and more widespread monitoring of this herbicide is recommended. Antifoulings containing Irgarol 1051 were banned from sale at UK chandlers in November 2001, with a total ban on application to all boats less than 25 metres overall after 24th November 2002.

Endosulfan

Statistics for endosulfan (both isomers) in waters of the Tamar show that the EQS of 3ng $l^{-1}$ has been exceeded at HMPs on the principal rivers, Lynher, Plym, Yealm, Tamar and Tavy between 1990 – 1994, with values of up to 6.8ng $l^{-1}$ (annual average) in the Tavy at Denham Bridge. For tidal waters in the vicinity of discharges e.g, 250m downstream of Ernesettle STW, the information is more up to date (1993 – 2001) although detection limits for endosulfan (7ng $l^{-1}$) are set at more than double the EQS, resulting in many *apparent* exceedences (using half DL for '<'values). Maximum individual values of up to 20ng $l^{-1}$ have been observed in the discharges to the Tavy from Bere Alston STW (1993), although more recently (2000-2001) maximum values are 3-10ng $l^{-1}$ (Marsh Mills and Ernesettle STW discharges).

It does not appear that these sources have significant effects on water quality however, as statistics for endosulfan in tidal waters sites away from the vicinity of discharges are for years 1990 – 1997 and show that concentrations are generally below the LOD of 2ng $l^{-1}$.

### 7.1.4 PCBs

The data on PCBs in waters and sediment are not adequate to assess site characteristics or spatial trends. The best data appears to be for mussels and flounder, though this is extremely limited.

Figure 44a illustrates similar distributions and concentrations of PCB congeners in mussels from three locations in the Tamar and Plymouth Sound. These values do not appear to be unduly elevated. Concentrations in livers of flounder from the Tamar (figure 44b) are an order of magnitude higher, as would be expected (bioconcentration in higher trophic level; higher lipid content) but are not outstandingly high.

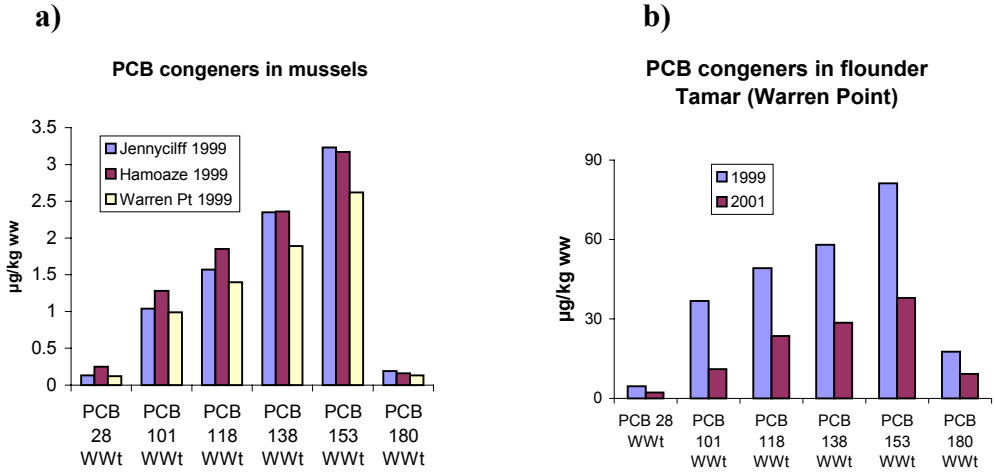



**Figure 44. PCB congeners in a) mussels from the Tamar and Plymouth Sound. b) liver of flounder from the Tamar.**

### 7.1.5 Hydrocarbons (Oil, PAHs)

Hydrocarbon oils

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, 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 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. GESAMP (1993) report studies detecting taints in fish and macro-crustaceans resulting from exposure during acute incidents, chronic discharges and in experimental studies. Experimental studies

indicate that taints can be detected when fish are exposed to concentrations of oil in water in the range 0.01 to 1 mg $l^{-1}$. 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 be still tainted days or weeks after a spill of fuel oil (GESAMP 1993).

There are no reports available for review concerning oil impact in Plymouth Sound and Estuaries. However, the EA database provided limited information on unspecified 'hydrocarbon oils' at a few sites in the cSAC which we include for reference purposes.

Data for 146 water samples (1992-1997) show hydrocarbon oil concentrations to be generally low at the sites monitored, with the exception of one or two sites, annual mean values were mostly <0.1mg $l^{-1}$ and the 90$^{th}$ percentile less than 300µg $l^{-1}$. Notable exceptions were in the Hamoaze, a non designated shellfishery near Jupiter Point in the mouth of the Lyhner where the mean, median and 90$^{th}$ percentile for 1992 were 3.2, 3.6 and 6.1 mg $l^{-1}$, respectively, and the River Tavy at Lopwell Dam where the mean, median and 90$^{th}$ percentile for 1994 were 0.2, 0.06 and 0.5 mg $l^{-1}$. In total, exceedences of bathing waters EQS 90$^{th}$ percentile value occurred at 4 out of 31 sampling sites (although none of these are actual designated bathing waters).

In the absence of recent data for concentrations in water and discharges, or the nature of the hydrocarbons, we cannot comment on the current water quality status with regard to hydrocarbons. It is recommended that this situation be addressed, particularly in the vicinity of shellfish beds.

PAHs

Highest concentrations of PAHs occur in major estuaries and generally reflect inputs from a wide range of combustion processes involving industrial sources. There is a limited amount of information in the EA dataset for PAH concentrations in waters of the Plymouth Sound and Estuaries cSAC, generally PAHs are monitored in freshwater at the HMP or abstraction points, and only occasionally in estuarine waters.

9 PAHs were listed on the database: naphthalene, chrysene, fluoranthene, pyrene, benzo(a)pyrene, benzo(b)fluoranthrene, benzo(k)fluoranthrene, ideno(123-cd)pyrene and benzo(ghi)perylene.

Highest concentrations in freshwater HMPs were for naphthalene (0.25-1130ng $l^{-1}$). The remaining 6 PAHs were present in concentrations of less than 77ng $l^{-1}$, which individually may be considered as low, but in combination may be significantly higher.

Concentrations greater than 1µg $l^{-1}$ (total PAHs) in estuaries are considered to be significant (Cole *et al.,* 1999), therefore total PAH concentration may be a more useful measure of water quality in future monitoring.

## 7.2 Non-Toxic Contaminants

### 7.2.1 Nutrient Quality Criteria.

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 Plymouth Sound and Estuaries cSAC, 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 N and P in estuarine and marine SACs, 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 Plymouth Sound and Estuaries cSAC, 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 phosphorous 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 threshold for eutrophication and is currently under review.

- The North Sea Status report stated that hypernutrification in sea water exists when winter (maximum) **TIN 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, 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** 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).
-

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 is 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 be grouped according to the following class boundaries (table 29):

**Table 29. 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 these thresholds would apply to the Plymouth Sound and Estuaries cSAC or how valid they may be. Nevertheless, in the absence of site-specific guidelines they at least represent benchmarks as to the potential threats, against which to draw comparisons. Based on these criteria, and published data from other estuaries, it is possible to attempt a brief analysis of nutrient monitoring observations supplied by the Agency including;

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

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.

We have used measurements of total inorganic nitrogen (TIN), nitrate, total reactive phosphate and ortho-phosphate as markers of nutrient status in different regions of the cSAC. (Nitrate typically makes up the largest proportion of TIN inputs to estuaries, with nitrite and ammonia usually accounting for < 10%).

{Note: 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 FW) P is thought to be limiting and at N:P ratios < 10:1 (mainly in SW) N is thought to be limiting (though there are 3 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). In many estuaries however enrichment may be such that nutrients are more likely to promote algal growth; turbidity may be the limiting factor instead (Parr *et al.,* 1999).

**Table 30. 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** |

Cole *et al*., (1999) made a comparison of the nutrient status of UK estuaries, having extrapolated freshwater values (from seawater values) on the basis of conservative mixing. Using these criteria, the projected classification for TIN is above average for the Tamar, Lynher and Yealm, grading them as A, B and B respectively. Projected TRP for the Yealm is high, almost twice the average whilst TRP is projected to be very low for the Tamar and Lynher resulting in grades D for the Yealm, and A and B for the Tamar and Lynher (table 30).

**Table 31. TIN and TRP in waters entering Plymouth Sound and Estuaries cSAC based on observations 1999-2001. (Data source: EA)**

| Estuary | Year | Median TIN conc. (mg $l^{-1}$) in freshwater | GQA TIN class | Median TRP conc. (mg $l^{-1}$) in freshwater | GQA TRP class |
|---|---|---|---|---|---|
| Tamar | 1999 | 2.84 | A | 0.05 | A |
| (Gunnislake) | 2000 | 2.9 | A | 0.05 | A |
| | 2001 | 2.34 | A | 0.04 | A |
| Lynher | 1999 | 3.2 | A | 0.06 | A |
| (Notter | 2000 | 3.49 | A | 0.03 | A |
| Bridge) | 2001 | 3.22 | A | 0.08 | A/B |
| Yealm | 1999 | 8.85* | B/C | 0.06 | A |
| (Newton | 2000 | 7.11 | B | 0.08 | A/B |
| Stream | 2001 | 6.27 | B | 0.06 | A |
| U/S STW) | | | | | |
| Yealm | 1999 | 2.66 | A | 0.08 | A |
| (Puslinch | 2000 | 2.66 | A | 0.07 | A |
| Bridge) | 2001 | 2.72 | A | 0.17 | B |

* 1998 data - not available for 1999

Actual EA data for TIN and TRP in waters entering the cSAC for subsequent years (1999-2001) allows cSAC waters to be classified according to the same scheme (table 31).

TRP values for the three selected estuaries are significantly lower than the projected FW concentrations described by Cole *et al.,* (1999), and still result in the classification of grade A and A/B for the Lynher. The Tamar and the Yealm would now be classed as grade A and A/B respectively (compared to B and D, previously). Note that one sampling site now used by the EA in the freshwater Newton Stream is upstream of a sewage treatment works (Newton Ferrers). There is no information in the EA database for freshwater below the STW.

TIN values for the selected estuaries are also lower than Coles' projections for the Tamar and Lynher, resulting in the classification of A. The Yealm itself is also classed as A but TIN values for Newton Stream result in B and B/C. It is not known for certain whether the discrepancies are artifactual (a result of using real measurements as opposed to modelled values) or the result of genuine changes in water quality. However the latter explanation seems unlikely since there is no

evidence of widespread temporal change in Agency data. Nevertheless, this example serves to illustrate the problems of assessing nutrient status.

There are other schemes which estimate the nutrient status from freshwater load inputs, thus encompassing point source discharges. Dong *et al.,* (2000) calculate estuarine nutrient loads by multiplying annual average of all nutrient concentration measurements for contributing rivers, by the annual freshwater flow, however there is scope for error in that diffuse freshwater sources entering directly into the estuary will not be accounted for, likewise estuarine sources such as those which occur in the Tamar 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. 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 distribution of key determinands in finer detail: Data for different parts of the cSAC and its catchment are treated separately in an attempt to further apportion sources of nutrients.

### 7.2.2 Phosphate

Riverine sources of phosphate entering the SAC have been assessed by comparison of monitoring data for harmonised monitoring points (HMP), or their equivalent, in the various catchments (figure 45).

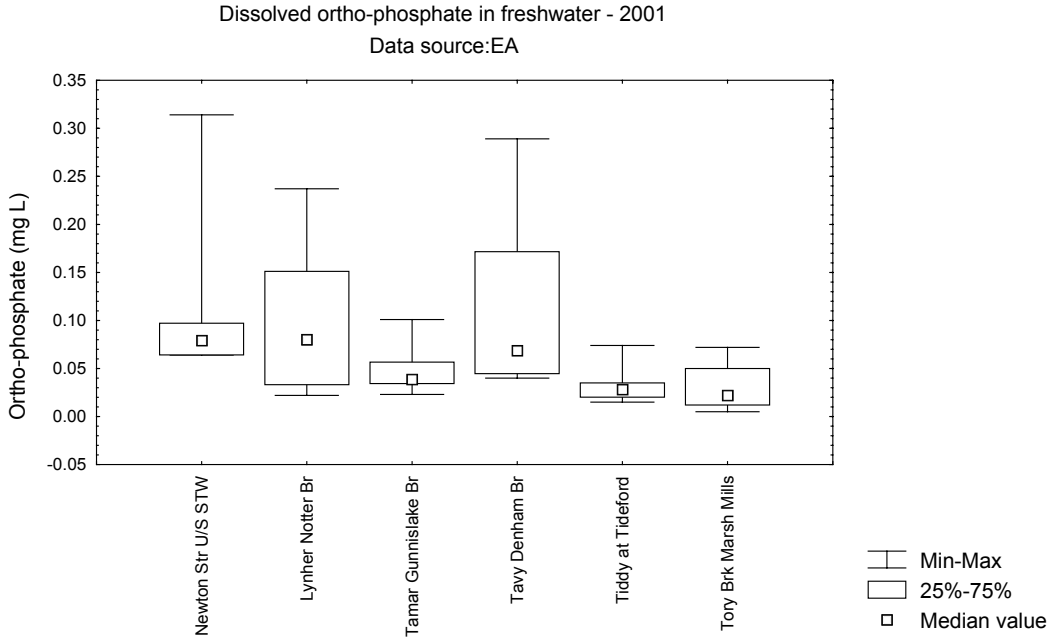



**Figure 45. Concentrations of dissolved Orthophosphate at harmonised monitoring points (or similar) in freshwater catchments feeding Plymouth Sound Estuaries. Data are for 2001. Data source EA.**

Median phosphate concentrations are somewhat elevated in freshwaters entering the Lynher and Tavy. Also phosphate levels in Newton Stream which joins the Yealm at Newton Ferrers are high, more so in waters at the confluence below the STW where the average phosphate concentration (1998-2000) was 0.39mg $l^{-1}$ (EA 2000)[1]. These levels have been relatively constant since 1990, whilst for the Lynher at Notter Bridge, and the Plym (Tory Brook at Marsh Mills), phosphate concentrations have been gradually increasing over the 11-12yr period. The trend is toward a decrease at the three other HMPs.

Elevated phosphate concentrations in a number of streams in the catchment areas are recorded in the EA database (1990-2002), (e.g. up to 8.6mg $l^{-1}$ in Milton Brook which joins the Tavy at Lopwell Dam) and 7.4mg $l^{-1}$ Coads Green Stream which runs into the Tiddy).

Data for phosphate in tidal waters of the cSAC are for the period 1990-1997, as the EA ceased this type of monitoring in 1997. (For clarification: routine monitoring ceased. Monitoring instead became targeted to particular estuaries, N.Cunningham, *pers comm.*). In tidal waters of the respective estuaries of the cSAC, elevated concentrations in riverine inputs are generally reflected (though diluted by the main river) in the vicinity of tributaries, e.g. the Yealm, where phosphate in Newton Creek dominates statistical plots, and the Plym where high concentrations occur (figure 46).

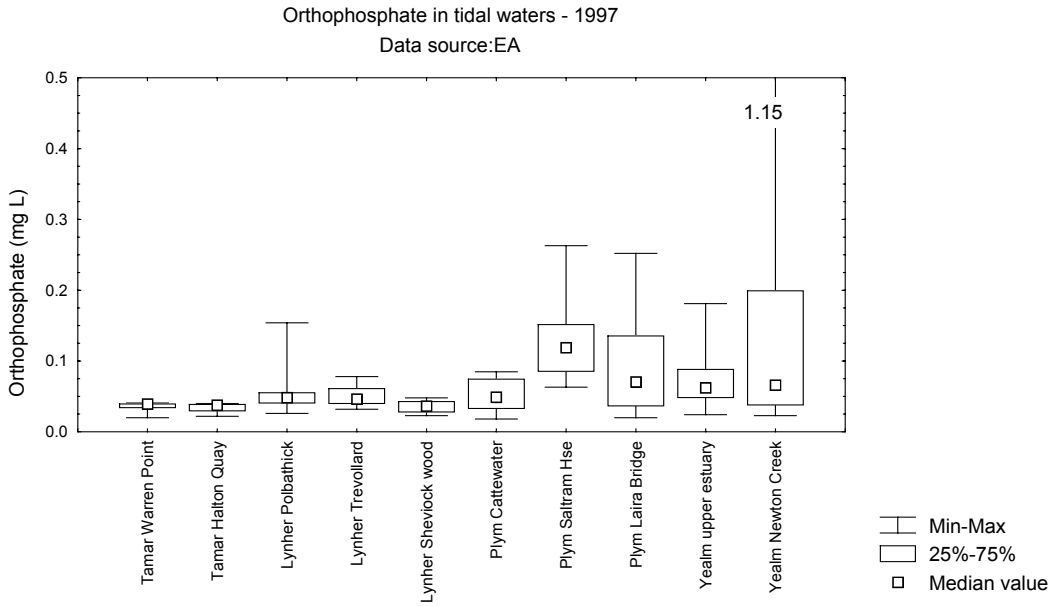



**Figure 46. Phosphate concentrations (mg $l^{-1}$) in tidal waters of Plymouth Sound and Estuaries. 1997.Data source: EA**

Similarly, for other tidal waters of the cSAC the more elevated phosphate concentrations (up to 0.26mg $l^{-1}$) occur near freshwater and point source inputs: River Plym by Saltram House, the Tamar at Morwellham, the Lynher at Polbathic and the

[1] http://www.environment-agency.gov.uk

Hamoaze at St Johns Lake, and reduce away from these sources; <0.01 – 0.02mg $l^{-1}$ at the NMP in Plymouth Sound.

Calculated as elemental P, the approximate background for the tidal waters (25$^{th}$ percentile) in component estuaries is in the range 1.63 – 27.9µg $l^{-1}$, invariably above the 0.1µg $l^{-1}$ criteria set by the EPA(US) to protect estuarine and marine organisms, but generally at the lower end of the range reported by Parr *et al* (1999) for coastal waters (7 – 165µg P $l^{-1}$).

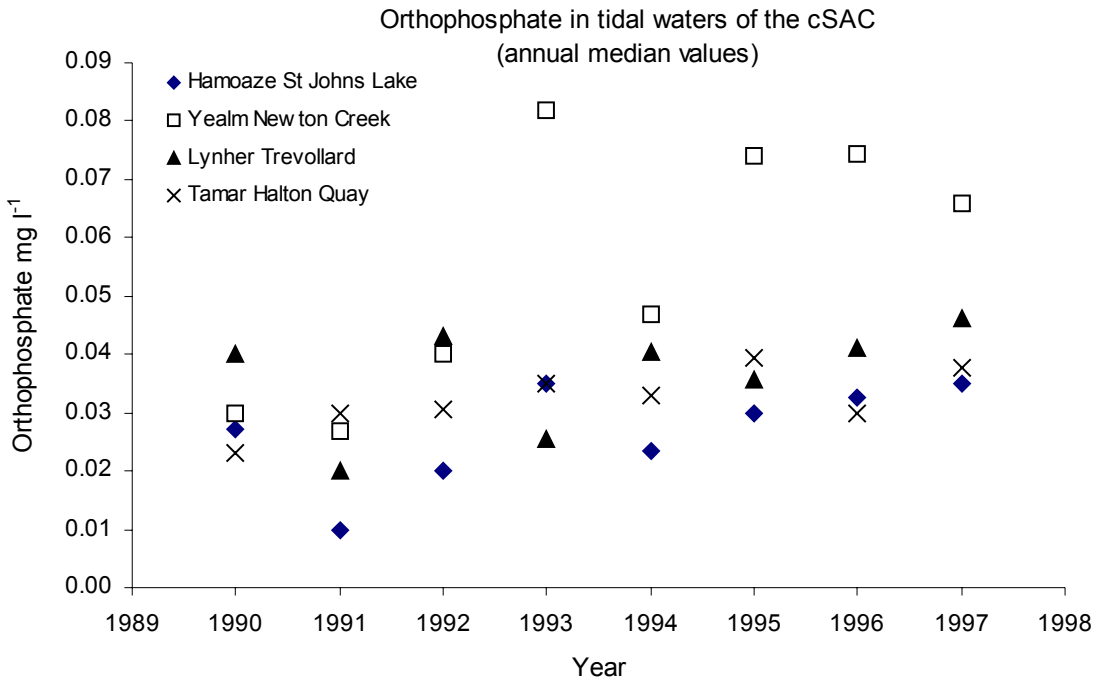



**Figure 47. Orthophosphate in tidal waters of the cSAC: examples of temporal trends since 1990.** Data source: EA

Statistical analysis of the data shows a general trend towards increasing phosphate levels for much of the tidal waters between 1990 and 1997, notably at all monitoring sites in the Lynher, all but one in the Yealm, and Tamar and Tavy, and 6 out of the 11 Hamoaze sites. Examples of these trends are shown in figure 47. Decreases have occurred in both the Plym and the Hamoaze at 3 sites, although phosphate concentrations in tidal waters of the Plym were still relatively high (up to 0.26mg $l^{-1}$) when monitoring ceased in 1997.

The freshwater catchment of the Tamar (and other estuaries within the cSAC) lies wholly within a region of intensive mixed arable and dairy farming and the lower catchment is underlain by impermeable bedrock with freely draining soil. Annual runoff is estimated at 775mm (Fraser *et al.,* 2000) and rapid runoff occurs once the soils become saturated in the early part of the winter. Livestock and fertilisers therefore represent a potentially large source of phosphates in freshwaters of the

cSAC and undoubtedly contribute to the phosphate load. However, for both fresh and tidal waters, the more elevated phosphate concentrations occur in the vicinity, or downstream, of STW discharges: Annual median phosphate concentrations in treated effluent from Lee Mill STW which discharges in to the freshwater Yealm, and Radford STW, discharging into the Plym at Cattewater, were increasing between 1991 and 1997 (annual maximum 12.3 and 8.9mg $l^{-1}$ respectively). Phosphate levels also gradually increased in discharges to the Tavy from Tavistock (Crowndale) STW between 1990 and 2002, annual maximum 8.1mg $l^{-1}$ (only 1 sample for 2002). In some cases other sources are also implicated; levels of phosphate in the Plym Estuary at Saltram house are probably attributable in part to discharges from Imerys China Clay works, both to Tory Brook on Lee Moor, and to the River Plym at Marsh Mills, which augment phosphate inputs from Marsh Mills STW discharge.

### 7.2.3 Nitrate

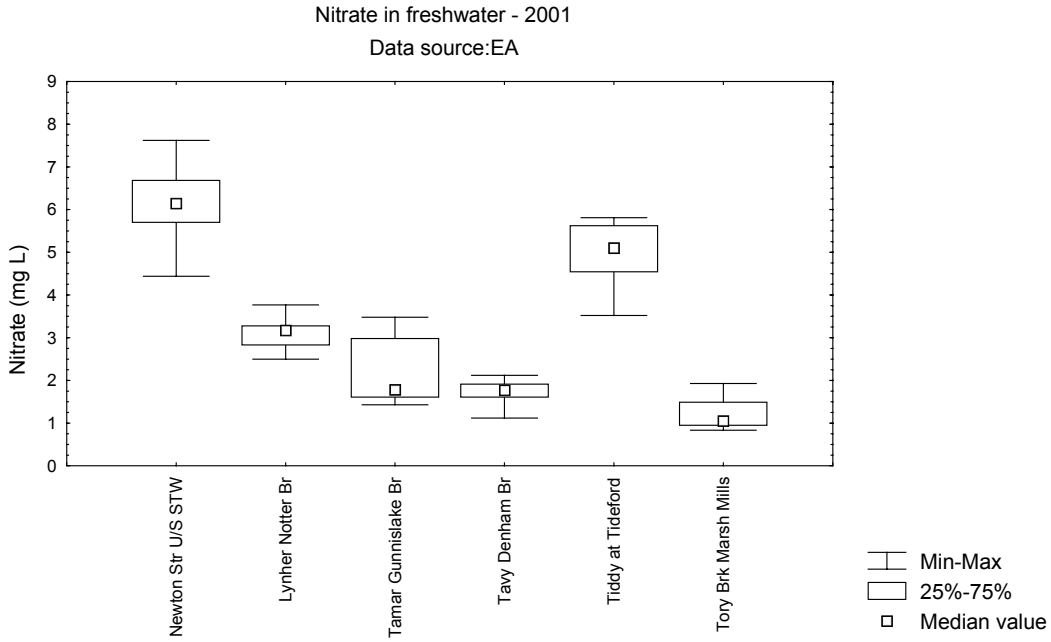



**Figure 48. Concentrations of nitrate at harmonised monitoring points (or similar) in freshwater catchments feeding Plymouth Sound Estuaries. Data are for 2001. Data source EA.**

Freshwater values for nitrate at HMPs or equivalent in the cSAC are shown in figure 48. In streams and rivers (e.g Newton Stream, Milton Brook, Tamar, Tavy, Tiddy, Wembury Stream) mean values (and 25$^{th}$ and 75$^{th}$ percentiles) are generally below the lower threshold of 10mg $l^{-1}$, only occasionally do values exceed this. The annual 25$^{th}$ percentile values in freshwaters for 2001 are calculated to be between 0.2 and 5.7 mg $l^{-1}$, which arguably approximates to a background reference for the area. Nitrate concentrations were increasing in Newton Stream, the Lynher and the Tamar 1990-2002, no other long term trends were apparent for HMPs.

Values for nitrate in tidal waters are generally for dissolved (filtered) nitrate as N), and have therefore been re-calculated here as nitrate values. Dissolved nitrate concentrations in tidal waters of the Plymouth Sound and Estuaries cSAC are for the period 1991 – 1999. Maximum values (up to 27.86mg $l^{-1}$) occur in the Lynher (Polbathic) and the Yealm (Newton Creek), but are below the EC nitrate Directive's 50 mg $l^{-1}$ threshold for any waters. No long-term trends are discernable from the annual data, mainly because individual sites were not generally monitored for more than three years during the period. Two exceptions are Halton Quay, in the Tamar, where annual median nitrate concentrations were increasing between 1991 and 1999, and Warren Point, also on the Tamar, where median concentrations were decreasing in the same period. Even so these observations are based on only five values.

Figure 49 summarises the most recent complete year's data available (1997) for nitrate in tidal waters of the cSAC. Ten sites with highest median concentrations are shown to give an indication of nitrate 'hotspots'. The highest median value (10.05mg $l^{-1}$) is for the Lynher Estuary at the confluence of the River Tiddy, whilst the most extreme concentration (26.8mg $l^{-1}$) was recorded in Newton Creek in the Yealm.

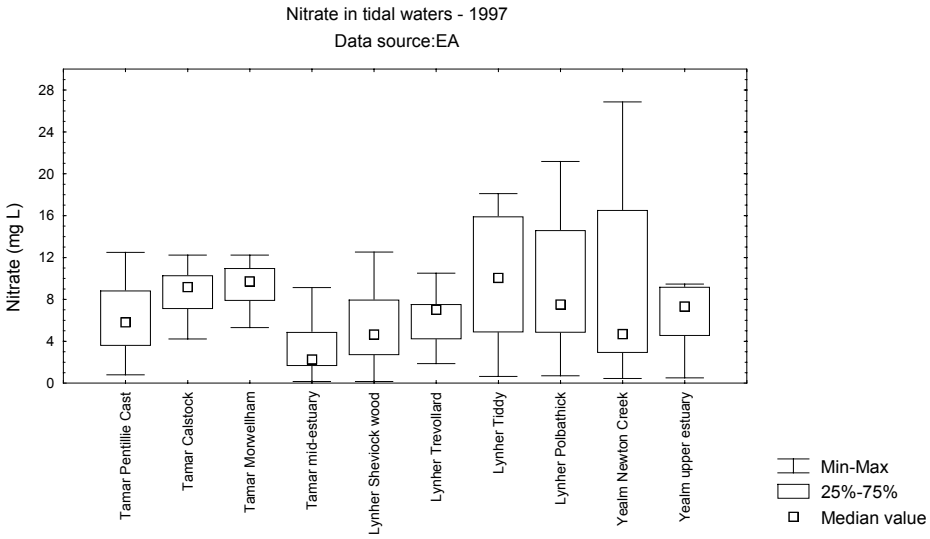



**Figure 49. Nitrate concentrations (mg $l^{-1}$) in tidal waters of Plymouth Sound and Estuaries 1997.Data source: EA**

Expressed as N, almost all mean annual nitrate values for the period 1991-9, (roughly 97%) for tidal waters sites within the SAC, are higher than the TIN value (0.144mg $l^{-1}$) considered to represent the threshold for hypernutrification in coastal waters (North Sea Quality Status Report), and 56% are above the (1mg $l^{-1}$) effects level suggested by Deegan *et al* (1997) as responsible for poor habitat quality for estuarine fish populations, (due in part to cloaking effects of macroalgal mats on *Zostera* beds).

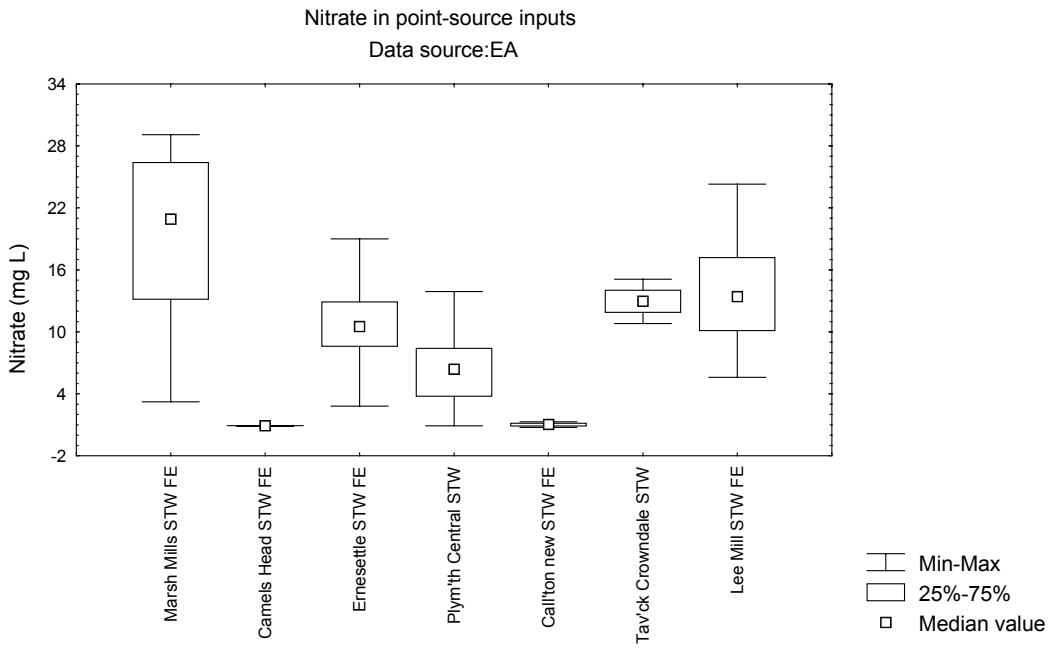



**Figure 50. Concentrations of nitrate in discharges to Plymouth Sound Estuaries. Data are for 2001 except Callington (New) and Tavistock (Crowndale) STWs – 2000, and Lee Mill STW - 1997. Data source EA.**

Recent values for nitrate in sewage discharges are shown in figure 50 and are relatively high suggesting that STWs are important sources, even so maximum values are below the 50mg $l^{-1}$ threshold guidelines for nitrate. On a temporal scale there are several increases in nitrate concentrations in treated effluent, notably at the STWs listed in table 32.

**Table 32. STWs where notable temporal increases for nitrate in final effluent discharges have occurred**

| STW | Receiving waters | Period | Nitrate mg $l^{-1}$ annual maximum |
|---|---|---|---|
| Plympton (Marsh Mills) STW | Plym | 1991-2002 | 28 |
| Plymouth (Ernesettle) STW | Tamar (Hamoaze) | 1991-2002 | 19 |
| Plymouth (Radford) STW | Plym (Cattewater) | 1990-1997 | 36 |
| Callington (New) STW | Lynher | 1991-2000 | 12.8 |
| Tavistock (Crowndale) STW | Tavy | 1990-2002 | 25 |
| Lee Mill STW | Yealm | 1990-1997 | 24.3 |

NB. Data for 2002 represent 1 sample only

Data for Ernesettle STW are exceptional in that nitrate concentrations in effluent dramatically increased in 2001 following the introduction of denitrification processes. (figure 51). Additional sewage flows are to be, or have been, transferred to Ernesettle following the closure of Saltash STW. South West Water have recently improved and upgraded Ernesettle sewage treatment works by adding secondary treatment and UV disinfection in addition to denitrification processes.

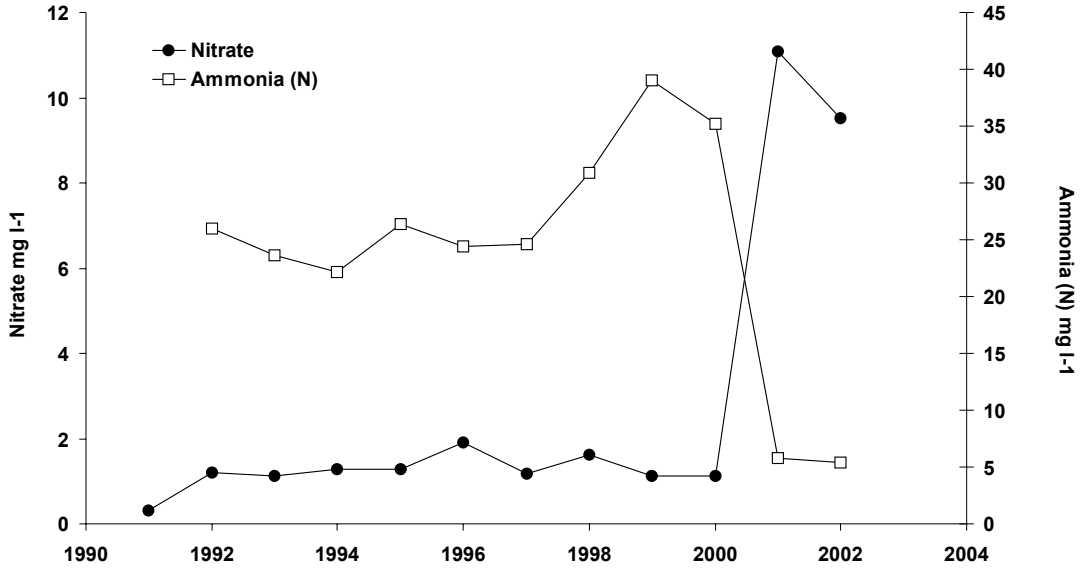



**Figure 51. Nitrate and ammonia (N) in discharges for Ernesettle STW showing nitrate increase in 2001 Data source:EA** NB. 3 values only for nitrate 2002

There is no up-to date monitoring information available for nitrate in the adjacent tidal waters to establish the influence of this sudden increase of N in the discharge.

Effects on many of the rare species in the cSAC are largely unresearched, but in view of their conservation importance, it would seem that an increase in nutrients should be avoided, as a precautionary requirement. Changes to consents (quantities and location) should therefore be considered carefully to avoid the risk of further enrichment.

For the current project we have briefly considered available EA information (statistics and raw data) on DO, turbidity and primary productivity as potential indicators of impact in different sections of the cSAC.

### 7.2.4 Ammonia

Whereas the effects of nutrient enrichment tend to be indirect, some forms of ammonia can be toxic to marine life. 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 $NH_3$ (N) $l^{-1}$ (26.3 and 37.4mg $l^{-1}$ total ammonia (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 $NH_4$ (H) $l^{-1}$), and tests on several life stages showed a No Observed Effect Concentration (NOEC) of 0.106mg $NH_3$ (N) $l^{-1}$ (3.34mg $NH_4$ (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.

Diverse invertebrate populations can survive, and flounder and salmonids pass through the Mersey Estuary with a mean unionised ammonia concentration of 0.008 mg $NH_3$ (N) $l^{-1}$ (Cole *et al,* 1999). 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 reduced at lower salinity levels, gradually decreasing until it reaches a point similar to that found for freshwaters (Seager *et al*., 1998, Miller *et al*., 1990). This may be of relevance, especially in estuaries such as the Tamar, where DO sags can occur at low salinities.

Ammonia does not accumulate in the sediments, although ammonifying microbial activity in sediments can result in ammonia release. This activity is greatest when large quantities of macroalgal biomass decline (Owens and Stewart, 1983) and is potentially toxic 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).

Ammonia is present in all natural waters, even if only at very low concentrations. It is derived either from the breakdown of organic nitrogen (mineralisation) or by the reduction of nitrate (a process known as denitrification). Ammonia 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.

The un-ionised form of the ammonium ion ($NH_3$) is the most toxic although ammonia as N is more commonly monitored. 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 .

Recent data for ammonia (N) in freshwater entering the cSAC (riverine sources) are summarised in figure 52. Values below detection limits (0.03mg $l^{-1}$) have been halved. Annual median concentrations are all below 0.1mg $l^{-1}$, with highest values recorded at sampling points in the vicinity of STWs (e.g. Newton Stream, Tory Brook).

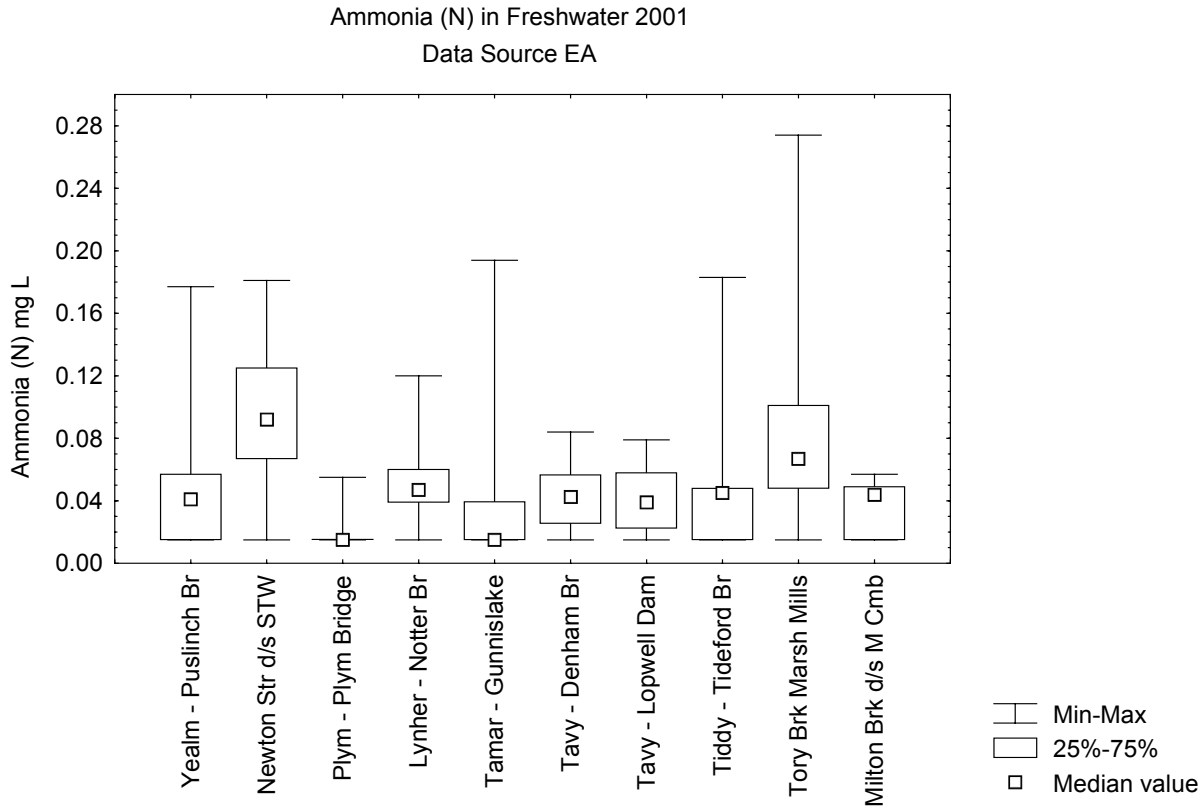



**Figure 52. Ammonia (N) in freshwater entering Plymouth Sound & Estuaries. Data source EA. Data are for 2001.**

For discharges, the highest median ammonia concentrations for 2001 were for effluents from Brixton, Camels Head and Landrake STWs (figure 53). *Note that figures 52 and 53 represent concentrations only and do not necessarily reflect ammonia loadings.*

Ammonia levels in discharges from Camels Head and Landrake STWs were consistently high throughout the year (mean, median and max >20mg $l^{-1}$, 25$^{th}$ percentiles >15mg $l^{-1}$). There have been general reductions in ammonia concentrations in discharges from several of the STWs 1992-2002, notably Wembury, Bere Alston, Gunnislake, Landrake and Plymouth (Radford), and also a recent significant reduction for Ernesettle STW brought about by the introduction of denitrification processes (see section 7.2.3 and figure 51).

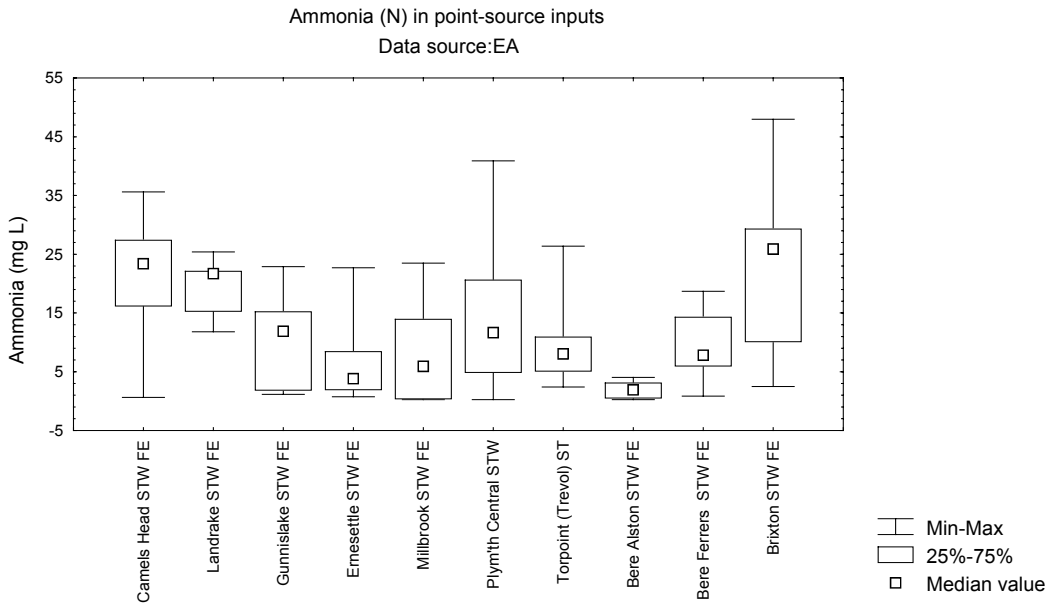



**Figure 53. Ammonia (N) in discharges to Plymouth Sound & Estuaries.. Data source EA.** Data are for 2001

Figure 54 shows temporal trends for ammonia in discharges from Camels Head STW, which were also decreasing between 1992 and 1997, however this trend has subsequently reversed.

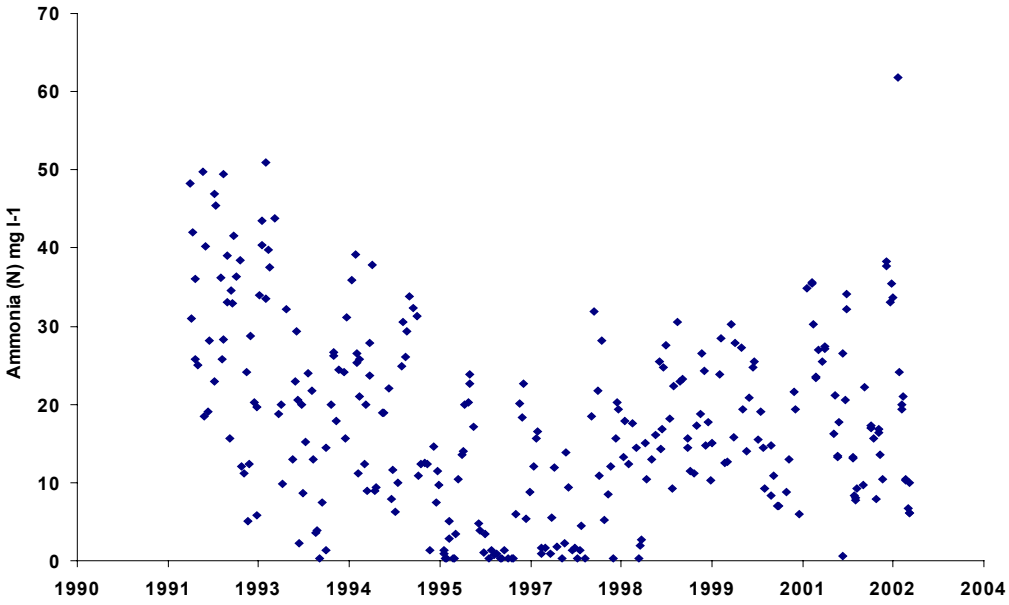



**Figure 54. Temporal trends for ammonia (N) concentration in discharges from Camels Head STW .** Data source EA. .

General increases are also indicated in effluent from Cargreen, Bere Ferrers and Torpoint STWs.

Ammonia standards for discharges appear to be set on a case-by-case basis, and are generally more stringent for discharges to sensitive waters (e.g 10mg $l^{-1}$ as 95$^{th}$ percentile).

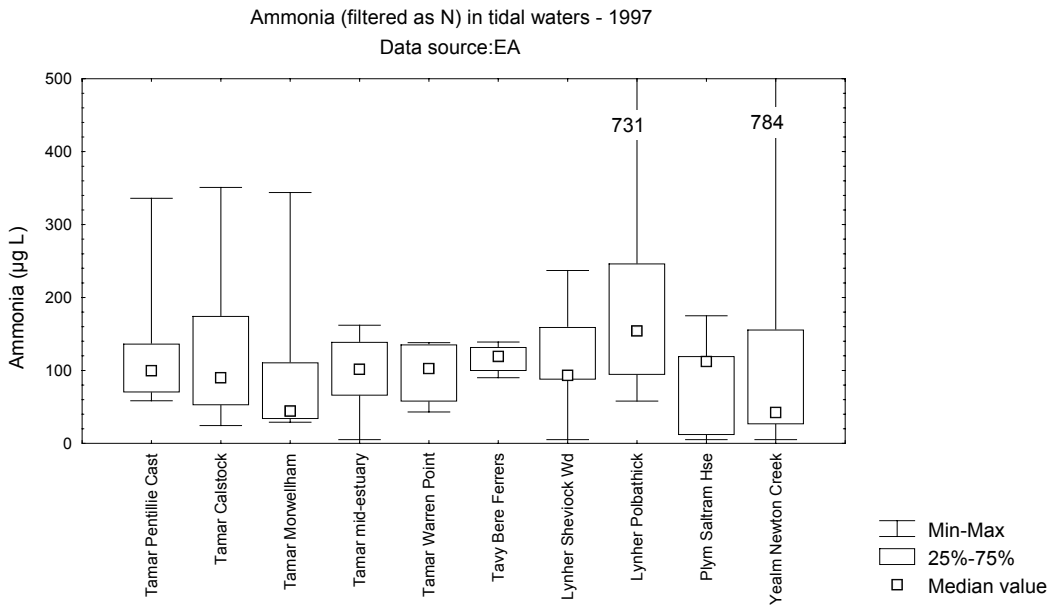



**Figure 55. Ammonia (filtered as N) in tidal waters of Plymouth Sound & Estuaries. Data are for 1997. Data source EA**

The most recent data (1997) for ammonia in tidal waters of Plymouth Sound and Estuaries are summarised in figure 55. Highest individual concentrations were recorded in the Yealm (Newton Creek) downstream of the STW[1], and in the Lynher (Polbathic) (max 784 and 731µg $l^{-1}$ respectively). The most elevated median concentrations for 1997 occur at Polbathic, the Tavy (near Bere Ferrers) and the Plym (at Saltram House).

There are few notable temporal trends for ammonia in tidal waters (1992-7), generally, concentrations at sampling sites in the Yealm appeared to be decreasing or are relatively unchanged, whilst most sites in the Lynher showed increases. Note that the ammonia data are for ammonia as N, and values for the more toxic 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 20˚C, and a salinity of about 30, 0.44 mg $l^{-1}$ total ammonia (N) relates to about 0.021mg $l^{-1}$ $NH_3$ (N), which is the proposed EQS.

Thus, it does not appear likely that the 21µg $l^{-1}$ EQS for $NH_3$ (N) is exceeded in the cSAC, although as monitoring of tidal waters ceased in 1997, further increases in ammonia concentrations from discharges should be avoided, as a precautionary requirement.

[1] No information for this discharge available

### 7.2.5 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 33 shows recommended EQS values for saline waters derived from the review of Nixon *et al.,* (1995).

**Table 33. Recommended EQSs for dissolved oxygen in saline waters (from Nixon *et al.*, 1995)**

| Saltwater use | EQS | Compliance statistic | Notes |
|---|---|---|---|
| Designated shellfishery | 70% saturation<br>60% saturation<br>80% saturation | 50%ile, mandatory standard<br>Minimum, mandatory standard<br>95%ile, guideline value | EC Shellfish Water Directive |
| Saltwater life | 5 mg $l^{-1}$<br>2 mg $l^{-1}$ | 50%ile<br>95%ile | |
| Sensitive saltwater life (e.g. fish nursery grounds) | 9 mg $l^{-1}$<br>5 mg $l^{-1}$ | 50%ile<br>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 34) and although this scheme has not been implemented, the class thresholds are a useful indication of the levels of DO that are likely to cause effects if organisms are exposed for a continuous period of greater than one hour.

**Table 34. 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.
Parts of Plymouth Sound and Estuaries cSAC may be particularly vulnerable to such problems, as these changes in water quality are likely to be greatest in semi-enclosed bodies of water with long retention times, and where stratification of the water column occurs (Cole *et al.,* 1999). Reduced DO levels could be anticipated in some areas of the cSAC such as the upper Tamar estuary, the Lynher and the Yealm, where nutrient levels are shown to be increasing.

Data for dissolved oxygen in waters of the cSAC are for the period 1990 – 2002 for HMPs and both designated and non-designated shellfisheries, and for 1990-1997 in other tidal waters. The data are expressed mg $l^{-1}$ enabling comparison with EQSs.

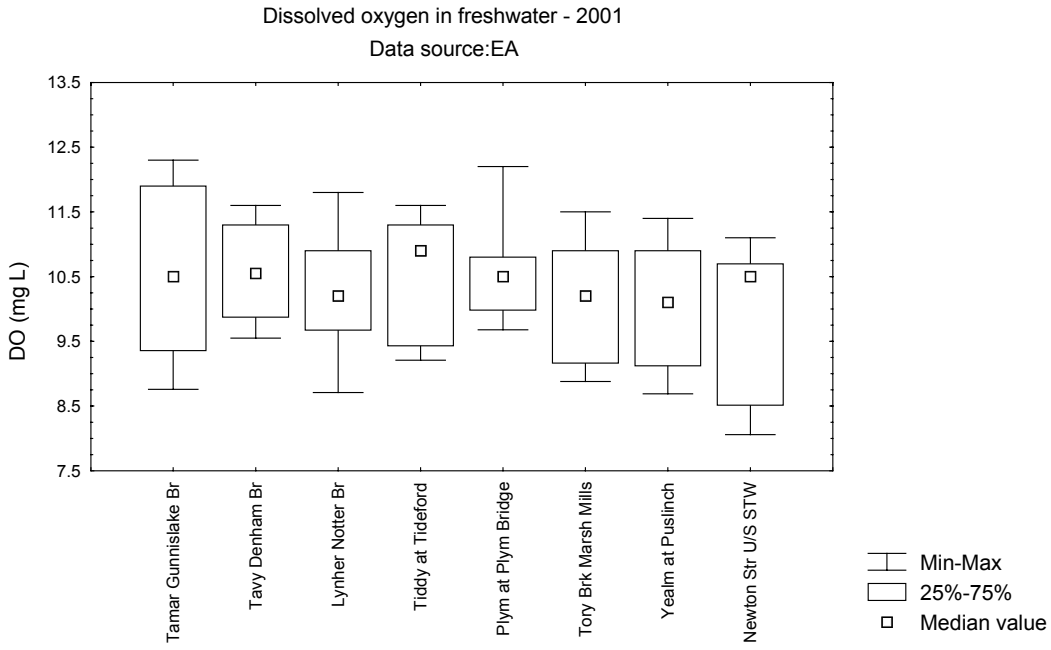



**Figure 56. Dissolved oxygen in freshwaters entering Plymouth Sound and Estuaries cSAC at HMP. Data source:EA**

Data for DO in freshwater entering Plymouth Sound and Estuaries at HMPs or similar in 2001 are summarised in figure 56. Between 1990 and 2002, lowest individual values have occurred in the Yealm (1998; Newton Stream, 1999; Puslinch Bridge, 0.9 and 1.1mg $l^{-1}$ respectively). Under the GQA scheme for DO proposed by Gunby *et al* (1995) (table 34), these low concentrations would result in a classification of 'D' for the Yealm, however annual percentile values do not fall below recommended EQS's set for estuaries (table 34).

Annual median values for DO in cSAC estuarine waters are generally in the upper range reported by MMPMG (1998) (4 - 11mg $l^{-1}$). For tidal waters (upper estuaries) lowest values for DO (0.82mg $l^{-1}$) also occurred in the Yealm (Wembury House, adjacent to the shellfishery at Thorn), and there were some very low concentrations recorded in the Tamar Estuary (e.g. off Pentillie Castle and Tamar Bridge, 0.93 and 2.9mg $l^{-1}$ respectively) in 1994. Not unsurprisingly summer values reflect the greatest oxygen depletion, however annual median DO fell below the 9mg $l^{-1}$ recommended EQS for sensitive saltwater life at several sites in the Lynher, Plym, Tamar and Yealm during the period covered. The most recent data (for shellfish waters) show the annual median DO in the Yealm at Wembury House for 2000 was 8.6mg $l^{-1}$ (min 6.5).

Similarly, for tidal waters of the lower estuaries, dissolved oxygen has been depleted during in the summer months (0.19mg $l^{-1}$ in the Hamoaze off Wilcove and Anthony Passage 1994). In the 8-year period (1990-1997), annual median DO fell below the threshold 9mg $l^{-1}$ recommended EQS for sensitive saltwater life at several sites in and around the Hamoaze (Lynher, the Dockyard, Millbrook, St Johns Lake). For shellfish waters, more recent data show that median DO in the Lynher (Near Jupiter Point) was 8.3mg $l^{-1}$ in 1999.

There are few temporal trends apparent in the data, DO concentrations appeared to be increasing at several lower estuarine sites, e.g Plymouth Sound sites, St Johns Lake, Tamar lower estuary) although there is no recent data to establish whether these trends continue. Data for the upper Tamar at Morwellham indicates that summer DO concentrations were gradually decreasing overall when monitoring ceased in 1997 although this trend is not statistically significant ($p>0.05$) (figure 57). Similar decreases are apparent for the Tamar at Calstock and Pentillie Castle, and the Yealm at Wembury House.

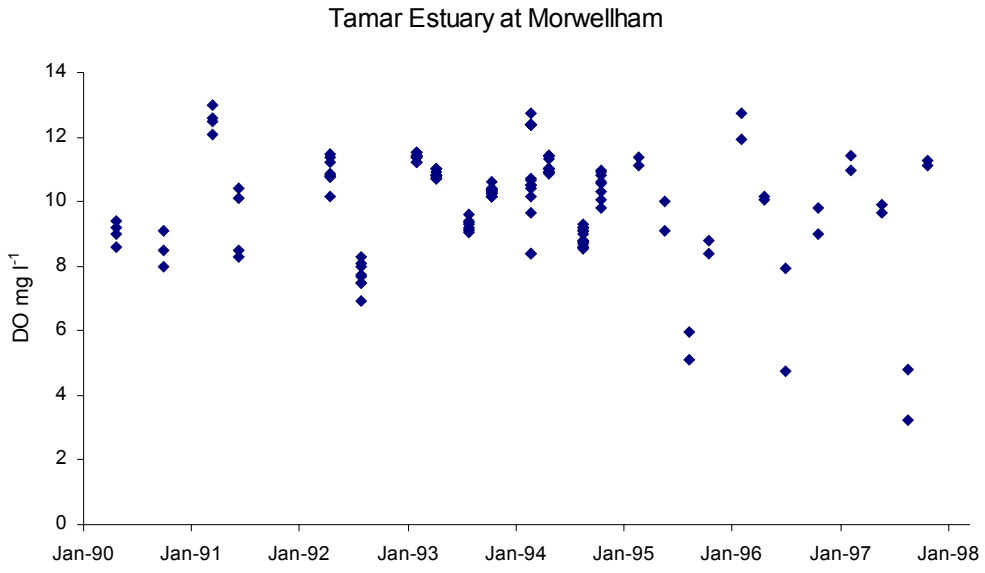



**Figure 57. Dissolved oxygen in tidal waters of the Tamar at Morwellham. Data source:EA**

With regard to the proposed GQA, 7% of DO measurements for tidal waters of the cSAC (n=7869) fell below the threshold GQA class A/B (8mg $l^{-1}$), a level at which effects are considered likely if organisms are exposed for continuous periods of greater than 1 hour. Indications are that this situation is more common in the upper estuaries where levels of less than 8mg $l^{-1}$ may persist for up to 6 hours, e.g raw data show that on August 20th 1997, DO levels in the Tamar at Morwellham was 3.25mg $l^{-1}$ at 0745 (low tide), and 4.8mg $l^{-1}$ at 1315 (high tide).

Generally recent values for HMPs do not indicate that DO concentrations are depleted in freshwaters entering the cSAC, which suggests that depletion is occurring in the tidal waters. Possible contributing factors are discussed in section 5.2.5 and can include organic enrichment, BOD, suspended solids and stratification of the water column, either singly or in combination. In view of the salmonid deaths which occurred in the upper Tamar in the late 1980's, it would seem prudent to reinstate monitoring in vulnerable areas.

### 7.2.6 Chlorophyll *a*

It is important to distinguish between natural blooms and those induced by "artificial" causes. 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. Elevated and prolonged 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. 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 such as the Plymouth Sound and Estuaries cSAC. 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 more often restricted to spring and summer months when estuarine concentrations in optimum growing conditions may exceed 50-80µg $l^{-1}$ (Monbet 1992).

In the UK, an indicator (mean) value for suspected eutrophic conditions is set at 10µg $l^{-1}$ chlorophyll *a* (Dong *et al.,* 2000). Data for mean annual chlorophyll *a* concentrations for selected upper estuarine sites in the cSAC are summarised in figure 58. Values are generally for the period April-September, although measurements taken February-October are included at some sites.

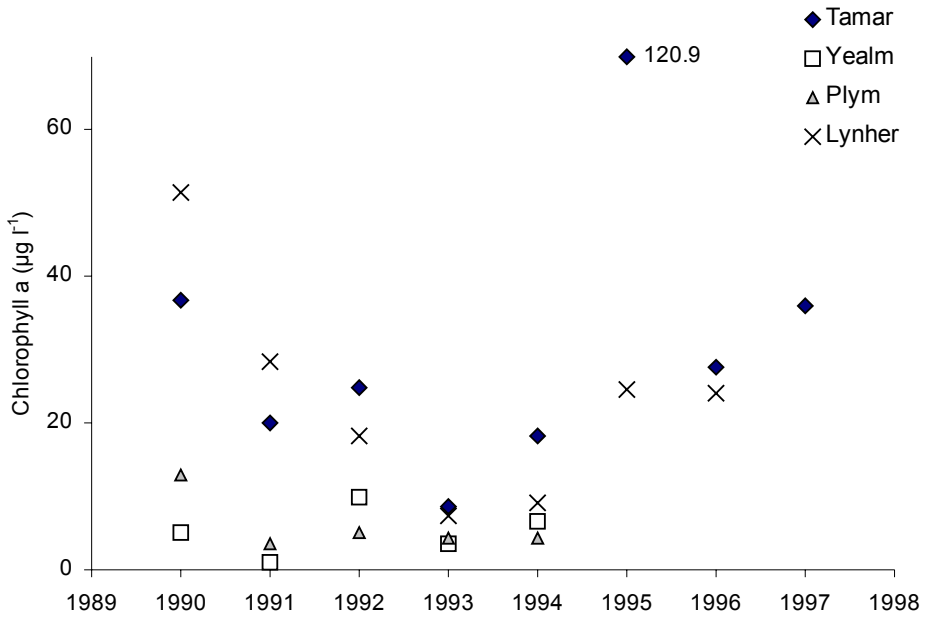



**Figure 58. Mean annual chlorophyll *a* (µg $l^{-1}$) for selected upper estuarine sites in Plymouth Sound and Estuaries cSAC.** Sites are Tamar Estuary – Morwellham, Yealm Estuary - Wembury House, Plym Estuary - by Saltram House, Lynher Estuary - Polbathic Lane. Data source EA.

Mean annual chlorophyll *a* values for the all sites in the Plym and Yealm (available data, 1990-1994) were generally low and not indicative of significant plankton blooms (maximum individual measurements 74 and 83µg $l^{-1}$ respectively). For the Tamar and Lynher (1990 – 1997), highest levels of chlorophyll *a* occurred in the uppermost reaches of the estuary (Lynher - by Sheviock Wood, off Trevollard and the Tiddy; the Tamar at Morwellham, Calstock and Pentillie Castle) where mean annual values were up to 120µg $l^{-1}$ and individual values up to 396µg $l^{-1}$ were recorded during summer months. Again, monitoring appears to have ceased in 1997 at a point when chlorophyll *a* concentrations appeared to be increasing.

The more elevated values indicate significant algal blooms. There is no information available at present to indicate which phytoplankton species are contributing to these blooms, but such levels, whether or not they are toxic species (discussed elsewhere), may be a result of the nutrient enrichment observed in the upper estuaries and are likely to have 'knock on' consequences for estuarine biota. These include fluctuations in dissolved oxygen (with the potential for sublethal and lethal effects on invertebrates and fish), increased turbidity and reduction in light levels (see relevant sections in this report).

For waters of the lower estuaries, Hamoaze and the Sound, mean annual concentrations of chlorophyll *a* rarely exceed 10µg $l^{-1}$, and maximum individual values are generally within the normal range during spring and autumn blooms (up to 80µg $l^{-1}$).


**Figure 59. Chlorophyll *a* in freshwaters entering Plymouth Sound and Estuaries cSAC 1990 – 2002.** Data source EA

Chlorophyll *a* concentrations in freshwaters entering the cSAC at HMPs (1990 – 2002) are shown in figure 59 and are generally below the UK indicator value of 10µg $l^{-1}$. This indicates that freshwater phytoplankton may not be entering the brackish water zone in great numbers. Die-off of these species is therefore probably not releasing significant amounts of DOC, contradicting the hypothesis of Morris *et al*., (1978) (discussed in section 5.2.2).

### 7.2.7 Turbidity

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.

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$^{o}$C or 500$^{o}$C) or remote sensing. The results of these methods are not readily inter-convertible, making comparisons problematic, and the

only EQS appears under the Bathing Waters Directive and relates to transparency using a secchi disc (guide value 90$^{th}$ percentile >2m, imperative 95$^{th}$ percentile >1m). These values are only applicable during the bathing season and may be waived in the event of 'exceptional weather or geographical conditions'.

Two principal methods are used by the EA for quantifying turbidity in Plymouth Sound and Estuaries cSAC: suspended solids (units mg $l^{-1}$, at 105$^{o}$C), and light scattering, measured using a turbidimeter calibrated with Formazin (units Formazin Turbidity Units, FTU). Turbidity data for the tidal waters are largely recorded in FTU, whilst suspended solid measurements are mainly reported for freshwaters and discharges. For the purposes of this report FTU units have been used to assess turbidity in tidal waters and suspended solids as a guide to the contribution made by discharges.

Data for tidal waters of the cSAC are for the period 1990 – 1997. Mean annual values are in the range 0.7 – 814 FTU and are generally highest for the uppermost estuarine reaches: the Tamar; Morwellham, Calstock, Pentillie Castle, the Lynher; by Sheviock Wood, off Trevollard, Tiddy, the Yealm; Newton Creek, Cofflete Creek and the Plym; Saltram House. For the Tamar and Lynher, mean annual turbidity in the upper estuaries was increasing over the period covered (figure 60), however, there is no recent data to establish whether this trend continued after monitoring ceased. Individual values of up to 4950 FTU have been recorded in the Tamar (Morwhellam 1997).

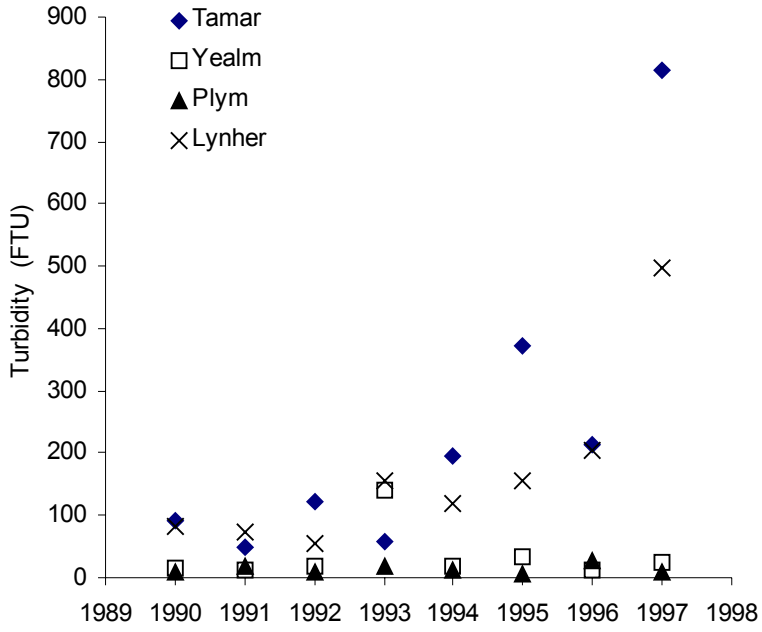



**Figure 60. Mean annual turbidity for selected upper estuarine sites in Plymouth Sound and Estuaries cSAC.** Sites are Tamar Estuary – Morwellham, Yealm Estuary – Newton Creek, Plym Estuary - by Saltram House, Lynher Estuary - Polbathic Lane. FTU = Formazin Turbidity Units and refers to the standard used to calibrate the turbidimeter. (Data source: EA)

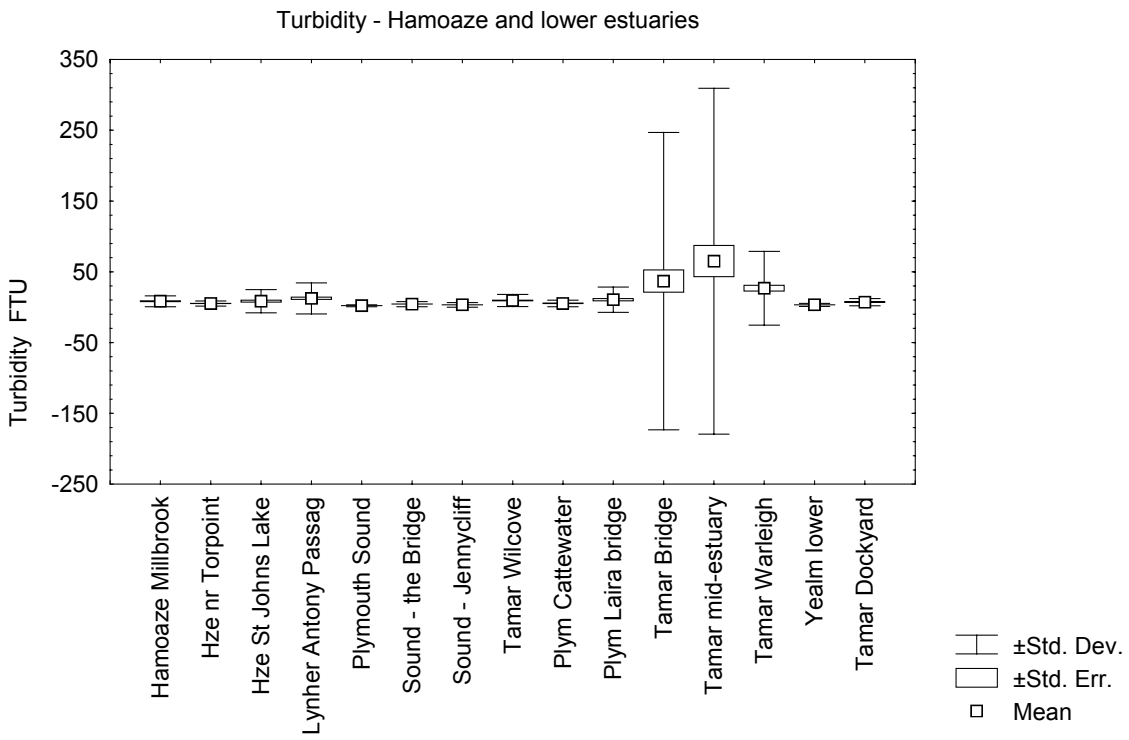



**Figure 61. Turbidity in the Hamoaze and lower estuaries of the cSAC 1990 - 1997.** FTU = Formazin Turbidity Units and refers to the standard used to calibrate the turbidimeter. (Data source: EA)

Data for the lower estuarine sites including the Hamoaze and Sound (1990 – 1997) are summarised in figure 61. Highest values (64 and 2600 FTU, mean and max respectively) occur in the Tamar, mid-estuary (near Cargreen), but for the majority of lower tidal waters, mean annual turbidity is generally below 20, and individual values rarely exceed 50 FTU.

The principal source of turbidity is often quoted as being sediment resuspension (Parr *et al.,* 1998) and peak levels are generally confined to a discrete area in the mid-upper reaches of the system, which moves up and down with the tide (Coles *et al*., 1999). The level of suspended solids depends on a variety of factors, including: substrate type, river flow, tidal height, water velocity, wind reach/speed and depth of water mixing (Parr *et al*., 1998). For the tidal waters of the Plymouth Sound and Estuaries cSAC, peak turbidity levels (the turbidity maximum) are in the upper reaches where there are significant silt deposits. However, the levels of turbidity in parts of the cSAC suggest additional sources: suspended solids in discharges, chemical flocculation and plankton may contribute to this load.

Suspended solids (@105°C) in freshwaters entering the cSAC at HMPs (or similar) for 2001 are summarized in figure 62, **(note that data summarised in figures 62 and 63 are for concentration only and do not represent loadings)** Values for the period 1990 – 2002 range from 0.2 – 570mg $l^{-1}$ and are generally at the lower end of the scale. There are no obvious temporal trends in the data, and values do not indicate that suspended solids in freshwater are a significant cause of elevated turbidity in the cSAC.

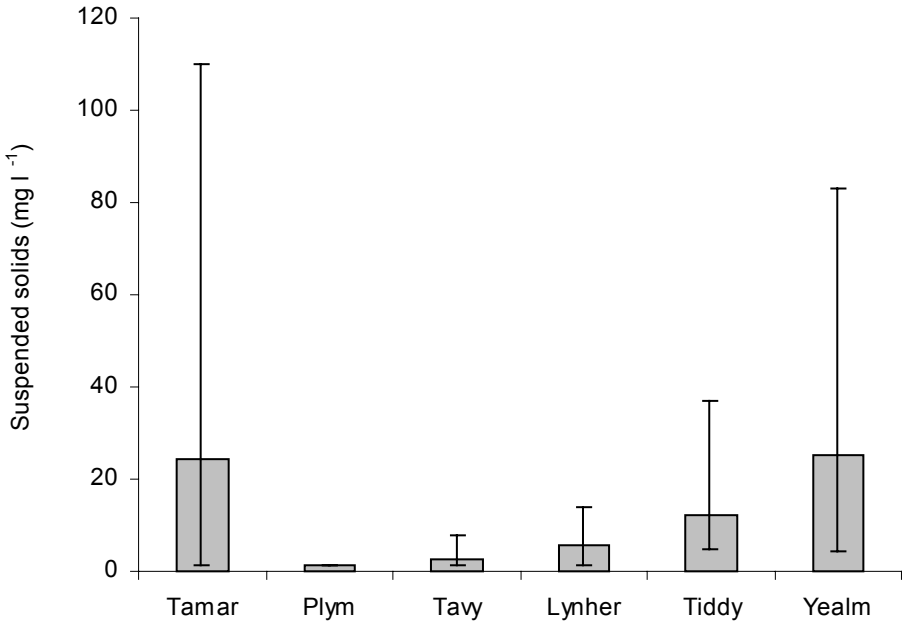



**Figure 62 Suspended solids in freshwaters entering the cSAC at HMPs or equivalent – Mean annual 2001. Error bars show range (min and max concentrations)**

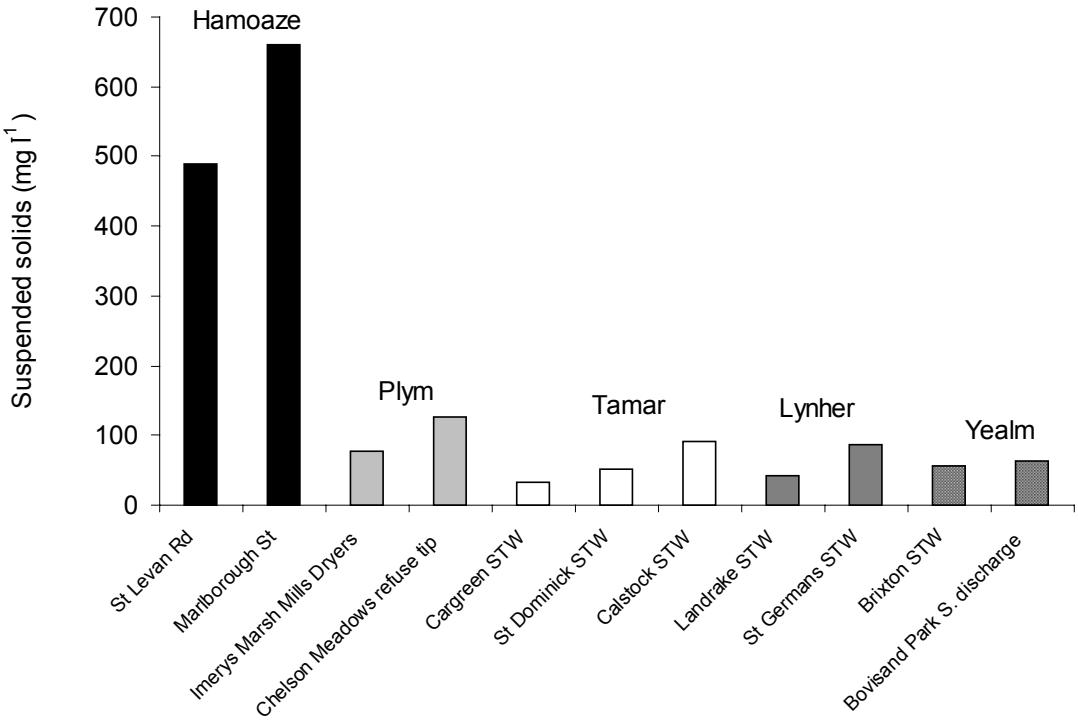



**Figure 63. Suspended solids (mg $l^{-1}$ @105°C) in discharges to the cSAC – Mean annual 2001.**

The highest levels (based on concentration) of suspended solids in waters entering the cSAC come from discharges, primarily STWs. Figure 63 shows the annual mean for 2001 for the principal discharges to each estuary. Of these, St Levans (mean and max, 488 and 1360mg $l^{-1}$) and Marlborough St (mean and max 660 and 2430mg $l^{-1}$) outfalls stand out with the highest concentrations. The data show a temporal trend toward lower levels of suspended solids in discharges (annual means) from these and several other STWs since 1990 (including Albert Rd, Camels Head, and Torpoint on the Hamoaze, Calstock, Gunnislake, St Dominick and Ernesettle on the Tamar, Brixton, Yealmpton and Newton Ferrers on the Yealm, and Radford, Plympton and Imerys (Marsh Mills dryers) (trade discharge) on the Plym, however these discharges still constitute a considerable source to the cSAC, and supplement suspended solids remobilised during dredging, in freshwater inputs, and urban and agricultural run-off.

Increases have occurred for suspended solids in STW discharges from St Johns on the Hamoaze, Cargreen and Bere Ferrers on the Tavy, St Germans on the Lynher and Chelson Meadows on the Plym (trade discharge), which all discharge into relatively enclosed waters in areas where they may significantly add to turbidity due to tidal resuspension.

To put turbidity levels into some perspective, Coles *et al* (1998) cited typical annual values for mean suspended solids (105$^{o}$C) around the English and Welsh coast as 1-110mg $l^{-1}$, and suggested that anything >100 mg $l^{-1}$ could be considered high. Annual mean suspended solids (105$^{o}$C) in the water column of the upper Tamar at Morwellham, during the period 1990 – 1997, ranged from 61 - 1039mg $l^{-1}$ and in the lower estuary 6 - 18mg $l^{-1}$. Further seaward, mean annual suspended solids in the water column of Plymouth Sound are very low, 2-9mg $l^{-1}$.

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 to higher trophic levels.

### 7.2.8 Microbiological Parameters

EQS for microbiological parameters are defined by standard values set by three EC Directives;

- Quality required for Shellfish Waters 91/923/EC – sets classification standards for harvesting areas in addition to guidelines for faecal coliforms in shellfish waters and flesh

- Quality required for Shellfish Hygiene 91/492/EC – set conditions for the production and placing on the market of live bivalve molluscs.

- Quality required for Bathing Waters 76/160/EC (currently under revision) – sets guideline and imperative standards for coliforms, faecal streptococci, salmonella and enterovirus in bathing waters

The standards in the Shellfish Waters Directive (Annex 3) are applicable only in designated shellfish waters and are designed to protect shellfish populations which are harvested for human consumption. EQS for waters under this directive is 300 faecal coliforms per 100ml as 75$^{th}$ percentile value (in intervalvular fluid and waters from which shellfish are taken for direct human consumption).

**Table 35. Classification of shellfish harvesting areas under the requirements of Shellfish Hygiene Directive 91/492/EC**

| | | |
|---|---|---|
| **Category A** | Less than 230 *E. coli*/100 g flesh, or Less than 300 faecal coliforms/ 100 g flesh | May go direct for human consumption if end product standard met |
| **Category B** | Less than 4,600 *E. coli*/100 g flesh (in 90% of samples), or Less than 6000 faecal coliforms/ 100 g flesh (in 90% samples) | Must be depurated, heat treated or relaid to meet Category A requirements |
| **Category C** | Less than 46,000 faecal coliforms/100 g flesh | Must be relaid for long period (at least two months) whether or not combined with purification, or after intensive purification to meet Category A or B. |
| | Above 60,000 faecal coliforms | Unsuitable for production |

Classification of shellfish harvesting areas in England and Wales is compiled by the Centre for Environment, Fisheries and Aquaculture Science, Weymouth (CEFAS) and has recently been updated. The following applies from 12th September 2001: The EEC Directive 91/492/EC is now implemented by means of the 1998 Regulations which themselves were amended by the Food Safety (Fishery Products and Live Shellfish) (Hygiene) (Amendment) Regulations 1999. Production areas have been classified according to the extent to which shellfish sampled from the area are contaminated with *E. coli*. The classification of a production area determines the treatment required before molluscs may be marketed:

Classifications of designated bivalve mollusc production areas in England and Wales are now revised annually and also include a list of areas prohibited for production under the regulations, and areas designated by food authorities as relaying areas. These designations have been made by the Food Standards Agency under the Food Standards Act 1999 (Transitional and Consequential Provisions and Savings) (England and Wales) Regulations 2000.

*To assess water quality in the cSAC with regard to microbiological parameters, current designations and classifications are presented, followed by interpretation of statistics and data provided by the EA from the WIMS database as a general guide.*

The following classifications apply to designated shellfish beds in Plymouth Sound and Estuaries cSAC:

**Table 36. Classification of shellfish beds in Plymouth Sound and Estuaries cSAC (Sept 2001)**

| Production area | Bed name | Species | Category | Notes |
|---|---|---|---|---|
| Yealm | Fox Cove | *C. gigas* Mussels | B | |
| | Thorn | *C. gigas* | B | 1 |
| | Happy Cove | *C. gigas* | B | 2 |
| Lynher | | *O. edulis* Mussels | C | 2 |
| Tamar | All beds | All species | Prohibited | 3 |
| Plym | All beds | All species | Prohibited | 3 |

1. Thorn is also a designated relaying area for bivalve molluscs (class B).
2. These beds may be subject to review before the periodic update because of insufficient sample results, either in number or covering sufficient period of time.
3. Shellfish from these areas must not be subject to production or be collected

Imperative standards given in the Bathing Waters Directive require there to be no more than 10,000 total coliforms or 2,000 faecal coliforms per 100ml. For bathing waters to comply, 95% of samples taken must meet these standards. Guideline standards for coliforms are 20 times more stringent. 80% of samples must not contain more than 500 total coliforms or 100 faecal coliforms per 100ml. Also 90% of samples must not contain more than 100 faecal streptococci per 100ml (table 37).

**Table 37. EQS Under the Bathing Waters Directive**

| | Unit | Guideline value | Imperative value |
|---|---|---|---|
| Faecal coliforms | per 100 ml | 100 80%ile | 2000 95%ile |
| Total coliforms | per 100 ml | 500 80%ile | 10000 95%ile |
| Faecal streptococci | per 100 ml | 100 90%ile | |
| Salmonella | per $l^{-1}$ | | 0 95%ile |
| Enterovirus | PFU 10 $l^{-1}$ | | 0 95%ile |

There are six EC Designated Bathing Waters in the area bounded by the cSAC. Below are their compliance records against the Imperative and Guideline standards of the EC Bathing Waters Directive. The bathing season runs from 15 May to 30 September and sampling begins two weeks before the start of the season. At least 20 samples are taken for coliform and faecal streptococci analysis at each designated bathing water. Table 38 shows compliance at the designated bathing waters 1991 – 2001.

**Table 38. Plymouth Sound and Estuaries cSAC EC Designated Bathing Water Compliance 1991 - 2001. (a) Imperative standards, (b) Guideline standards (EA 2002)**

| **(a) Imperative Standards** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1991 | 1992 | 1993 | 1994 | 1995 | 1996 | 1997 | 1998 | 1999 | 2000 | 2001 |
| Wembury | Pass | Pass | Fail | Pass | Pass | Pass | Pass | Pass | Pass | Pass | Pass |
| Bovisand | Pass | Pass | Fail | Pass | Pass | Pass | Pass | Pass | Fail | Pass | Pass |
| Plymouth Hoe (E) | Fail | Fail | Fail | Fail | Pass | Fail | Pass | Pass | Pass | Pass | Fail |
| Plymouth Hoe (W) | Fail | Fail | Fail | Fail | Pass | Fail | Fail | Fail | Pass | Pass | Pass |
| Kingsand | - | - | - | - | - | - | - | Fail | Fail | Fail | Pass |
| Cawsand | - | - | - | - | - | - | - | Fail | Fail | Fail | Pass |

| **(b) Guideline Standards** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1991 | 1992 | 1993 | 1994 | 1995 | 1996 | 1997 | 1998 | 1999 | 2000 | 2001 |
| Wembury | Pass | Pass | Fail | Fail | Fail | Pass | Pass | Fail | Pass | Pass | Pass |
| Bovisand | Fail | Fail | Fail | Pass | Fail | Fail | Pass | Fail | Fail | Pass | Pass |
| Plymouth Hoe (E) | Fail | Fail | Fail | Fail | Fail | Fail | Fail | Fail | Pass | Fail | Fail |
| Plymouth Hoe (W) | Fail | Fail | Fail | Fail | Fail | Fail | Fail | Fail | Fail | Fail | Fail |
| Kingsand | - | - | - | - | - | - | - | Fail | Fail | Fail | Pass |
| Cawsand | - | - | - | - | - | - | - | Fail | Fail | Fail | Pass |

Note: Kingsand and Cawsand were not designated until 1998

Recent Improvements to wastewater treatment include:

Plymouth Hoe (East and West)
SWW have made significant investments to improve the wastewater treatment facilities at STWs affecting the bathing waters at Plymouth Hoe. These improvements have also been designed to improve the quality of Shellfish Waters in the area. Both continuous and intermittent storm discharges have been the subject of the investments programmes. In 1998 a new STW was completed at Plymouth (Central) and a new tunnel sewer was constructed under the Hoe for storm attenuation. However, the bathing waters continue to have a poor compliance record and further work is underway to improve the performance of the new installations (EA pers comm.).

Kingsand and Cawsand
These bathing waters were not designated until 1998 up to which time they had not been regularly monitored. Once identified, SWW were required to install a new STW as the waste water from the two villages was discharged without treatment to the streams which flow across the associated beaches. Four new pumping stations were completed prior to the 2001 Bathing Season and the foul flows redirected to Millbrook STW for treatment. Since the scheme was implemented, the quality of the Bathing Water has improved significantly and passed both the Imperative and Guideline standards in 2001.

Data for faecal coliforms in waters of the cSAC confirms the above classifications and designations. Data for 2001 are summarised in figure 64 and show faecal coliforms numbers to be highest in waters of Plymouth Hoe (mean and max for Hoe east - 837 and 11,360 per 100ml). The mean annual value for faecal coliforms is also relatively high at Wembury Beach (mean and max 226 and 4200 per 100ml) although 95$^{th}$ percentile complies with the EQS for bathing waters.

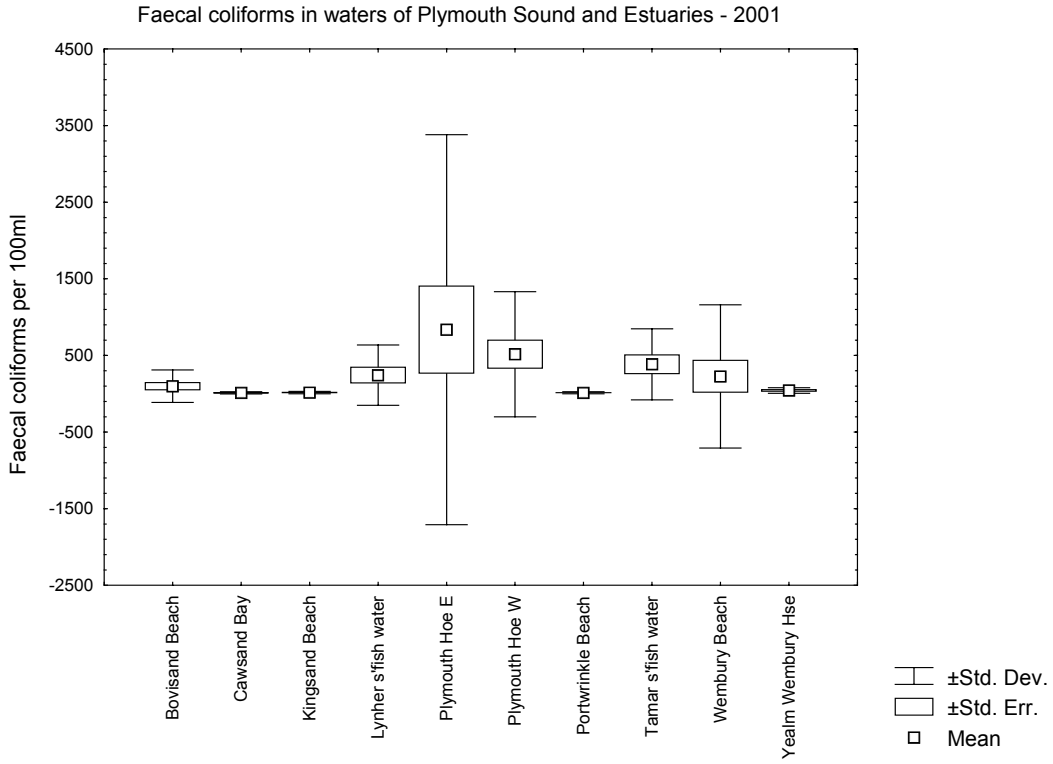



**Figure 64. Faecal coliforms in waters of Plymouth Sound and Estuaries cSAC. Data source: EA.** NB For statistical purposes, values below the limit of detection have been assigned a nominal value of half the limit of detection (LOD = 10 per 100ml).

The mean annual value for faecal coliforms in 2001is also relatively high at Wembury Beach (mean and max 226 and 4200 per 100ml), and has been gradually increasing. Although the 95$^{th}$ percentile still complies with the EQS for bathing waters, these were the highest values recorded in the dataset (1995 – 2001).

The data also confirms that improvements to STW have resulted in significant reductions in numbers of faecal coliforms, notably at Cawsand and Kingsand where

mean annual values (per 100ml) have dropped by 1534 and 2840 (respectively) between 2000 and 2001. A marked reduction is also apparent in the Yealm at Wembury House (mean annual for 2000 = 13591, and for 2001 = 42 per 100ml). Long term (since early 1990's) trends for decreasing numbers of faecal coliforms are apparent at Bovisand and Portwrinkle beaches. For shellfish waters, there have been reductions in numbers of faecal coliforms since 1992 in the Tamar (Warleigh Pt at the confluence of the Tamar and Tavy) although values are still relatively high (mean and max 384 and 1718 per 100ml in 2001), no significant temporal trends are evident in the Lynher (near Jupiter Point).

Data for total coliforms are restricted to bathing waters and complied with bathing waters imperative EQS in 2001 (1000 per 100ml as 95$^{th}$ percentile). With the exception of Plymouth Hoe, where mean numbers of total coliforms increased in 2001, temporal trends for total coliforms also reflect improvements in sewage treatment and are generally decreasing.

There are fewer recorded values for faecal *Streptococci* in waters of the cSAC, and the available data are primarily for the early 1990's. However, the EQS imperative value for bathing waters (100 per 100ml as 90$^{th}$ percentile) has been exceeded at several estuarine sites (inc Halton Quay and Warren Point on the Tamar, and the Hamoaze by the Dockyard) although it is stressed that these are not designated bathing waters and the EQS is used in this case as a guide to general water quality. The most recent data for faecal *Streptococci* are for 2000 and shows that the beach stream and tidal waters at Kingsand contained very high numbers, 2970 and 267 per 100ml (both 90$^{th}$ percentiles). There are no other recent data to comment upon.

Data for enterovirus are also restricted to designated bathing waters. Enterovirus is commonly found in sewage, species include strains responsible for meningitis and polio in humans, in addition to milder illness such as stomach upset and conjunctivitis. Bathing water EQS require 0 PFU (plaque forming units) per 10L as a 95$^{th}$ percentile. With the exception of Cawsand Bay and Plymouth Hoe, all sites have complied with this imperative since 1994. However, enterovirus was consistently recorded in waters of Plymouth Hoe (E&W) (max 17.5 PFU per 10L 95%ile) until 2001 when it was not detected. Enterovirus was also detected in waters of Cawsand Bay in June 1998 and July 2001(2, and 1 PFU per 10L, respectively). Such numbers may appear insignificant but Gantzer *et al* (1999) suggest that conventional methods of detection generally underestimate actual numbers of enterovirus present therefore the problem may be more serious.

No data was available to consider salmonella in waters of the cSAC.

Microbiological parameters such as faecal coliforms are generally monitored in the estuarine environment to indicate the presence of other human derived microbial pathogens, and are principally associated with sewage discharges. In rural areas, animal-derived slurry in run-off from waterside fields and farms may provide an additional source of coliforms. The marine environment is hostile to most microbial pathogens and they rapidly die off, especially in the presence of sunlight. However they may become associated with suspended particles and can accumulate to some extent in sediments, surviving for days or weeks. This is therefore a consideration

when permitting dredging operations close to bathing waters or shellfish waters during the bathing or harvesting seasons (respectively). Microbial pathogens also accumulate in filter feeding organisms to levels that can be harmful to themselves (microbial toxins), to humans and perhaps other consumers (e.g. birds and marine mammals). In addition, the aesthetic appearance of the site could be damaged.

# 8 SEDIMENT STATUS AND QUALITY STANDARDS

## 8.1 Metals

The NMP surveys between 1992-95 (MPMMG, 1998) concluded that sediments of Tamar could be characterised as containing high concentrations including Hg and As. The latter was attributed to mineralisation and historic mining activity within the catchment, though as detailed in an earlier section, it is not always easy to separate natural and anthropogenic components. Apparent levels of contamination (Hg, Cd, As, Cr, Cu, Pb, Ni, Zn) decrease significantly at intermediate and offshore sites, though this partly reflects the changing characteristics of the sediments from fine silts rich in binding sites in the upper estuaries, to coarser sediments offshore. Sieving and normalisation procedures are required to compensate for such granulometric and geochemical effects, to allow meaningful comparison of contamination levels (Langston *et al*., 1999; MPMMG, 1998;). For example normalisation of Pb, Cr, Ni concentration in sediment to Al content demonstrates effectively their enhancement in Tamar sediments, compared to expected values for 'normal' UK sediments of similar Al content (MPMMG, 1998; Rowlatt *et al*., 1998). In the current report we have used our own data, for sediments sieved at 100µm, to examine sediment quality (*see footnote below*[1])

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

[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 oxyhdroxide 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 for the examples shown on the following pages in the current exercise. A study of microwave-digested Irish Sea sediments conducted in our own laboratory has shown that, following sieving at this mesh size, further normalisation confers no significant additional advantage when comparing contaminant trends. Sieving fulfils a further function - to place emphasis on particles which are accepted by benthic organisms. Sieving at 100µm was the preferred option for comparisons made in this project. It is stressed that this is only one of the options for classifying sediments, others may be equally suitable; the point is that some adjustment has to be made for grain size otherwise comparisons are uncontrolled and of little value.

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 their application as discussed by Grimwood and Dixon (1997) in the context of List II metals, including possible fundamental differences in sediment geochemistry (as discussed in the footnote on the previous page) and the use of test species which are not indigenous to the UK, 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 and identify instances where efforts should be made to minimise further inputs of these substances to the cSAC.

Guideline values for principal metals in sediments are summarised below (table 39); a full list of guideline values is provided in Annex 5. The status of metals in sediments of the cSAC are based on MBA's own published and unpublished records[1].

**Table 39. Interim marine sediment quality guidelines (ISQGs) and probable effect levels (PELs) for metals (from CCME, 1999)**

| Metal | ISQG ($mgkg^{-1}$) dry weight | PEL ($mgkg^{-1}$) dry weight |
|---|---|---|
| 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 |

With the possibility of biological effects in mind, we have summarised data for metals in Plymouth Sound Estuaries inter-tidal sediments by partitioning sites into 'zones' according to the interim sediment guideline criteria for each metal (Figures 65- 66). Green zones denote areas where no harm to the environment is predicted (below

[1] Note: these data have been collected at intervals over the last 30 years in connection with research projects and were not intended as a monitoring programme. The quality of the data is considered to be good. Methodologies have been successfully validated in numerous intercalibration exercises, including Quasimeme. The sediment measurements described here are for the <100μm fraction (without further normalisation) and are concentrated nitric acid digests (Langston *et al.,* 1994 a,b).

ISQG's), grey zones are where effects cannot be excluded (between ISQG's and PEL's) and red zones are where harmful effects are expected (above PEL's).

In sediments of the cSAC all of the seven metals in table 39 are, to some extent, in concentration ranges where adverse effects to biota cannot be excluded. There are 'red zones' for many of the metals in the major rivers, tributaries and upper estuaries of the cSAC.

Arsenic sediment concentrations are within the range where harmful effects to biota are expected for much of the Tamar, Tavy and to a lesser extent, the Plym. Arsenic concentrations in the Tamar and Tavy are a result of the area's mining history (discussed in section 5.1.1). Though harmful effects cannot be excluded in the Yealm (upper site) concentrations at the mouth appear to be harmless (also for the single sample from Plymouth Sound). At Rame and Whitsand, just outside the SAC harmful effects cannot be excluded according to the CCME criteria, but would seem unlikely.

Sediment concentrations of Zn, Cu and Pb in the SAC generally exhibit similar distributions to As and are dominated primarily by mineralisation. Cu and Pb are in the 'red' category throughout most of the Tamar/Tavy. Elsewhere (apart from one anomalously high value in the lower Plym - associated perhaps with battery disposal) effects of sediment Cu and Pb on biota seem unlikely but cannot be excluded (grey zone), except for the mouth of the Yealm and at Whitsand (green zone). This characterisation broadly applies to Zn, though the Rame and Cawsand samples are also below the ISQG threshold value.

Hg levels in sediments of the upper sections of the Tamar, Tavy and Lynher estuaries suggest some effects are likely here. Unusually the same applies to sediments of the Yealm Estuary (the source of this enrichment is unknown and should perhaps be investigated further). At other stations around the SAC Hg concentrations generally fall into the 'grey zone' range.

Cadmium distributions are quite different and reflect the different source of this pollutant metal. Although there is a degree of enrichment (grey zone) in the upper Tamar (perhaps associated with mineralisation) the most significant levels (red zone) occur in the upper Plym, and probably reflect historic industrial discharges, inputs from the Plympton STW and possible run-off from Chelson Meadows disposal site. Sites in the Yealm Estuary, Plymouth Sound, Rame and Whitsand are below the threshold for Cd.

Cr levels are fairly uniform in the estuarine sediments and are by and large in the 'green' zone with no adverse effects predicted.

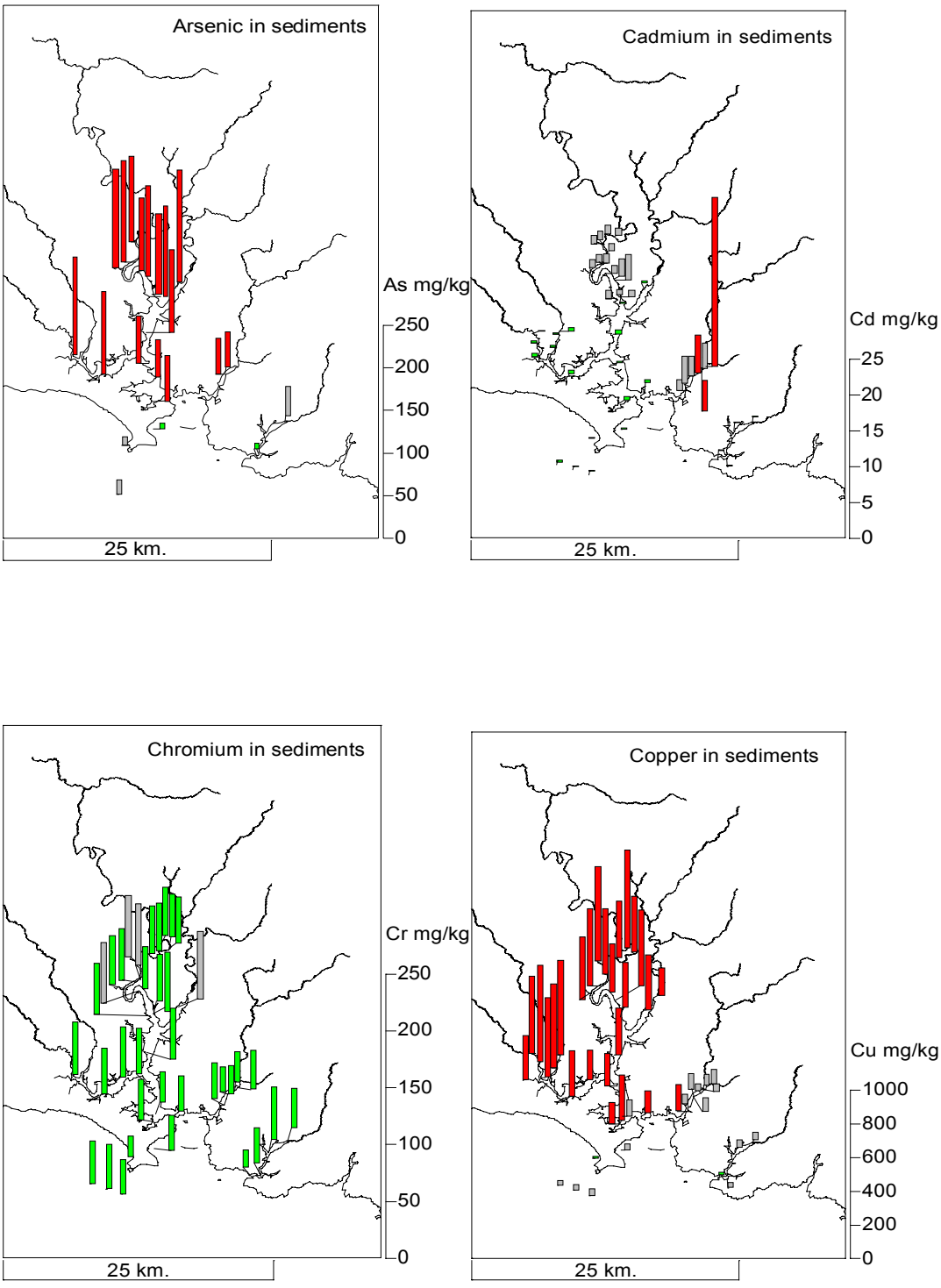



**Figure 65. Arsenic, Cadmium, Chromium and Copper in sediment. Classification of the Plymouth Sound and Estuaries cSAC into zones based on interim marine sediment quality guidelines (ISQG's) and probable effect levels (PEL's) (from CCME 1999).** Red = effects expected; Grey = possible effects cannot be excluded; Green = no harm to the environment expected.

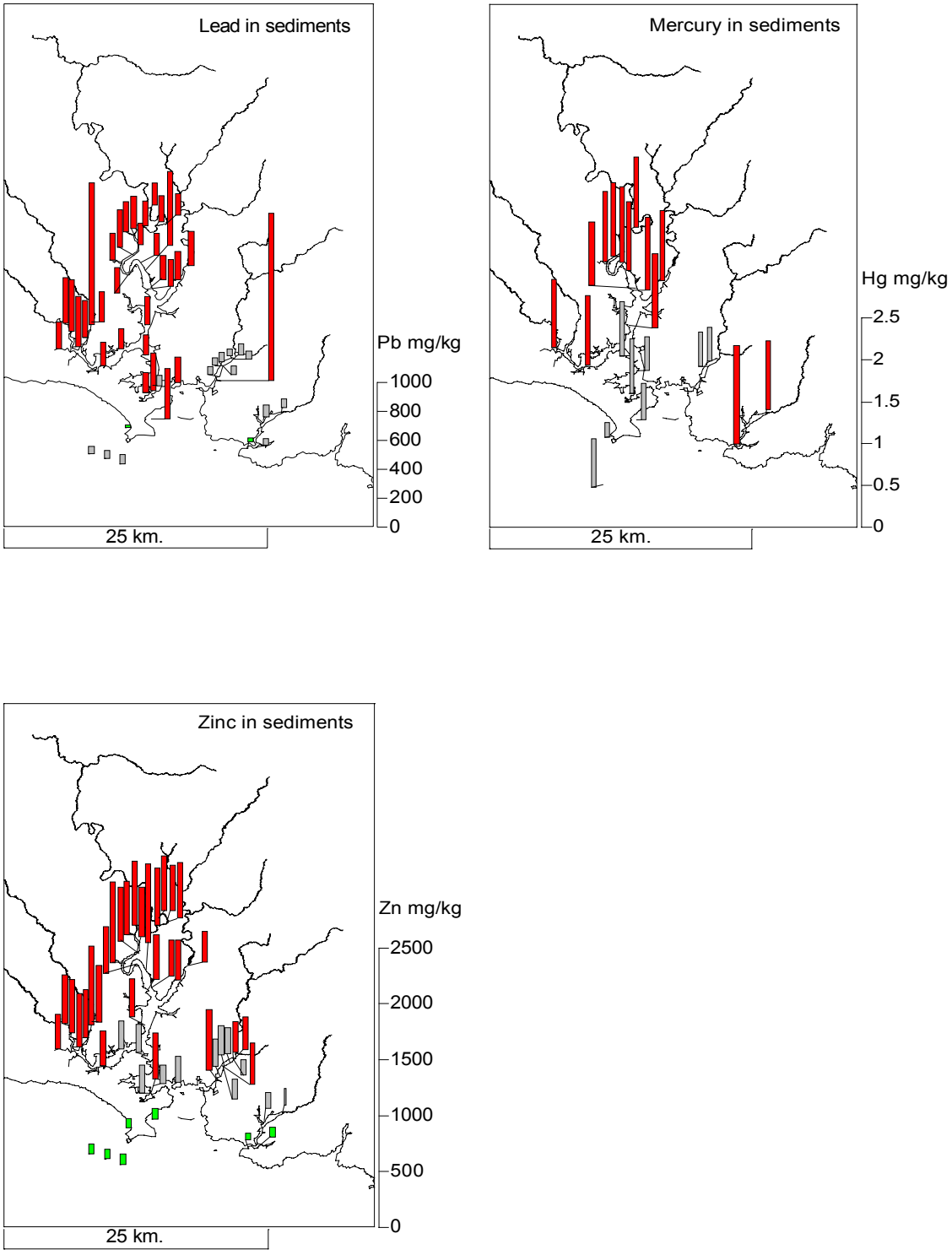



**Figure 66. Lead, Mercury and Zinc in sediment. Classification of the Plymouth Sound and Estuaries cSAC into zones based on interim marine sediment quality guidelines (ISQG's) and probable effect levels (PEL's) (from CCME 1999).** Red = effects expected; Grey = possible effects cannot be excluded; Green = no harm to the environment expected.

Thus, sediments at a number of sites in the Plymouth Estuaries contain levels of metals which are likely to exert pressures on biota, though these are probably chronic rather than acute. Information on Plymouth Sound itself is rather sparse but suggests impact is likely to be low. It would be useful to gather up to date and more extensive data for the system as a whole.

## 8.2 TBT

Environment Canada has not produced guideline values for TBT in sediments presumably because of insufficient information on toxicity levels. However, the Oslo-Paris Commission (1994) has drawn up a set of ecological assessment criteria for the identification of possible problem areas relating to TBT in the aquatic environment (table 40). These are derived from a diverse body of information, including national limit values (e.g. EQS), toxicity thresholds, sediment quality and body burden data. It should be stressed that these are 'guidelines' arising from evaluation of the best available evidence. The mean TBT concentration (±sd) in Tamar sediments collected in October 1991 was 0.023 (±0.008)µg $g^{-1}$ (as Sn) (Gibbs and Langston 1994). Based on OSPARCOM guideline ecotoxicological assessment criteria for sediments (Oslo and Paris Commissions, 1994), much of the Tamar would be classified as a 'problem area' though arguably these guidelines may be overcautious.

**Table 40. OSPAR provisional ecotoxicological assessment criteria guidelines for TBT (Oslo and Paris Commissions, 1994)**

| Sample type | TBT concentration range (as TBT) | TBT concentration range (as Sn) |
|---|---|---|
| | | |
| Water | 0.1 –1 ng $l^{-1}$ | 0.04-0.4 ng $l^{-1}$ |
| Sediment (1% organic C) | 0.0001-0.001 µg $g^{-1}$ | 0.00004-0.0004 µ $g^{-1}$ |
| Mussel (dw) | 0.05-0.5 µg $g^{-1}$ | 0.02-0.2 µg $g^{-1}$ |

Perhaps a more realistic evaluation, based on limited publications and research into sediment toxicity of TBT, would be that effects on benthic organisms might be expected to occur in the range 0.02 - 0.3µg $g^{-1}$ dw sediment (Langston *et al.,* 1990; Langston and Burt, 1991; Austen and McEvoy, 1997; Allen *et al*., 2000). Tamar sediments probably come into the lower end of this range. The above data are, however, now ten years old, and, since results from that time suggest little short-term temporal change, efforts should now be made to demonstrate that Favourable Condition and 'stand still' requirements are being met and if necessary to minimise further inputs of these substances to the cSAC.

These recommendations are borne out by bioaccumulation (Tamar mussel) data from 1991 (Gibbs and Langston 1994). Typical concentrations at that time (~0.5 - 1µg $g^{-1}$ (as Sn) were above the OSPAR guideline range (table 40). Also, a summary of water monitoring data for the SAC collected by EA/CEFAS between 1995 and 1999 still places the median value an order of magnitude above the EQS (Allen *et al.,* 2000).

## 8.3 Organic Substances - Pesticides, Herbicides, PAHs

In general, these compounds have low water solubility and are therefore likely to sorb strongly to suspended solids and sediments (discussed in section 5.1.4). The majority of organics are also lipophilic, and therefore liable to accumulate and/or biomagnify in marine organisms.

*Pesticides and herbicides* - The EA dataset contains very little information about levels of pesticides and herbicides in sediments and for many of these substances, the most recent monitoring took place in 1997. In some instances detection limits are set above the interim marine sediment guidelines (ISQGs – see annex 5). However, there are indications that levels of certain substances are elevated in sediments.

DDT and its derivatives

Sediment quality guidelines (CCME 1999) for DDT and its derivitives DDE and DDD are for total isomers (*p,p'* and *o,p'*). Values in the EA dataset are few and for individual isomers but nonetheless are indicative of the level of sediment contamination. For much of the DDT monitoring, limits of detection used (up to 12µg $kg^{-1}$ dw) are set above the ISQG and PEL therefore we have included only positive results. Table 41 summarises the available data for the different isomers of DDT and DDE.

**Table 41. DDT and DDE in sediments of the cSAC. Data source:EA**

| Site | Year | Maximum concentration µg $kg^{-1}$ dw | | |
|---|---|---|---|---|
| | | DDT (*op*) | DDT (*pp*) | DDE (*pp*) |
| NMP Plymouth Sound | 1994 | 9.3 | 6.7 | 5.2 |
| Hamoaze opp dockyard | 1996 | | 8.4 | 3.6 |
| Hamoaze Torpoint Gas works | 1999 | | 1.6 | |
| Plym d/s Marsh Mills STW | 1992-93 | | 3.7 | |
| Tamar - Halton Quay | 1994-97 | | 11.4 | |
| Tamar - Halton Quay | 1997 | | | 58.4 |
| Tamar Warren Pt | 1996 | | 1 | |

Values indicate elevated levels in sediments of the cSAC. ISQG and PEL for DDT (total of both isomers) are 1.22 and 7.81µg $kg^{-1}$ dw respectively, and for DDE, 2.07 and 374µg $kg^{-1}$ dw. The implications from the data are that sum totals of *o, p'* and *p,*

*p*' isomers exceed ISQGs and in some cases the level at which effects to marine biota are expected. Additionally, DDE concentrations are lower than those of the parent compound DDT, which implies that there may have been more recent inputs of DDT.

DDT and its metabolites can be toxic to marine life, and have been identified as endocrine disruptors which are liable to bioaccumulate and magnify along food chains.

Lindane

Gamma-HCH (lindane) concentrations exceed both ISQG (0.32µg $kg^{-1}$) and PEL - probable effect level, (0.99µg $kg^{-1}$) values. Figure 67 shows lindane in sediments of tidal waters. The more elevated concentrations occur in the vicinity of STWs indicating that these are an important source of much of this insecticide (see sections 5.1.4 and 7.1.3). Trade discharges from the Chelson Meadow disposal site are also implicated as a source of lindane in the Plym.

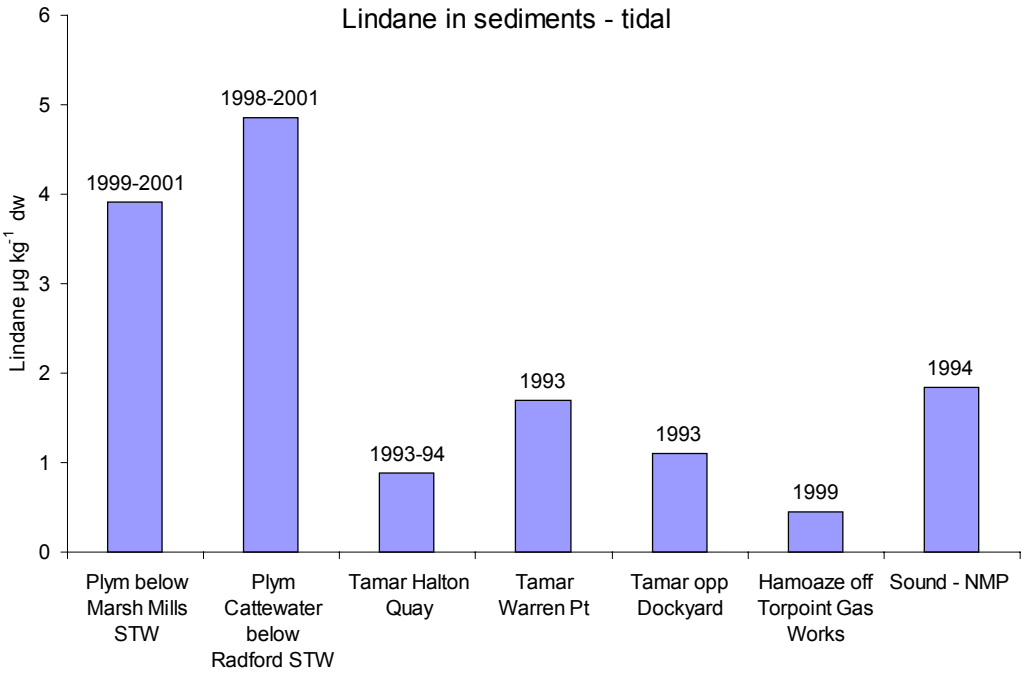



**Figure 67. Lindane (µg $kg^{-1}$ dw) in sediments of Plymouth Sound and Estuaries cSAC.** Data Source: EA . Mean values for period shown

Data for freshwater sediments also show levels to be highest near STWs (mean values for Kelly Brook below Callington STW and the Tavy below Crowndale STW 1990-2000 are 11, and 0.99µg $kg^{-1}$ dw respectively. Lindane in sediments at HMPs also exceeded guideline and probable effects levels between 1990-1992 (max 4.8µg $kg^{-1}$ in the Tamar). There are no recent results for HMPs or several other sites within the cSAC. Some biodegradation of lindane is thought to occur, and a half-life of several days to a year is reported in water and aquatic sediments (Cole *et al* 1999). Figure 68 shows lindane in sediments downstream of Marsh Mills STW and illustrates that despite reductions in water sample concentrations (see section 7.1.3), lindane can

persist in sediments. Concentrations appear to fluctuate somewhat from year to year (this may be due to sampling inconsistencies and/or sediment movement) but there is no overall temporal trend apparent.

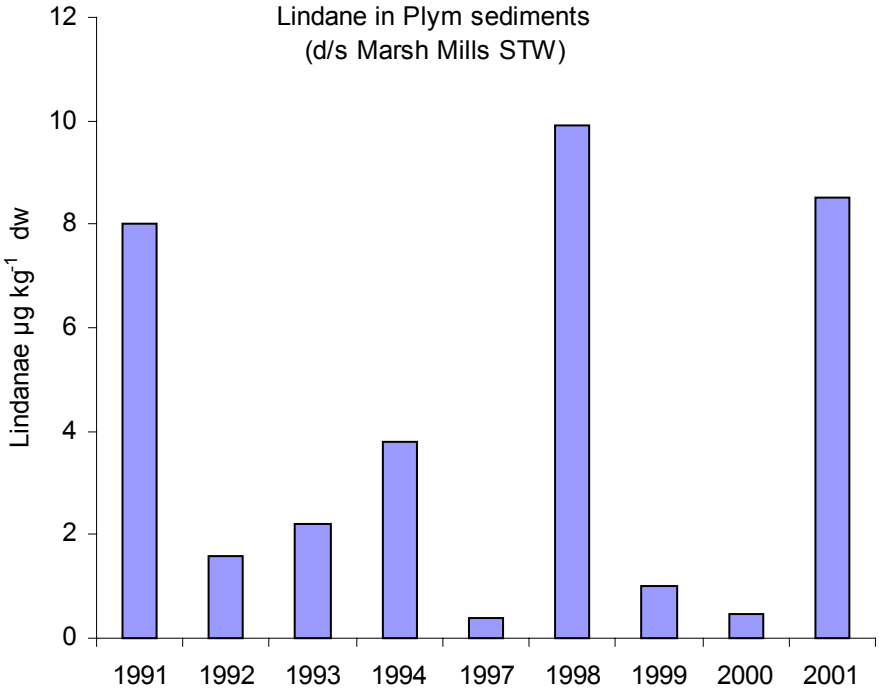



**Figure 68. Temporal trends in concentrations of lindane (annual mean µg $kg^{-1}$ dw) in sediments of the Plym Estuary below Marsh Mills STW**

For pesticides dieldrin and endrin, ISQGs are 0.71µg $kg^{-1}$ and 2.7µg $kg^{-1}$, respectively. Concentrations of these list 1 and red list substances in sediments of the cSAC may be slightly elevated: up to 1.4 µg $kg^{-1}$ (dieldrin) and 1.5µg $kg^{-1}$ (endrin) was recorded in sediments at Halton Quay on the Tamar in 1994. In the same year, 4.5µg $kg^{-1}$ endrin was recorded in sediments at the NMP site south off Plymouth Sound. These organochlorines have been banned from use as pesticides in the UK, and their persistence in the marine environment remains a concern. High levels in sediments of the upper estuaries may be due a combination of such persistence in sediments, and run-off from agricultural land with a history of pesticide usage. The source of endrin in marine sediments off Plymouth Sound is more difficult to hypothesize as the site is not adjacent to land, one possibility is the sewage sludge which until recently was dumped SW of Rame Head (see section 5.1.1).

PAHs

Sediment concentrations of several PAHs are included in the EA dataset. ISQGs and PELs are often exceeded, notably those depicted below.

Anthracene

The ISQG and PEL values for anthracene in sediments (46.9 and 245µg $kg^{-1}$) are exceeded at several sites in the cSAC, notably the upper Tamar (Halton Quay and Warren Point, max 397µg $kg^{-1}$), the Hamoaze (opposite the Dockyard and off Torpoint gas works, max 7396µg $kg^{-1}$), and Plymouth Sound (Jennycliff Bay, max 48.2µg $kg^{-1}$) Mean values are shown in figure 69.

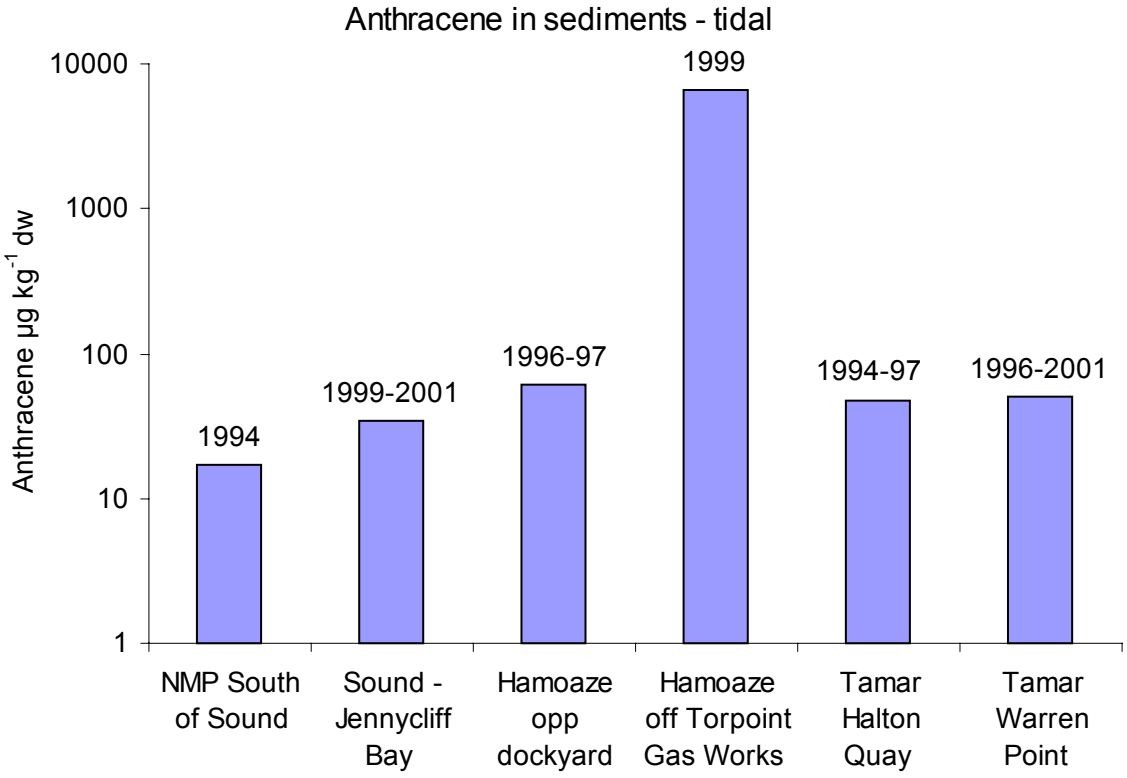



**Figure 69. Anthracene in sediments of Plymouth Sound and Estuaries. Note log scale .** Data Source: EA . Mean values for period shown.

Benzo(a)anthracene

Maximum values for benzo(a)anthracene in sediments have also occurred in the Hamoaze (up to 12049µg $kg^{-1}$ off Torpoint gas works). The ISQG of 74.8µg $kg^{-1}$ has been exceeded at all sites listed and values in excess of the PEL (693µg $kg^{-1}$) are recorded for the upper Tamar at Warren Point and both sites in the Hamoaze.

Benzo(a)pyrene

ISQG and PELs for B(a)P in marine sediments are 88.8 and 763µg $kg^{-1}$. Concentrations of B(a)P in excess of the guideline value have been recorded at all sites (figure 70) and the upper value at which effects to marine life might be expected was exceeded in sediments of the Hamoaze (opposite the dockyard, and off Torpoint gas works - max 10583µg $kg^{-1}$).

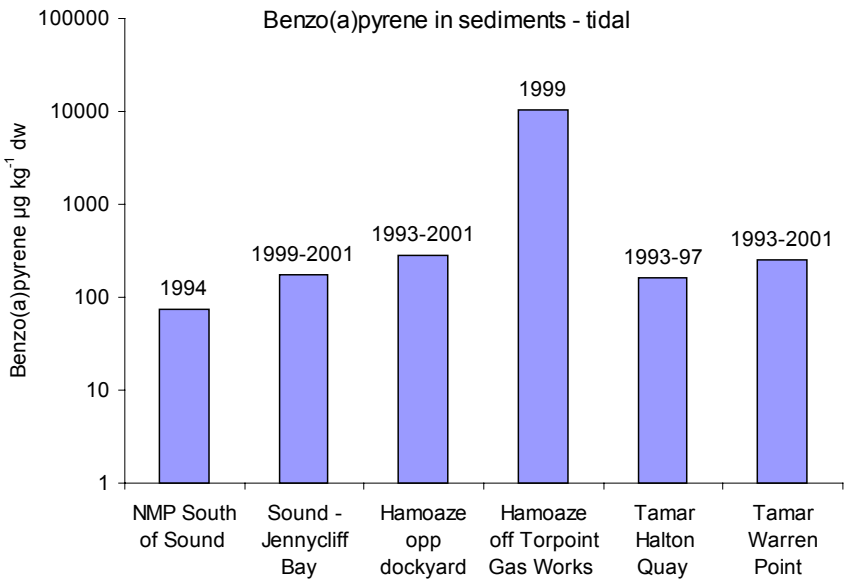



**Figure 70. Benzo(a)pyrene in sediments of Plymouth Sound and Estuaries. Note log scale** . Data Source: EA . Mean values for period shown.

Similarly, concentrations of other individual PAHs, notably chrysene, phenanthrene, naphthalene and pyrene are recorded, which are well in excess of guideline, and probable effect levels for marine sediments. Principal 'hotspots' are: the Hamoaze - off Torpoint gasworks (pyrene and chrysene), and opposite the dockyard (naphthalene), upper Tamar - Warren Point (phenanthrene). In the Hamoaze, a possible localised source of PAHs is Thanckes oil Depot at Torpoint, although there is no information in the EA dataset for PAHs in discharges from this depot, or indeed in any discharges from the dockyard. The source of PAHs in sediments of the NMP site south of the Sound may be sewage sludge which was, until recently, dumped in the vicinity. General sources of PAHs are discussed in section 5.1.3.

# 9. MODELS

A main concern of estuarine science is to calculate the transport of contaminants from rivers, through estuaries and into oceans. Direct measurements of hydrodynamics, water flow and concentrations of contaminants involved in the transport can be difficult, time consuming and expensive to make. Modelling in any estuary is also immensely difficult, tides, weather, intertidal and mudflat zones, waves, hydraulics, dredged channels and shipping all influence the movement of water (Varney 1992). However, the need to model and predict fluxes and distributions has resulted in has resulted in the development of several flexible catchment and estuarine modelling programs, some of which can be tailored to establish the distributions of dissolved and adsorbed contaminants in different estuaries as well as calculating their residence times in the estuary.

*Dispersal and biological effects of contaminants*

*ECoS – Estuarine Contaminant Simulator*

ECoS is a general simulator and allows the definition of the physical aspects of any estuary including its size, shape, tidal/river flows and sediment reservoirs. ECoS contains a segmented physical mixing model that can account for the transport and dispersal of contaminants by river flow and tides, water solubility, degradation, disequilibria, air-water exchange, partitioning onto suspended particulates and sediment interactions. The chemical behaviour of contaminants in EcoS is defined by the characteristic $K_D$-salinity relationships (Turner and Millward 1994). EcoS, like most models, uses the averages of measurements throughout tidal cycles, therefore a pre-requisite is the availability of accurate and reliable data. Parameters can be altered so that their effects on distributions can be observed.

The early one-dimensional version of net solute and particulate transport described under the section on PAHs was in fact a forerunner of the ECoS simulation shell and as acknowledged by the authors, lacked specific validation (Harris *et al*., 1984). In addition to the dispersion of benzo-a-pyrene, other aromatic hydrocarbons (benzene, toluene, ethylbenzene, propyl benzene, naphtalene, 1-methyl naphthalene, 2-ethyl naphthalene and phenanthrene), representing a range of characteristics, were considered. A model of Cd speciation and dispersion was also developed, representing a compound which is lost primarily by flushing - in contrast to the hydrocarbons, where losses via volatilisation, photo-oxidation and microbial action also have to be accounted for. Examples are given of simulated spatio-temporal distributions at the head and mouth of the estuary.

The turbidity maximum, and the effects of run-off and tidal range, are reproduced by the model. Essentially the dispersal model concludes what is seen to some extent in observations (see, for example, the section 5.1.2 - TBT) - that the distribution of toxins depends on the balance between water flows and tidally-driven particle movement and hence on the partition between dissolved and particle-adsorbed phases. Thus, simulated distributions of both Cd and benzo-a-pyrene appear to be dominated by concentrations at the head of the estuary as a result of the predominance of particle-bound transport. Behaviour of Cd is more akin to weakly bound benzene when inputs are placed towards the mouth.

The distribution of toxic effects in mussels (as signified by rates of food absorption and respiration in the energy balance of mussels) is exemplified in similar fashion (Harris *et al.,* 1984). For hydrocarbons, respiration and food absorption are assumed to increase and decrease, respectively, as a linear function of the accumulated compound: both combine to reduce growth potential (scope for growth). Despite the considerable assumptions made, simulated regions of negative growth in the estuary nevertheless appear to closely reflect the (simulated) areas high in suspended naphthalene. The various constraints on the model are discussed by Harris *et al* (1984) which again fall mainly into the category of the need for further validation i.e. axial profiles of contaminant distributions. Among a shortlist of other topics needing investigation are vertical and lateral heterogeneity; particle and solute fluxes across the bed, sediment mixing and structure, kinetics of uptake and loss and impact of

body burdens in infaunal organisms. The current model is therefore seen as a basis for progress rather than an end in itself.

Two dimensional models of estuarine processes usually provide a better representation and are often site-specific (Varney 1992). A two dimensional EcoS-based simulation of the estuarine cycling of nitrogen and carbon shows of the development a late summer oxygen sag in the Tamar Estuary (Wood *et al,* 1996). The model suggests that the sag is dependant on the retention, in the fine sediment trapped in the estuary, of organic carbon generated by local primary production. Primary production depends on the particulate dynamics through both the availability of light and the cycling of nitrogen.

*Nutrient modelling*

Using models to estimate nutrient status is also inherently problematic. Parameters such as the local geology and sediment type, land use, volume, dilution and flushing rate, rainfall, vertical mixing, and wave exposure, influence the nutrient status of environmental waters and are unique to each estuary.

A project taking into account a wide range of physical characteristics in order to determine the relative contribution of diffuse and point source inputs to the Tamar Estuaries complex was recently undertaken (Fraser *et al.,* 2000). Models used were P-EXPERT, EXPORT COEFFICIENT MODELLING and INCA-N (Integrated Nitrogen in Catchments). It was also intended that the information gained be used to develop a catchment-wide list of consent licences likely to have an effect under the Habitats Directive. The aims of the work appear to have been achieved and estimates of nutrient budgets to the system as a whole have been made (discussed in relevant section of the current report). The secondary objective, to simulate catchment dynamics in the Tamar system, was also successful. The study showed that current effluent inputs do not contribute a significant proportion of the total catchment nitrogen loads, in periods when observed flows remain at a medium-high level.

However, efforts to apply the approach to another system (the Fal) appear to have been thwarted by lack of good quality data, therefore the model may have limited application in SACs. The authors aim to refine INCA, but stress the need for high resolution, reliable data.

There are also limitations in that models appear to predict nutrient loading to the estuary as a whole and do not take into account site-specific variability, such as that which occurs in the more enclosed and low-flow areas within the system.

*Sediment dynamics*

Available observations of tidal and sediment properties (e.g. Uncles *et al*., 1985, 1996; Uncles and Stephens 1989) have been used recently to provide improved fine-tuning of predictions for hydrodynamics and equilibrium sediment dynamics (Friedrichs *et al.,* 1998). By assuming a mobile, finite-size pool of easily erodible bed sediment, a new set of functions has been established (combining solutions for non-linear tidal velocity with the one-dimensional advection-dispersion equation for

sediment concentration). This reproduces the positioning and intensity of the turbidity maximum in the Tamar Estuary and its response to variations in river flow. Thus, the model simulates migration of the mobile bed-source material in conjunction with the seasonal migration of the high turbidity region. When river flows are low (summer and early fall), this unconsolidated material is placed by the model near the head of the estuary; in high run-off periods it moves much further seaward and, in extremes, may spread out over a large distance within 5-15km of the mouth (Friedrichs *et al.,* 1998). These predicted distributions are consistent with observations.

Generally, modelling appears to be a valuable tool provided that the limitations are acknowledged. Models can provide a quick exploratory analysis and indicate where further data collection is appropriate. However, it seems unlikely that models will obviate the need for field studies, as these provide the basic information, and are necessary to keep abreast of temporal changes and anomalies within the system.

# 10. CONCLUSIONS AND RECOMMENDATIONS

This report sets out the status of Plymouth Sound and Estuaries cSAC as regards ***available evidence*** on water and sediment quality and environmental impact. Wherever possible, we have used UK EQS values to identify problem areas. However, for many substances, the UK has not set benchmark values and we have drawn on proposed standards or guidelines adopted in other countries, and published literature on dose/effect levels, to assess environmental quality and links to impact. It is also important to recognise that environmental concentration data for many chemicals is limited or non-existent for the cSAC (as elsewhere). Improved strategies for chemical monitoring are needed and biological effects-type monitoring must accompany the suite of chemical measurements that are made, to ensure a more acceptable degree of environmental protection.

Table 42 is a very general, quick-reference summary of principal issues affecting water quality within the cSAC, based on available information, and highlights (i) areas of the system where problems are perceived, or may arise, (ii) sources of contaminants and (iii) threatened features/biota. Below there follows a brief synopsis of these issues and summary suggestions for future R&D.

**Table 42. Principal areas of concern which may be affecting environmental quality in the Plymouth Sound and Estuaries cSAC.** (Findings for each of the numbered 'contaminant categories' are explained in more detail in the accompanying text).

| Principal problems | Area | Potential Sources | Most vulnerable features/biota |
|---|---|---|---|
| 1) Organotins (TBT, TPT?) | Widespread<br>NB estuaries | Sediments, shipping, discharges | Molluscs (primarily gastropods, also some bivalves |
| 2) Metals (esp. As, Cu, Cd, Hg, Zn,) | Estuaries<br>NB Tamar and Tavy | Historic mining and industry (point source and diffuse)<br>STW and run-off | Invertebrates (primarily molluscs and crustaceans), species composition, fish and birds |
| 3) Nutrients, DOC, (Chlorophyll *a*) | Upper estuaries esp Tamar, Yealm, Lynher<br><br>Hamoaze | Sewage discharges, diffuse sources (latter increasingly important) | Phytoplankton, Invertebrates, fish (estuarine and migratory, esp. early life stages), seabirds, mammals, *Zostera* beds (and associated diverse fauna). |
| 4) Low DO | Yealm, Upper Tamar, Hamoaze (St Johns Lake), Lynher | O2 demand in sediments, perhaps enhanced by STW outfalls. Also related to freshwater flows and possibly water abstraction | Salmonids |
| 5) Microbiological parameters | Inner Sound, Yealm (Wembury beach) Lynher, Tamar, Plym | Sewage discharges, farm animals (run-off from land) | Bivalves, birds, other marine organisms at risk from microbial pathogens |
| 6) Hydrocarbons: PAHs, anthracene, phenanthrene chrysene, naphthalene, pyrene, benzo(a)pyrene | Tamar (Hamoaze and upper) and Plymouth Sound sediments | Road run-off, industrial sources e.g gasworks oil depot, dockyard discharges<br>Sediments | Bivalves, species composition, fish, seagrasses and shoreline communities |
| 7) Pesticides and herbicides: DDT (and its derivitives) Lindane, dieldrin, endrin, endosulfan, simazine, trifluralin, Irgarol 1051 | Plym, Tamar (Hamoaze and upper), Plymouth Sound | Land run-off, discharges<br>crop spraying<br>Sediments<br><br>Antifouling compounds | Invertebrates (esp. crustacea), fish, sea birds and mammals, species composition, Zostera |
| 8) Radionuclides | Sediments – Hamoaze and Tamar | Dockyard | Marine biota (genotoxicity) |

On balance of available evidence it appears that the cSAC/SPA is environmentally degraded in several areas particularly in relation to historic mining areas, urban centres and shipping. Most of these appear to be chronic rather than acute issues.

There have been a number of significant reductions in industrial and sewage pollution in recent years which have lead to improvements in environmental quality. As the major point sources around the estuary are progressively upgraded it is anticipated that diffuse sources (urban, agricultural and mining run-off, sediments) may well become the most significant contributors and may delay further improvement.

1) TBT

In the early 1990s, following legislation, highest values (up to 20 ng $l^{-1}$) often occurred upstream at the turbidity maximum - linked to internal interactions and transport within the estuary. This contrasts with the situation prior to 1987 when direct inputs from ships and leisure vessels, situated towards the mouth of the estuary, were a dominant feature. The reductions in TBT levels in the water column of the Tamar, particularly in the Hamoaze, are also probably linked to containment processes introduced by the naval base at Devonport in 1988. TBT levels in mussels from the Hamoaze closely mirror declining trends exhibited in the water column. Mussels appear to be a valid surrogate for measurement of TBT in water.

In contrast, sediment concentrations in the Tamar Estuary did not change significantly following legislation confirming their importance in internal cycling of TBT in the Tamar. Data on TBT partitioning have been used to refine the ECoS model. Simulations made in the early 1990s confirmed that losses of butyltins (TBT+DBT) from the Tamar could be offset by continuing, albeit low-level inputs, which appeared to be responsible for the 'steady-state condition at the time.

The potential for desorption illustrates that sediments can act as continuing sources as well as sinks, for TBT. The continued presence of TBT in sediments implies a continuing and long-term potential hazard to the marine environment. Tamar sediments probably come into the lower end of the range where effects from TBT might be expected.

TBT concentrations in Plymouth Sound water declined markedly following legislation in 1987. Levels in front of the MBA Laboratory on Plymouth Hoe declined from around 15ng Sn $l^{-1}$ in 1987 to 2ng Sn $l^{-1}$ in 1992. However at a site in Batten Bay levels still regularly exceeded the EQS of 2ng $l^{-1}$ throughout this period. Furthermore a summary of water monitoring data for the SAC collected by EA/CEFAS (Allen *et al*., 2000) between 1995 and 1999 also places the median value an order of magnitude above the EQS.

Surveillance of imposex in *N. lapillus* populations (up to ~1993) demonstrated that imposex was still prevalent, and visibly-unaffected females were still a rarity. The breeding capacity of a partially-sterilised population just outside the Sound, monitored for a number of years, had markedly increased during this time. However, significant recolonisation of areas denuded of *N. lapillus* had yet to occur (mid 1990s).

The netted whelk *Nassarius reticulatus* is slightly less sensitive to TBT than the dog-whelk *Nucella lapillus*. There is no evidence that female *N. reticulatus* are sterilized by imposex. Nevertheless *N. reticulatus* is a useful alternative to *N. lapillus* as an imposex-based TBT indicator at contaminated sites around the Sound where *Nucella* is absent. In the five years following the 1987 TBT restrictions, concentrations in water and tissues at some of the more polluted sites decreased by factors of 5 to 10 times. However, the intensity of imposex declined very slowly. This was attributed to the longevity of the snails, the limited reversibility of penis length and limited recruitment.

Much of the available data are however, now ten years old, and, since results from that time suggest little short-term temporal change, efforts should now be made to demonstrate that Favourable Condition and 'stand still' requirements are being met and if necessary to minimise further inputs of these substances to the cSAC.

2) Metals

Metal characteristics in water and sediment from the upper Tamar and Tavy Estuary complex are still dominated by historic mining activity, which reached its peak in the latter part of the 19$^{th}$ century. EQS values for dissolved metals are seldom exceeded, though concentrations of As, Cu, Pb, Zn and, surprisingly, Hg exceed sediment quality guidelines at a range of estuarine sites. Monitoring data for metals in species such as *Fucus vesiculosus, Nereis diversicolor, Scrobicularia plana* and *Littorina littorea,* provide useful information on spatial variation in bioavailability around the cSAC.

With the exception of Sn (and Hg in sediments) the Yealm is relatively uncontaminated compared to the Plym and Tamar complex and acts as a useful reference as to the status of many metals. The presence of elevated Sn levels in Yealm biota in earlier surveys may have reflected inputs of TBT from small vessels (prohibited 15 years ago). There is also the possibility of a TBT contribution from trade discharges in the Yealm. Plympton STW, Chelson Meadow disposal site and other discharges to the Plym are further potential sources of impact on the SAC. However for many of the risks there are inadequate data on which to place a reasonable assessment (e.g. TBT, metals).

Very little is known of impact at offshore sites. Tentative observations of induction of a metallothionein–like protein (a biomarker for metal exposure) in transplanted mussels suggest impact increased inshore, reflecting Tamar sources, but with some anomalies close to the sewage sludge disposal grounds. These observations were made prior to the cessation of dumping in the late 1990s. It would be useful to conduct similar surveys at this site and others around the SAC, using improved metallothionein assays and other biomarkers, to gauge the success of legislation on recovery of the site and to map biological responses more thoroughly.

3) Nutrients, DOC

The Tamar and Lynher Estuaries have been regarded as displaying a tendency towards being eutrophic and there is a recognition that diffuse sources may play an increasingly important role in this process (Fraser *et al*., 2000; Tamar Estuaries Consultative Forum, 2001). Thus, temporal trends for nitrogen and phosphorus indicate that nutrient concentrations are increasing in much of the cSAC. This may be due in part to an increase in diffuse source inputs due to changing land use in the catchment areas, although the weight of evidence suggests that localised enrichment occurs in the vicinity of point source inputs. The issue already appears to have been taken on board by SWW as there is a current programme of upgrading several STWs which discharge into the cSAC and its tributaries, although very few sites which are due to be upgraded under AMP3 will have nutrient reduction. The major drivers are UWWTD, Bathing Waters and Shellfish Waters Directives, the latter two of which are most concerned with microbiological standards (EA pers comm.). Thus, despite a number of completed improvements to sewage treatment, the most recent data indicate that nutrient concentrations in discharges are still increasing, quite considerably in some cases (e.g nitrate in discharges from Ernesettle STW).

Although nitrate in tidal waters did not appear to be exceptionally high in the late 1990s, levels were increasing and continued surveillance is important. In estuarine and marine ecosystems there is a complex interaction of nutrients between sediment and overlying water, which in the case of N, for example, involves a range of processes including nitrification, denitrification, mineralisation, assimilation and fixation which may all vary spatially and temporally. Phosphorous behaviour, transformations and fluxes are also affected by environmental conditions, particularly low $O_2$. Thus as SOD and BOD levels vary across the seasons, sediments may oscillate between being sources and sinks for $PO_4$. Suspended solids loadings and adsorption/desorption characteristics (e.g. Kp values) will also determine P (and N) concentrations and the ratio of dissolved to particulate forms.

The complexity of the nitrogen and phosphorous 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 any attempt at evaluating the significance of sediment as sources or sinks of N and P is difficult. In order to construct more meaningful budgets the needs are to determine N and P removal rates to sediment, estuarine mixing behaviour, and to look at export rates from the estuary on suspended particles, at different salinities, tidal states, flow rates and seasons.

In terms of ecological impacts it is difficult to establish, precisely, the effects of nutrients. Many of the gaps in our knowledge are discussed at length by Parr *et al* (1999). There is no published evidence to indicate that estuarine benthos are directly affected by nutrient enrichment in the SAC. However since primary productivity is linked to nutrient status, secondary productivity of the benthos will also probably be linked, indirectly. The consequences could be beneficial (in terms of knock-on effects such as increased food items for tertiary consumers, e.g. birds and fish) as well as negative (e.g increased algal smothering of seagrass beds and intertidal flats.) If the

increase in primary productivity involves harmful microlagal blooms the consequences can be highly detrimental (e.g. concentration of PSP transmitting toxins in shellfish).

Effects on many of the rare species in the cSAC are largely unresearched, but in view of their conservation importance, it would seem that an increase in nutrients should be avoided, as a precautionary requirement. Changes to consents (quantities and location) should therefore be considered carefully to avoid the risk of further enrichment.

4) Low dissolved oxygen

Historically DO sags have been associated with large numbers of salmonid deaths in the upper Tamar Estuary. These DO sags occur during low river flow (particularly drought conditions) and are partly caused by natural mechanisms including stratification (most prolonged during neap tides) and large amounts of suspended solids at the turbidity maximum (most pronounced during spring tides).

Detailed water quality surveys of the Tamar by EA, PMSP laboratories and others illustrate that careful selection of chemical determinands and simple analogue calculations can provide useful information on apparently complex estuarine profiles. However, many of these surveys were conducted almost two decades ago. Although many of the process affecting distributions are likely to be the same, conditions may have changed. In view of the legacy of contaminants in sediments (NB metals) this combined format should be considered for future surveys to update our understanding of contaminant behaviour in estuaries of the Plymouth Sound SAC.

5) Microbiological parameters

Values for faecal coliforms in the cSAC indicate a sewage-related problem in the area of the Hoe. The Bathing Water Directive has been a significant driver for recent improvements to STWs and sewerage facilities in the cSAC, however, there is still scope for improvement. SWW have completed a scheme to incorporate secondary treatment and UV disinfection to the current processes at STWs to improve water quality. This has alleviated the problem somewhat, although waters at Plymouth Hoe have repeatedly failed guideline standards, and Plymouth Hoe (E) failed the imperative standard in 2001. Careful monitoring of the situation is strongly recommended.

6) PAHs

Levels of PAHs in sediments of the Tamar, in particular the Hamoaze, are high, and exceed both interim guideline values and the level at which effects to marine life are expected. Low molecular weight PAHs can be acutely toxic to aquatic organisms, but the major concern is that some PAHs form carcinogenically-active metabolites

(benzo[a]pyrene is the prime example) posing a hazard to sediment and bottom dwelling fish and organisms). In future, more monitoring data for PAHs, particularly in Hamoaze discharges, would be valuable when considering consents.

7) Pesticides

Surveys show that despite the reduction in concentrations of pesticides such as lindane, dieldrin and endrin in environmental waters, they continue to be detected in sediment, and in the case of lindane, in surprisingly high concentrations. In general, organic pesticides are highly toxic to aquatic organisms, but restrictions and bans on their use, coupled with their relatively rapid removal from the water column has resulted in low estuarine concentrations. However accumulation and persistence in sediments can be a hazard for sediment dwelling organisms. Several of these substances (lindane, DDT) have been identified as endocrine disruptors, and bioaccumulation and biomagnification in food chains could pose a threat to fish, sea birds and marine mammals. Indications that concentrations of DDD and DDE in sediments of the cSAC are lower than that of the parent compound suggest more recent inputs of DDT (see sections 5.1.4 and 8.3) and warrant investigation.

8) Radionuclides

Results of the available monitoring data for 2000 suggest that the radiological significance of current levels of radionuclides discharged into the SAC is low. However the published data are not extensive. Discharges of tritium from the Devonport Dockyard are expected to rise in the near future as a result of a recent substantial increase in the consent. Although the biological impact is predicted to be minimal, more data and fundamental studies on tritium behaviour, bioaccumulation and effects on marine biota would be welcome.

**Further evidence of impact and possible areas of concern include:**

Endocrine disruption caused by phthalates and other EDs.

High concentrations of phthalates (esp. DEHP) have been reported in waters of the inner Sound. DEHP has a high affinity for sediments and for partitioning to biota where toxic or endocrine disrupting effects cannot be ruled out (see section 5.1.4). There are no data or statistics for phthalates in tidal- or fresh-water, discharges or sediments in the EA dataset and no recent information regarding phthalates in the cSAC is available. Wastewater discharges constitute possible sources of phthalates and the organisms which may be at risk are primarily molluscs and fish.

On balance of evidence it is likely that a number of other endocrine disrupting effects could occur widely in marine environments. As yet no direct evidence is available

that this is occurring in the Plymouth SAC: indeed, preliminary observations in male flounders sampled in 1997 did not reveal any indication of feminisation (Allen *et al.,* 1999). Nevertheless, in view of the potential for effects it would seem desirable to attempt to establish whether or not endocrine disruption is taking place in resident fish and invertebrate populations (sex steroid titres, vitellogenin, gonad development, sex ratios, and secondary sex characteristics). As with TBT-induced imposex, the effects may remain undetected until thorough investigations take place. The review by Allen *et al* (2000) considers the Plymouth SAC as an area of high priority for further ED studies.

Oyster embryo assays

MPMMG have conducted oyster embryo assays which essentially involved the collection, (twice annually, summer and winter) of surface water samples from estuaries in the UK. These were incubated in the laboratory with a fixed number of freshly fertilised embryos of *Crassostrea gigas*. The developing embryos integrate the adverse effects of many contaminants in the sample and if the water quality is poor, they fail to develop normally to D-shaped larvae. Tamar water has been used in this assay for three consecutive years (1993-5), and the percentage net response has increased every year culminating with 100% embryos failing to develop normally in 1995. Failure to reach the normal larval state can be caused by everything from lethal effects to subtle interferences with embryonic development, but the endpoint is a simple expression of water quality in comparison to a clean reference sample of seawater. Thus, poor water quality, which was deteriorating significantly until 1995, was indicated in the cSAC. No specific compound is implicated as being responsible for this failure, although, in reality, it is probably due to a combination of contaminants and not one single compound.

Biodiversity indices

Diversity indices are frequently used to assess the effects of environmental degradation on the biodiversity of natural assemblages of organisms. MPMMG (1998) included a summary of principal univariate statistics to examine biological diversity within benthic communities at coastal and estuarine sampling sites around the UK including Plymouth Sound and the Tamar:

*Abundance* - Contaminated sites (such as the Tyne and Wear) contained highest densities (>10000 $m^{-2}$) dominated by a restricted range of principal species (*Polydora*, *Capitella* and *Ophryotrocha*), probably indicating the effects of organic enrichment. Numbers in the Tamar were ~6100 $m^{-2}$, which compares well with the average abundance for UK estuarine sites in the survey of 6449 $m^{-2}$.

*Species richness* is indicated by the number of taxa per 0.1$m^2$, and both the Tamar and offshore Plymouth Sound scored 100, compared to averages for estuarine sites and offshore sites, 29 and 54 respectively.

*Shannon-Weiner diversity index* expresses the relationships between the occurrence of species and the apportioning of individuals among those species. The Tamar scored ~3.5, and intermediate and offshore Plymouth Sound sites, >5. For comparison, the average for estuarine sites was 2.21, and for intermediate and offshore sites, 3.59 and 4.05. Evenness is a complementary measure of the allocation of individuals across species: low values are associated with samples from sites numerically dominated by only one or two species which is generally indicative of stressed communities. The evenness statistic for the Tamar was ~0.5, close to the mean of 0.503 for estuarine sites. Offshore (Plymouth Sound) the score was ~1, higher than the average 0.738.

It is evident from these indices that biodiversity in Plymouth Sound and estuaries fares reasonably well in comparisons with other UK estuaries. However, MPMMG acknowledges that sites such as the Plymouth cSAC have relatively more extensive salinity regimes, along with variable substrate types that provide a wider array of niches for colonisation, than most others used in the comparisons. Therefore, this data can only be used as a rough guide in characterising the site.

*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 Plym and Tamar, 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 Tamar, none of the six sites sampled appeared to be completely undisturbed. St Johns Lake (N), Clifton, Cargreen and Weir Quay were classified as moderately disturbed, whilst St Johns Lake sites (SE, and SW) were grossly disturbed. All three sites in the Plym, between Laira Bridge and Marsh Mills, were assessed in this study as being undisturbed. However, given the proximity of Chelson Meadows landfill site, Marsh Mills STW and the china clay deposits entering the Plym via Tory Brook, this classification appears to be somewhat anomalous.

*Taxonomic distinctness* - Using data on free-living marine nematodes in mud samples from 16 localities/habitat types in the UK including the Tamar, Warwick *et al* (1999) looked at the taxonomic distinctness (TD - which captures phylogenetic diversity rather than simple species richness, and is more linked to functional diversity), and variation in taxonomic distinctness (varTD), as a measure of biodiversity. These two parameters, in combination, can be used to pick out degraded locations. Low-to-average TD and low-to-normal VarTD identify the Tamar 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.

Thus, biological indices indicate that biodiversity in the cSAC is not overtly impaired, compared with other UK estuaries. It should be remembered however that the cSAC is fairly unique in its wide range of salinities and variety of interest features (i.e. large

shallow inlets and bays, estuaries, subtidal sandbanks, reefs, salt meadows, intertidal mudflats and sandflats). With such a wide range of habitats within its boundaries, biodiversity within the cSAC might be expected to be well above average.

In comparing existing chemical and biological classifications for Plymouth Sound and estuaries cSAC it is clear that there may be inconsistencies. This is not surprising since site-specific biological effects information is extremely limited, and the available chemical data are not necessarily designed to accurately predict complex biological responses. In the absence of truly integrated studies, compliance with environmental standards and guidelines has been used extensively to gain a 'first-impression' of impact on biota. Thus, 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). 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 have been used here merely help to highlight some of those sites and conditions which merit closer investigation.

**Recommendations for Future Research**

Most high quality chemical survey data and interpretation for the Plymouth SAC is now of the order of 10 years old, or more. Many of the measurements made since then have been largely focused on compliance monitoring and are not adequate to characterise the character of the site as a whole. Co-ordinated chemical and biological surveys are needed for a better evaluation of impact from consented discharges and for a more accurate assessment of the 'health' of the site as a whole. These need to be targeted (on economic grounds) at the most important issues and well-designed (on scientific-grounds) so that they answer, adequately, the questions being asked by the regulatory agencies.

Further up-to date survey of TBT, metals, PAHs, selected pesticides and nutrients in sediment, water and biota should be conducted to examine spatial and temporal trends in contaminants.

With regard to TBT, this should coincide with collection of contemporary information on imposex levels and population data for neogastropods (*Nucella, Nassarius)* at established sites, and ascertaining the prognoses for re-colonisation at others. These studies are needed to judge both the effectiveness of current legislation, and as baselines for the impending IMO ban on TBT-based antifouling paint scheduled for 2003.

Since an increasing percentage of the contaminant burden in the environment is likely to reside in sediment there is a need for research on persistence, toxicity and bioavailability. This should include studies on the combined effects of TBT, metal, PAHs, selected pesticides and nutrients. Results would contribute to the derivation of more appropriate 'Quality Standards' for sediments

Among the variables which might affect retention of contaminants in the Plymouth Sound SAC are resuspension events, dredging, burial of sediment, storage and the influence of major bioturbators and their ability to bury or redistribute contaminants.

To accompany targeted chemical data, it is essential to extend biological impacts studies, and hence to establish cause and effect linkages. Comparisons with EQS and sediment guidelines may give a useful approximation of risk, particularly if only one stressor is involved: however, predicting total exposure risks in receiving waters or sediments which are subjected to complex mixtures (which may interact in terms of toxicity) tends to compound the uncertainties surrounding the EQS approach. Biological-effects techniques are now available which would allow screening of the SAC, including possible problem discharges. By selection of an appropriate suite of indicators/biomarkers, a sampling strategy could be tailor-made to establish with greater certainty the causes and extent of damage. These include chemical and biomonitoring procedures 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 further details). These should be used alongside more traditional ecological survey procedures, some of them multivariate, to identify changes in the abundance and diversity of species, and possible causes. When these procedures are used in combination in well-designed survey programmes, they can provide insight into which areas may be degraded and which pollutants are responsible. They are equally amenable for measuring long-term trends e.g in the assessment of recovery or deterioration. The scheme should be developed as a rolling programme to monitor the health of the environment within the cSAC i.e. to ensure that conditions remain favourable for the continued survival of biota.

It would seem advisable to initiate a series of baseline studies on radionuclide content and genotoxic effects in key bioindicator species (e.g shrimps, clams, phytoplankton) particularly with a view to monitoring the effects of change in discharge limits for tritium. The potential impact on marine biota caused by radionuclide remobilisation

during dredging operations in the Tamar, are unknown and appear to be an important area for research.

Research is needed to address the notable lack of firm data on endocrine disruptors and to confirm the presence or absence of their effects in the cSAC.

Modelling the dispersal of contaminants and the distribution of toxic effects has proved feasible using the modelling shell ECoS. Constraints on the model are mainly related to the need for further validation e.g. axial profiles of contaminant distributions along estuaries. Among a shortlist of other topics needing investigation are vertical and lateral heterogeneity; particle and solute fluxes across the bed; sediment mixing and structure; kinetics of uptake and loss and impact of body burdens in a range of species (particularly infaunal organisms like *Scrobicularia plana*). The current model is therefore seen as a basis for progress rather than an end in itself.

# 11. BIBLIOGRAPHY


Ackroyd, D.R. (1983). Removal and remobilization of heavy metals during estuarine mixing. (Thesis) 261p. Plymouth Polytechnic, 1983.

Ackroyd, D. R., A. J. Bale, Howland, R.J.M , Knox, S., Millward, G.E. and Morris , A.W. (1986). Distributions and behaviour of dissolved Cu, Zn and Mn in the Tamar estuary. Estuarine, Coastal and Shelf Science. 23: 621-640.

Ackroyd, D. R., G. E. Millward, and Morris A.W. (1987). Periodicity in the trace metal content of estuarine sediments. Oceanologica Acta. 10: 161-168.

Ahel, M., K. M. Evans, Fileman, T.W. and Mantoura, R.F.C. (1992). Determination of atrazine and simazine in estuarine samples by high-resolution gas chromatography and nitrogen selective detection. Analytica Chimica Acta. 268: 195-204.

Allen, Y.T., Matthiessen, P., Scott, A.P., Haworth, S., Feist,S. and Thain, J.E. (1999). The extent of oestrogenic contamination in the UK estuarine and marine environments – further surveys of flounder. Sci. Total. Envir. 233, 5-20.

Allen, Y.T., Hurrell, V., Reed, J. and Matthiessen, P. (2000). Endocrine Disruptors and European Marine Sites in England. Centre for Environment Fisheries and Aquaculture Science (CEFAS). Contract C01042 for English Nature. 159p

Allison, D.M.and Sawyer, L.J. (1987). The UK Ministry of Defence's experiences, practices, and monitoring programmes for the application, maintenance and removal of erodable organotin antifouling paints. In: Oceans 87. Proceedings. Vol. 4. International organotin symposium. p.1392-1397. New York: Institute of Electrical and Electronics Engineers.

Anderson, M.J., Miller, M.R. and Hinton, D.E. (1996a) In vitro modulation of 17-beta -estradiol-induced vitellogenin synthesis: Effects of cytochrome P4501A1 inducing compounds on rainbow trout (*Oncorhynchus mykiss*) liver cells Aquatic Toxicology 34(4):327-350

Anderson, M.J.,Olsen, H., Matsumara, F. and Hinton, D.E. (1996b) In vivo modulation of 17- beta -estradiol-induced vitellogenin synthesis and estrogen receptor in rainbow trout (*Oncorhynchus mykiss*) liver cells by beta-napthoflavone. Toxicology and Applied Pharmocology 137:210-218

Anon. (1993). Consultation paper on the methodology for identifying sensitive areas (Urban Waste Water Treatment Directive) and methodology for designating vulnerable zones (nitrates directive) in England and Wales. March 1993. DOE, MAFF and Welsh Office.

Armitage, M. J. S., Burton, N. H. K., Atkinson, P. W., Austin, G. E., Clark, N. A., Mellan H. J. and Rehfisch, M. M. (2002) Reviewing the Impact of Agency Permissions and Activities on Bird Populations in Special Protection Areas: Level 1 Interpretation. BTO Research Report No. 296. 156pp. The National Centre for Ornithology, Thetford, Norfolk.

Aston, S. R., I. Thornton, Webb, J.S., Milford, B.L. and Purves, J.B. (1975). Arsenic in stream sediments and waters of South-west England. Science of the Total Environment. 4: 347-358.

Bale, A.J. (1983). The characteristics, behaviour and heterogeneous chemical reactivity of estuarine suspended particles: an interim report. Characterisation of the natural variability, behaviour and properties of estuarine particles. 76pp. Institute for Marine Environmental Research, (IMER Miscellaneous Publications No. 5)

Bale, A.J. and Morris, A.W. (1981). Laboratory simulation of chemical processes induced by estuarine mixing: the behaviour of iron and phosphate in estuaries. Estuarine Coastal and Shelf Science,13, 1-10.

Bale, A.J., A. W. Morris and Howland, R.J.M. (1985). Seasonal sediment movement in the Tamar estuary. Oceanologica Acta. 8: 1-6.

Bedding ND, McIntyre AE, Perry R, Lester JN (1982). Organic contaminants in the aquatic environment 1. Sources and occurrence. Science of the Total Environ. 25: 143-167.

Belcher, J.H. and Swale, E.M.F. (1978). *Skeletonema potamus* (Weber) Hasle and *Cyclotella atomus* Hustedt (Bacillariophyceae) in the plankton of rivers in England and France. *British Phycological Journal*, 13, 177-182

Berg, C. M. G., P. J. M. Buckley, Huang, Z.Q. and Nimmo, M.. (1986). An electrochemical study of the speciation of copper, zinc and iron in two estuaries in England. Estuarine, Coastal and Shelf Science. 22: 479-486.

Berg, C. M. G., S. H. Khan, Daly, P.J. , Riley, J.P. and Turner, D.R. (1991). An electrochemical study of Ni, Sb, Se, Sn, U and V in the estuary of the Tamar. Estuarine and Coastal Shelf Science. 33: 309-322.

Besten, P.J. den, Elenbaas, J.M.L., Maas, J.R. Dieleman, S.J. herwig, H.J. & Voogt, P.A. (1991) Effects of cadmium and polychlorinated biphenyls (Clophen A50) on steroid metabolism and cytochrome P-450 monooxygenase system in the sea star *Asterias rubens* L. Aquatic Toxicol., 20, 95-110.

Bird, D. J (2002). Environmental Factors Affecting Migratory Fish in The Severn Estuary with Particular Reference to Species of Shad and Lamprey. Report for the Environment Agency Wales. Severn Estuary Research Group, University of the West of England, Bristol

Bird, P., Comber, S.D.W., Gardner, M.J., Ravenscroft, J.E. (1996) Zinc inputs to coastal waters from sacrificial anodes. Science of the Total Environment, 181(3), 257-264

Blackburn, M. A., S. J. Kirby and Waldock, M.J. (1999). Concentrations of alkyphenol polyethoxlates entering UK estuaries. Marine Pollution Bulletin. 38: 109-118.

Blaber, S.J.M (1970) The occurrence of a penis-like outgrowth behind the right tentacle in spent females of *Nucella lapillus* (L.). Proceedings of the Malacological Society of London, 39, 231-233.

Blanchard, M. (1997). Spread of the slipper limpet *Crepidula fornicata* (L.1758) in Europe. Current state and consequences. Scientia Marina, 61(9):109-118.

Boalch, GT (1983). Recent dinoflagellate blooms in the Plymouth area. British. Phycol. J., 18, 200-201,

Boalch, GT; Potts, GW (1977) The first occurrence of *Sargassum muticum* (Yendo) Fensholt in the Plymouth area. Journal of the Marine Biological Association of the United Kingdom. Plymouth . 57, 1, 29-31.

Boalch, GT; Holme, NA; Jephson, NA; Sidwell, IMC (1974) A resurvey of Colman's intertidal traverses at Wembury, South Devon. Journal of the Marine Biological Association of the United Kingdom. 54, no. 3, pp. 551-553,

Boström, C. and Bonsdorff, E. (1997). Community structure and spatial variation of benthic invertebrates associated with *Zostera marina* (L.) beds in the northern Baltic Sea. Journal of Sea Research, 37(1/2):153-166

Bryan, G.W. Pollution due to heavy metals and their compounds. In Marine Ecology Vol. 5., O.Kinne (Ed.), John Wiley and Sons Ltd, part 3, 1984.

Bryan, G.W., and Gibbs, P.E. Polychaetes as indicators of heavy-metal availability in marine deposits, in *Oceanic Process. in Mar. Pollut.,* Vol. 1. *Biol. Process. and Wastes in the Ocean,* Capuzzo, J.M., and Kester, D.R., Eds., Krieger, Melbourne, USA, 1987, Chap. 4.

Bryan, G.W., Langston, W.J. 1(992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Environmental Pollution, 76(2): 89-131

Bryan, G.W. and Hummerstone, L.G. (1973a). Brown sea weed as an indicator of heavy metals in estuaries in south-west England. J. Mar. Biol. Ass. UK., 53: 705-720.

Bryan, G.W. and Hummerstone, L.G. (1973b). Adaptation of the polychaete Nereis diversicolor to estuarine sediments containing high concentrations of zinc and cadmium. Journal of the Marine Biological Association of the United Kingdom, 53, 839-857,

Bryan, G.W., Langston, W.J., and Hummerstone, L.G. (1980) The use of biological indicators of heavy metal contamination in estuaries, with special reference to an assessment of the biological availability of metals in estuarine sediments from South-West Britain. Mar. Biol. Ass. U.K. Occasional Publication No. 1, 73 pp.

Bryan, G.W., Langston, W.J., Hummerstone, L G., Burt, G.R., and Ho, Y.B. (1983). An assessment of the gastropod, *Littorina littorea*, as an indicator of heavy metal contamination in U.K. estuaries, J. Mar. Biol. Assoc. U.K., 63, 327, .

Bryan, G.W., Langston, W.J., Hummerstone, L.G., and Burt, G.R..(1985). A guide to the assessment of heavy-metal contamination in estuaries using biological indicators, Mar. Biol. Ass. U.K., Occasional Publication No. 4, 92 pp.

Bryan, G.W., Gibbs, P.E., Hummerstone, L.G. & Burt, G.R., 1986. The decline of the gastropod Nucella lapillus around south-west England: evidence for the effect of tributyltin from antifouling paints. Journal of the Marine Biological Association of the United Kingdom, 66, 611-640.

Bland, S., D. R. Ackroyd, J.G. Marsh and G.E. Millward. (1982). Heavy metal content of oysters from the Lynher estuary, U.K. Science of the Total Environment. 22: 235-241.

CCME. (1992). Canadian water quality guidelines, prepared by the taskforce on water quality guidelines of the Canadian Council of Ministers of the environment, Eco-Health branch, Ottawa, Ontario, Canada

Clarke, K. R. and R. M. Warwick (2001). A further biodiversity index applicable to species lists: variation in taxonomic distinctness. *Marine Ecology Progress Series.* 216: 265-278.

Clifton, R.J. and Hamilton, E.I. (1979) Lead-210 chronology in relation to levels of elements in dated sediment core profiles. *Estuarine and Coastal Marine Science*, 8, 259-269.

Chiou, C.T., Malcolm, R.L., Brinton, T.I and Kile, D.E. (1986). Water-solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids. Environmental Science and Technology, 20:502-508

Coggan, R.A.; Dando, P.R. (1988) Movements of juvenile Dover sole, Solea solea (L.), in the Tamar Estuary, south-western England. Journal of Fish Biology, 33, Supplement A, 177-184.

Cole, J.A. (1988).Gunnislake Pumping Station – Interim report on arsenic pollution risk. WRc Report to SWW. CO 1976-M/EV 8829. 19pp.

Cole, S., Codling, I.D.,; Parr, W. and Zabel, T. (1999) Guidelines for managing water quality impacts within UK European marine sites. 441p. Swindon: WRc, 1999.

Collier, A. (1992). Determination of organotin/TBT in water and sediment samples taken from Chelson Meadow disposal site. Devonport Management Limited. 25pp

Crouch, W. 1894. On the occurrence of *Crepidula fornicata* (L.) off the coast of Essex. Essex Naturalist, 8: 36-38.

Crouch, W. 1895. On the occurrence of *Crepidula fornicata* in Essex. Proceedings of the Malacological Society, 1: 19.

CSL (2000) Environmental endocrine disruptors: Review of research on top predators. Report for DETR, 111pp

Dahl, B. and Blanck, H. (1996). Toxic effects of the antifouling agent Irgarol 1051 on periphyton communities in coastal water microcosms Marine Pollution Bulletin 32(4):342-350

Currás, A., Sánchez-Mata, A. and Mora, J. (1993). [Comparative study of benthic macrofauna collected from sediments within a seagrass bed (Zostera marina) and an adjacent unvegetated area.] Cahiers de Biologie Marine. Paris 35:91-112

Dando, PR; Demir, N AF: Journal of the Marine Biological Association of the United Kingdom, 65, 1, 159-168, 1985.

Darbyshire, E. (1996). Water quality profiling in the upper Tamatr Estuary during the summer of 1995. Tidal Waters Quality – Report No: TWQ/96/08. Environment Agency, Exeter.

.Davison, D.M. and .Hughes, D.J. (1998). Zostera Biotopes (volume I). An overview of dynamicsand sensitivity characteristics for conservation management of marine SACs. ScottishAssociation for Marine Science (UK Marine SACs Project). 95 pp

De Montaudouin, X. and Sauriau, P.G., (1999). The proliferating Gastropoda Crepidula fornicata may stimulate macrozoobenthic diversity. Journal of the Marine Biological Association of the United Kingdom, 79(6):1069-1077).

Dong, L.F., Nedwell, D.B., Underwood, G.J.C. and Sage, A.S. (2000). Environmental limitations of phytoplankton in estuaries. Final Report. 51p. + appendix. Colchester: University of Essex, (DETR contract No CW0694; Northeast Atlantic Marine Research Programme No. 97)

Doyotte, A., Mitchelmore, C.L., Ronisz, D., McEvoy, J., Livingstone, D.R. and Peters, L.D. (2001) Hepatic 7-ethoxyresorufin O-deethylase activity in eel (Anguilla anguilla)from the Thames estuary and comparisons with other United Kingdom estuaries Marine Pollution Bulletin 42(12):1313-1322

Duffy M, Fisher S, Greenhill B, Starkey DJ, Youings J (1994) The new maritime history of Devon. Volume II: From the late eigthteenth century to the present day. Conway Maritime Press Limited, London, pp 272

Durrance EM, Laming, D.J.C., Eds. (1982) The geology of Devon: 346pp

EA (2000). Endocrine-disrupting substances in the environment: The Environment Agency's strategy. Environment Agency 23p.

EA (1996) Local environment agency plan - Tamar estuary and tributaries - consultation report. Environment Agency, pp xi,215

Eagle, R.A., Hardiman, P.A., Norton, M.G. and Nunny, R.S. (1979). Fish Res. Tech. Report, No 50, MAFF Direct. Fish Res., Lowestoft.

Elliott, M. and Griffiths, A.H. (1987). Contamination and effects of hydrocarbons on the Forth ecosystem, Scotland. Proceedings of the Royal Society of Edinburgh, 93B, 327-342

English-Nature (2000) Plymouth Sound and estuaries European marine site. English Nature's advice given under Regulation 33(2) of the Conservation (Natural Habitats & c.) Regulations 1994,. English Nature

Ehrhold, A., Blanchard, M., Auffret, J.P. & Garlan, T., 1998. The role of Crepidula proliferation in the modification of the sedimentary tidal environment in Mont Saint-Michel Bay (the Channel, France). Comptes Rendus de L'Acadamie des Sciences. Paris, 327, 583-588.

Evans K.M., Fileman T.W., Ahelm M., Mantoura R. and Cummins, D. (1993). Fate of organic micropollutants in estuaries (triazine herbicides and alkyl phenol polyethoxylates). National Rivers Authority, R&D Note 306

Fernandes, M. B., M. A. Sicre, Broyelle, I., Lorre, A. and Pont, D. (1999). Contamination by polycyclic aromatic hydrocarbons (PAHs) in French and European rivers. Hydrobiologia 410: 343-348.

Fonseca, M.S., (1992). Restoring seagrass systems in the United States. In: Restoring the Nation's Marine Environment. Maryland Sea Grant College, Maryland, USA. 79-110 pp.

Franklin, A. and Pickett, G.D. (1974). Recent research on introduced oyster pests in England and Wales. Unpublished, International Council for the Exploration of the Sea. (Paper, No. CM 1974/K:15.)

Fraser, A.I., Butterfield, D., Uncles, R., Johnes, P. and Harrod, T.R. (2000) Fal and Helford special areas of conservation (cSAC) and the Tamar Estuaries complex cSAC/special protection area (pSPA): Estimation of diffuse and point-source nutrient inputs. SSLRC report to the EA. 89pp

Freshney E.C., Keown M.C. and Williams M. (1972) Geology of the coast between Tintagel and Bude (explanation of part of one-inch geological sheet 322, new series). H.M.S.O., pp viii, 92

Fretter, V. and Graham, A., (1981). The Prosobranch molluscs of Britain and Denmark, part 6. Journal of Molluscan Studies, Supplement 9: 309-313.

Friedrichs, C.T., Armbrust, B.D. and de Swart, H.E. (1998). Hydrodynamics and equilibrium sediment dynamics of shallow, funnel-shaped tidal estuaries. In: Physics of Estuaries and Coastal Seas, Dronkers and Scheffers (Eds). Balkema, Rotterdam, 315-327

Fry, D.M. (1995). Reproductive effects in birds exposed to pesticides and industrial chemicals. Environ. Health Perspect. 103, 165-171.

Geileskey, S (2000). Dogwhelk populations and the influence of tributyl-tin induced imposex around the Cornish and southwest Devon coasts. Environment Agency.

Gantzer, C., Senouci, S., Maul, A., Lévi, Y. and Schwartzbrod L. (1999) Enterovirus detection from wastewater by RT-PCR and cell culture Water Science and Technology 40(2):105–109

GESAMP - Joint Group Of Experts On The Scientific Aspects Of Marine Pollution (GESAMP) (1993). Impact of oil and related chemicals and wastes on the marine environment. GESAMP Reports and Studies No. 50. IMO. London. 180pp

Gibbs, P.E. and Bryan, G.W., 1986. Reproductive failure in populations of the dog-whelk, *Nucella lapillus,* caused by imposex induced by tributyltin from antifouling paints. Journal of the Marine Biological Association of the United Kingdom, **66,** 767-777.

Gibbs, P. E. and W. J. Langston (1994). Tributyltin (TBT)contamination of estuarine sediments. Department of the Environment Contract PECD 7/8/175, 1 September 1990 - 31 December 1993. Final Report, Plymouth Marine Laboratory: 78.

Gibbs, P.E., Bryan, G.W., Pascoe, P.L. & Burt, G.R., 1987. The use of the dog-whelk, *Nucella lapillus,* as an indicator of tributyltin (TBT) contamination. Journal of the Marine Biological Association of the United Kingdom*,* **67**, 507-523.

Gibbs, P.E., Bryan, G.W., Pascoe, P.L. & Burt, G.R., 1990. Reproductive abnormalities in female *Ocenebra erinacea* (Gastropoda) resulting from tributyltin-induced imposex. Journal of the Marine Biological Association of the United Kingdom*,* **70**, 639-656.

Gundlach, E.R.and Hayes, M.O. (1978).Vulnerability of coastal environments to oil spill impacts. Marine Technology Society Journal, 12:18-27.

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

Hallers-Tjabbes, C.C; Kemp, J.F; Boon, J.P. (1994) Imposex in whelks (*Buccinum undatum*) from the open North Sea: relation to shipping traffic intensities. *Marine Pollution Bulletin* **28**, 311-313.

Harris, J.W. (1988). Roadford environmental investigation water quality model of the Tamar Estuary. Modelling oxygen levels in the Tamar Estuary. PML, Prospect Place , Plymouth.

Harris, J.R.W., Bale, A.J., Bayne, B.L., Mantoura, R.F.C., Morris, A.W., Nelson, L.A., Radford, P.J., Uncles, R.J. (1984) A preliminary model of the dispersal and biological effect of toxins in the Tamar Estuary, England. Modelling the Fate and Effect of Toxic Substances in the Environment, 22:1-4.

Harris, J.R.W., Hamlin, C.C. and Stebbing, A.R.D., 1991. A simulation study of the effectiveness of legislation and improved dockyard practice in reducing TBT concentrations in the Tamar estuary. *Marine Environmental Research*, **32**, 279-292.

Harris, M.P. (1992). Investigation into the oxygen levels, in association with salmonid deaths in the upper reaches of the Tamar Estuary 1989. Environmental Protection Report TWU/89/013, National Rivers Authority, South West Region, 8p.

Hartley, P.H.T. (1939).The Saltash tuck-net fishery and the ecology of some estuarine fishes. Journal of the Marine Biological Association of the United Kingdom, 24, 1-68.

Hatcher, P.G. and McGillivary, P.A. (1979)Sewage contamination in the New York Bight. Coprostanol as an indicator Environmental Science and Technology 13(10):1225-1229

Hiscock, K., (1987). The distribution and abundance of Zostera marina in the area of Littlewick Bay, Milford Haven, with an account of associated communities and hydrocarbon contamination of sediments. Surveys undertaken in 1986. Final report to the Institute of Petroleum., London. Field Studies Council, Pembroke, Wales. 34 pp

Hiscock, K. and Moore, J. (1986) Surveys of harbours, rias and estuaries in southern Britain: Plymouth area, including the Yealm. Volume 1 - Report. 143p. Peterborough: Nature Conservancy Council, NCC CSD Report 752; FSC/OPRU/36/86

Holt, T.J., Hartnoll, R.G., & Hawkins, S.J., (1997). Sensitivity and vulnerability to man-induced change of selected communities: intertidal brown algal shrubs, *Zostera* beds and *Sabellaria spinulosa* reefs. Peterborough, English Nature, Research Report No. 234

Howard,A.G., Apte, S.C., Comber, S.D.W and Morris, R.J. (1988). Biogeochemical control of the summer distribution and speciation of arsenic in the Tamar Estuary. Estuarine Coastal and Shelf Science,27, 427-443.

Hunt, S. and Hedgecott, S. 1992. Revised Environmental Quality Standards for chromium in water, WRc report to the Department of the Environment DoE 2858/1.

IACMST (1994). Report of the Marine Environmental Data Working Group. Inter-Agency Committee on Marine Science and Technology. Working Group Report No 2

Jacobs, R.P.W.M., (1980). Effects of the Amoco Cadiz oil spill on the seagrass community at Roscoff, with special reference to the benthic infauna. Marine Ecology Progress. Series, 2: 207-212

Jackson, , R.H., Williams, P.J. le B. and Joint, I.R. (1987). Freshwater phytoplankton in the low salinity region of the Tamar Estuary. Estuarine Coastal and Shelf Science,25, 299-311

Jobling S, Reynolds T, White R, Parker MG and Sumpter JP (1995). A variety of environmentally persistant chemicals, including some phthalate plasticizers, are weakly estrogenic. Environ. Health Perspect. 103: 582-587.

Johnson, D. and T. J. Lack (1985). Some responses of transplanted *Mytilus edulis* to metal-enriched sediments and sewage sludge. Marine Environmental Research 17: 277-280.

Johnson, W. W. and Finley, M. T. (1980) Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates, Resource Publications 137. U.S. Department of the Interior, Fish and Wildlife Service, Washington, DC pp10-38

Jones, H., Crane, R. and Zabel, T. (1996). Proposed provisional environmental quality standards for Azinphos-methyl in water. WRc Report No. DoE 2348(P)

Keil, R.G., Montiucon, D.B., Prahl, F.G. and Hedges, J.I. (, 1994). Sorptive preservation of labile organic matter in marine sediments. Nature 370(6490): 549-552

Kelley, D. (2002). Abundance, growth and first-winter survival of young bass in nurseriesof south-west England. Journal of the Marine Biological Association of the United Kingdom, 82, 307-319.

Kirby, M.F., Morris, S., Hurst, M., Kirby, S.J., Neall, P.,Tylor, T. and Fagg, A. (2000). The use of cholinesterase activity in flounder (*Platichthys flesus*) muscle tissue as a biomarker of neurotoxic contamination in UK estuaries. Marine Pollution Bulletin, 40(9):780-791

Kirubagaran, R. and Joy, K.P. (1991). Changes in adrenocortical-pituitary activity of the catfish, *Clarias batrachus* (L.) after mercury treatment. *Ecotoxicol. Environ. Safety*, 22, 36-44

Klyuev, N.A., Brodskii, E.S., Murenets, N.V., Tarasova, O.G. and Zhil'nikov, V.G. (1993) Determination of organic pollutants in Danube water by the chromatography-mass spectrometry method. Water Resource 20(4):83-91

Knox, S., Turner,D.R. , Dixon, A.G., Liddicoat,M., Whitfield, M. and Butler E.I. (1981). Statistical analysis of estuarine profiles: II Application to arsenic in the Tamar estuary (S.W.England). Estuarine Coastal and Shelf Science,13, 357-371

Knox, S., Langston, W.J., Whitfield, M., Turner,D.R. and Liddicoat, M. (1984). Statistical analysis of estuarine profiles: II Application to arsenic in the Tamar estuary (S.W.England). Estuarine Coastal and Shelf Science,18, 623-638

Knox, S., M. Whitfield, et al. (1986). Statistical analysis of estuarine profiles: III. Application to nitrate, nitrite and ammonium in the Tamar estuary. Estuarine, Coastal and Shelf Science. 22: 619-636.

Knudsen F.R. and Pottinger T.G. (1999). Interaction of endocrine disrupting chemicals, singly and in combination, with estrogen-, androgen-, and corticosteroid-binding sites in rainbow trout (*Oncorhynchus mykiss*). Aquatic Toxicology 44: 159-170.

Kocan, R.M., Marty, G.D. Okihiro, M.S., Brown, E.D. and Baker, T.T. (1996) Reproductive success and histopathology of individual Prince William Sound Pacific herring 3 years after the Exxon Valdez oil spill. Canadian Journal of Fisheries and Aquatic Sciences. 53(10):2388-2393

Langston, W.J. (1980). Arsenic in U.K. estuarine sediments and its availability to benthic organisms. J.Mar.Biol.Ass.U.K., 60, 869-881.

Langston, W.J. (1982). The distribution of mercury in British estuarine sediments and its availability to deposit-feeding bivalves. J.Mar.Biol.Ass.U.K., 62, 667-684.

Langston, W.J. (1983). The behaviour of arsenic in selected United Kingdom estuaries. Can.J.Fish.Aquat.Sci., 40, supplement 2, 143-150.

Langston, W. J. and Burt, G. R. (1991) Bioavailability and effects of sediment-bound TBT in deposit-feeding clams, Scrobicularia plana. Marine Environmental Research, 32,61-77.

Langston, W. J. and N. J. Pope (1995). Determinants of TBT adsorption and desorption in estuarine sediments. Marine Pollution Bulletin. 31: 32-43.

Langston, W.J., Bryan, G.W., Burt, G.R. and Pope, N.D. (1994a) Effects of sediment metals on estuarine benthic organisms, R&D Note 203, National Rivers Authority , 141pp

Langston, W.J., Bryan, G.W., Burt, G.R.(1994b). Heavy metals in UK estuaries:PML data and mapping programme,R&D Note 280, National Rivers Authority, 85pp.

Langston, W.J., Bryan, G.W., Burt, G.R. and Pope, N.D. (1994c) Effects of sediment metals on estuarine benthic organisms, Project Record 105/2/A, National Rivers Authority , 49pp

Langston W.J , Bebianno, M.J and Burt, G.R. (1998) . Metal handling strategies in molluscs. In : Langston W.J and Bebianno, M.J (Eds) Metal metabolism in Aquatic Environments, Kluwer Academic Publishers, 219-283

Langston, W.J., Burt, G.R. and Pope, N.D**.** (1999) Bioavailability of metals in sediments of the Dogger Bank (central North Sea): a mesocosm study (Estuarine Coastal and Shelf Science (519-540)

Langston, W. J., Chesman, B. S., Burt , G.R. , Pope, N.D. and McEvoy, J. (2002) Metallothionein in liver of eels *Anguilla anguilla* from the Thames Estuary: an indicator of environmental quality? Marine Environmental Research, 53, 263-293

Law R. J, Fileman TW and Matthiessen P (1991). Phthalate esters and other industrial organic chemicals in the North and Irish Seas. Wat.Sci.Tech. 10:127-134.

Law, R.J., Dawes, V.J., Woodhead, R.J., Matthiessen, P. (1997). Polycyclic aromatic hydrocarbons (PAH) in seawater around England and Wales. Marine Pollution Bulletin 34(5):306-322

Leah, R., Johnson, M.S., Connor, L. and Levene, C.F (1997b). Polychlorinated biphenyls in fish and shellfish from the Mersey Estuary and Liverpool Bay. Marine Environmental Research. 43(4):345-358

Lewis S, Howe, A.J., Comber S, Reynolds P, Mascarenhas R, Sutton A and Rogers H (1998). Proposed environmental quality standards for phthalates in water. DoE Report No. 3929/3, 205pp

Lewis, F.G. III and Stoner, A.W. (1981). An examination of methods for sampling macrobenthos in seagrass meadows. Bulletin of Marine Science 31:116-124

Lindsay, P. and Bell, F.G. (1997) Contaminated sediment in two United Kingdom estuaries. Environmental and Engineering Geoscience, 3, 375-387.

Luoma, S. N. and Bryan, G. W. (1982) A statistical study of environmental factors controlling concentrations of heavy metals in the burrowing bivalve *Scrobicularia plana* and the polychaete *Nereis diversicolor*, Estuarine and Coastal Shelf Science, **15:** 95-108

Maddock, L, Harbour, D.S. Boalch, G.T. (1989) Seasonal and year-to-year changes in the phytoplankton from the Plymouth area, 1963-1986. Journal of the Marine Biological Association of the United Kingdom, 69, 1, 229-244,

Mantoura, R.F.C. and Woodward, E.M.S. (1983). Conservative behaviour of riverine dissolved organic carbon in the Severn Estuary: chemical and geochemical implications. Geochimica et Cosmochimica Acta, 47:1293-1309

Marine Pollution Monitoring Management Group (MPMMG) (1998). National Monitoring Programme. Survey of the quality of UK coastal waters. 80p. London: Stationery Office

Martin, W.J., Ravi Subbiah, M.T., Kottke, B.A., Birk, C.C. and Naylor, M.C. (1973) Nature of faecal sterols and intestinal bacterial flora. Lipids 8:208

Matthiessen, P., Thain, J.E., Law, R.J. and Fileman, T.W. (1993) Attempts to assess the environmental hazard posed by complex mixtures of organic chemicals in UK estuaries. Marine Pollution Bulletin, 26(2): 90-95

Matthiesson, P.,. Allen, Y. T. (1998). Oestrogenic endocrine distribution in flounder (*Platichthys flesus* L.) from United Kingdom estuarine and marine waters. Science Series Technical Report. CEFAS. 107: 48.

Malins, D.C., McCain, B.B., Landahl, J.T, Myers, M.S., Krahn, M.M., Brown, D.W., Chan, S.L. and Roubal, W.T. (1988). Neoplastic and other diseases in fish in relation to toxic chemicals: an overview. Aquatic Toxicology 11:43-67

McKeown M.C., Edmonds E.A., Williams M, Freshney E.C., Masson Smith D.J. (1973) Memoirs of the geological survey of Great Britain. Geology of the country around Boscastle and Holsworthy. (Explanation of the inland areas of one-inch geological sheet 322 and 1:50 000 geological sheet 323, new series). H.M.S.O., London, pp x, 148

MBA, 1957. Plymouth Marine Fauna. Marine Biological Association, Plymouth. pp.457.

MCA (2002) (Marine Coastguard Agency). National contingency plan for marine pollution from shipping and offshore installations http://www.mcagency.org.uk/

Mears, M. (1997). Yealm estuary. Management plan 1997. Draft, Yealm Estuary Management Plan Steering Group: ii,64.

Miller, A.E.J. (1999). Seasonal investigations of dissolved organic carbon dynamics in the Tamar estuary, U.K. Estuarine, Coastal and Shelf Science, 49(6):891-908

Millward, G.E. and Herbert, I. (1981). The distribution of mercury in the sediments of the Plym Estuary. Environmental Pollution , series B, 2, 265 –274.

Minchin, D., McGrath, D. and Duggan, C.B. (1995). The slipper limpet, Crepidula fornicata (L.), in Irish waters, with a review of its occurrence in the north-eastern Atlantic. Journal of Conchology, 35: 247-254.

Mommaerts, J. P. (1969). On the distribution of major nutrients and phytoplankton in the Tamar Estuary. *Journal of the Marine Biological Association of the United Kingdom*. 49: 749-765.

Moore, A. and Waring, C.P. (1996) Sublethal effects of the pesticide diazinon on olfactory function in mature male Atlantic salmon parr Journal of Fish Biology 48(4):758-775

Moore, J. J., Smith J. and Northen, K.O. (1999). Marine Nature Conservation Review. Sector 8. Inlets in the western English Channel. Area summaries, Joint Nature Conservation Committee: 171.

Morris, A. W., Bale A. J. and Howland, R.J.M.. (1981). Nutrient distributions in an estuary: evidence of chemical precipitation of dissolved silicate and phosphate. Estuarine, Coastal and Shelf Science. 12: 205-216.

Morris, A. W., Howland, R. J. M. and Bale, A.J. (1986). Dissolved aluminium in the Tamar estuary, southwest England. *Geochimica et Cosmochimica Acta*. 50: 189-197.

Morris, A.W., Loring, D.H., Bale, A.J., Howland, R.J.M., Mantoura, R.F.C., Woodward, E.M.S. (1982). Particle dynamics, particulate carbon and the oxygen minimum in an estuary. Oceanologica Acta, 5, 349-353.

Morris, A.W., Mantoura, R.F.C., Bale, A.J. and Howland, R.J.M. (1978) Very low salinity regions of estuaries: important sites for chemical and biological reactions. *Nature*, 274(5672), 678-680.

National Rivers Authority. (1995) Pesticides in the aquatic environment. Water Quality Series. National Rivers Authority, (26), 92p

Nixon, S.C., Gunby, A., Ashley, S.J., Lewis, S. and Naismith, I. (1995). Development and testing of General Quality Assessment schemes: Dissolved oxygen and ammonia in estuaries. Environment Agency R&D Project Record PR 469/15/HO.

Norris, D.O, Donahue, S., Dores, R.M., Lee, J.K., Maldonado, T.A., Ruth, T. &Woodling, J.D. (1999). Impaired adrenocortical response to stress by brown trout, Salmo trutta, living in metal-contaminated waters of the Eagle River, Colarado. *Gen. Comp. Endocrinol*., 113, 1-8.

Okamura, H., Aoyama, I., Takami, T., Maruyama, T., Suzuki, Y., Matsumoto, M;.,Katsuyama, I., Hamada, J., Beppu, T., Tanaka, O., Maguire, R.J., Liu, D., Lau, Y.L. and Pacepavicius, G.J. (2000). Phytotoxicity of the new antifouling compound Irgarol 1051 and a major degradation product. Marine Pollution Bulletin 40(9): 754-763

Owen, R., Knap, A., Toaspern, M. and Carbery, K. (2002) Inhibition of coral photosynthesis by the antifouling herbicide Irgarol 1051. Marine Pollution Bulletin, 44(7): 623-632

Page, D. S. (1995). A six-year monitoring study of tributyltin and dibutyltin in mussel tissues from the Lynher River, Tamar estuary, UK. Marine Pollution Bulletin. 30: 746-749.

Parr, W., Wheeler, M. and Codling, I. (1999). Nutrient status of the Glaslyn/Dwyryd, Mawddach and Dyfi estuaries - its context and ecological importance. WRc Final Report to the Countryside Council for Wales.

Readman J.W., Mantoura R.F.C., Rhead M.M. (1984) Transfer processes in cohesive sediment systems. Distribution, composition and sources of polycyclic aromatic hydrocarbons in sediments of the River Tamar catchment and estuary. In: Parker WR, Kinsman DJJ (eds). Plenum Press, pp 155-170

Readman JW, Mantoura RFC, Rhead MM, Brown L (1982) Aquatic distribution and heterotrophic degradation of polycyclic aromatic hydrocarbons (PAH)in the Tamar Estuary Estuarine, Coastal and Shelf Science, pp 369-389

Readman, J.W., Preston, M.R. and Mantoura, R.F.C. (1986a) An integrated technique to quantify sewage, oil and PAH pollution in estuarine and coastal environments Marine Pollution Bulletin 17(7)298-308

Reay, P. (1998). The Plymouth Sound and Estuaries Marine Conservation Review. Report to English Nature and the Environment Agency.

Reddy, P.S., Tuberty, S.R. and Fingerman, M. (1997). Effects of cadmium and mercury on ovarian maturation in the red swamp crayfish, Procambarus clarkii. Ecotoxicol. Evnvir. Safety. 37, 62-65.

RIFE (2001). Radioactivity in Food and the Environment. RIFE-6. Food Standards Agency and Scottish Environment Protection Agency. Report produced by CEFAS: ISSN 1365-6414. 183p

Rodriguez, E.M., Lopez Greco, L.S. & Fingerman, M. (2000). Inhibition of ovarian growth by cadmium in the fiddler crab *Uca pugilator* (Decapoda: Ocypodidae). *Ecotox. Env. Safety*, **46**, 202-206

Rowlatt, S., Limpenny, D., Hull, S., Jones, B., Whalley, C., Salmons, M., Jones, L., Lovell, D. & Deacon, C. (1998). Assessment of metals in estuarine waters. Environment Agency, Research and Development Technical Report P7, Bristol, UK, 32p.

Scarlett, A., Donkin, M. E., Fileman, T.W.and Donkin, P. (1997). Occurrence of the marine antifouling agent Irgarol 1051 within the Plymouth Sound locality: Implications for the green macroalga *Enteromorpha intestinalis*. Marine Pollution Bulletin 34(8): 645-651.

Scarlett, A.,. Donkin, P., Fileman, T.W., Evans, S.V. and Donkin, M.E. (1999). Risk posed by the antifouling agent Irgarol 1051 to the seagrass, *Zostera marina*. Aquatic Toxicology. 45: 159-170.

Sheahan DS, Waldock MJ and Matthiessen P (2000). An evaluation of the approach to aquatic environmental risk assessment of phthalates. CEFAS Report, 25pp.

Spence, S.K., Bryan, G.W., Gibbs, P.E., Masters, D., Morris, L. and Hawkins, S.J. (1990). Effects of TBT contamination on *Nucella* populations. *Func. Ecol.* 4, 425-432.

Southward, A.J. (1991). Forty years of changes in species composition and population density of barnacles on a rocky shore near Plymouth. Journal of the Marine Biological Association of the United Kingdom. Plymouth. 71(3):495-513

Southward, A. J., Hawkins, S. J. and Burrows, M. T. (1995) 70 years observations of changes in distribution and abundance of zooplankton and intertidal organisms in the western English Channel in relation to rising sea temperature. Journal of Thermal Biology, 20:127-155.

Southward, A.J. and Boalch, G.T. (1994). The effects of climate change on marine life: past events and future predictions. Exeter Maritime Studies, 9, 101-143.

Southward, A.J.; Roberts, E.K. (1987). One hundred years of marine research at Plymouth. Journal of the Marine Biological Association of the United Kingdom, 67, 465-506.

Southward, A.J.; Butler, E.I.; Pennycuick, L. (1975). Recent cyclic changes in climate and in abundance of marine life. Nature, 253: 714-717

Spooner, G. M. and. Moore H. B (1940). The ecology of the Tamar Estuary. VI An account of the macrofauna of the intertidal muds. Journal of the Marine Biological Association of the United Kingdom. 24: 283.

Stang, P.M. and Seligman, P.F., 1987. *In situ* adsorption and desorption of butyltin compounds from Pearl Harbour, Hawaii sediment. In: *Oceans '87 Proceedings, Vol. 4. InternationalOrganotin Symposium*, New York: Institute of Electrical and Electronics Engineers, pp. 1386-1391.

Staples, C.A. (1997). Aquatic toxicity of eighteen phthalate esters - A review, ET&C, 16, 875-891.

Stebbing, A. R. D., Cleary,J.J., Brinsley, M., Goodchild, C. and Santiago-Fandino,V. (1983). Responses of a Hydroid to Surface-Water Samples from the River Tamar and Plymouth Sound in Relation to Metal Concentrations. Journal of the Marine Biological Association of the United Kingdom 63(3): 695-711.

Suffet, I.H. and MacCarthy, P. (editors) (1989) Aquatic humic substances: influence on fate and treatment of pollutants. xxx, 864p.. Washington, D.C.: American Chemical Society

Suter, G.W.; Rosen, A.E. (1988) Comparative toxicology for risk assessment of marine fishes and crustaceans. Environmental Science and Technology, 22:548-556

Tamar Estuaries Consultative Forum (1998) Plymouth Sound and estuaries nature conservation review 1998. Tamar Estuaries Consultative Forum, Plymouth, pp iv, 127 + appendices

Tamar Estuaries Consultative Forum (2001) Tamar Estuaries Management Plan 2001-2006. Tamar Estuaries Consultative Forum, Plymouth, pp 36.

Taylor, D. (1979). The effect of discharges from three industrialized estuaries on the distribution of heavy metals in the coastal sediments of the North Sea. Estuarine and Coastal Marine Science, 8, 387-393, 1979

Thomas, P. (1989). Effects of Aroclor 1254 and cadmium on reproductive endcrine function and ovarian growth in Atlantic croaker. *Mar. Env. Res*., 28, 499-503.

Tipping, E., Marker, A.F.H., Butterwick, C. Collett, G.D., Cranwell, P.A., Ingram, J.K.G., Leach, D.V., Lishman, J.P., Pinder, A.C., Rigg, E. and Simon, B.M. (1997) Organic carbon in the Humber rivers. Science of the Total Environment 194-195: 345-355

Tolosa, I., Readman, J.W., Blaevoet, A., Ghilini, S., Bartocci, J. and Horvat, M. (1996) Contamination of Mediterranean (Cote d'Azur) coastal waters by organotins and Irgarol 1051 used in antifouling paints. Marine Pollution Bulletin, 32(4): 335-341

Ton, P., Tovignan, S. and Davo Vodouhê, S. (2000) Endosulfan deaths and poisonings in Benin. Pesticides News 47:12-14

Toole, J., Baxter, M.S. and Thomson, J. (1987) The behaviour of uranium isotopes with salinity change in three U.K. estuaries. Estuarine, Coastal and Shelf Science, 25:283-297.

Tronczynski, J. (1985) Biogéochimie de la matière organique dans l'estuaire de la Loire: origine, transport et évolution des hydrocarbureset des acides gras. Thèse de Doctorat de 3ème cycle de l'Université Paris 6, Paris:176pp

Turner, A. and Millward, G.E. (1994) Partitioning of Trace-Metals in a Macrotidal Estuary - Implications for Contaminant Transport Models. Estuarine Coastal and Shelf Science, 39:45-58.

Uncles, R. J. and J. A. Stephens (1989). Distributions of suspended sediment at high water in a macrotidal estuary. Journal of Geophysical Research. 94C: 14395-14405.

Uncles, R. J., Elliott, R. C. A. and Weston, S.A. (1985). Observed fluxes of water, salt and suspended sediment in a partly mixed estuary. Estuarine, Coastal and Shelf Science. 20: 147-167.

Uncles, R.J., Bale, A.J., Howland, R.J.M., Morris, A.W. Elliott, R.C.A. (1983). Salinity of surface water in a partially-mixed estuary, and its dispersion at low run-off. Oceanologica Acta, 6:289-296

Uncles, R. J., Barton M. L. and Stephens, J.A. (1994). Seasonal variability of fine-sediment concentrations in the turbidity maximum region of the Tamar Estuary. Estuarine Coastal and Shelf Science. 38: 19-39.

Uncles, R. J.,. Barton, M. L. (1996). Mixing processes in estuaries and coastal seas Seasonal variability of mobile mud deposits in the Tamar Estuary. C. Pattiaratchi. Washington DC, American Geophysical Union: 374-387.

van Zoest, R, and van Eck, G.T.M. (1990) Behaviour of particulate polychlorinated biphenyls and polycyclic aromatic hydrocarbons in the Scheldt estuary. Netherlands Journal of Sea Research, 26(1): 89-96

Waldock MJ (1983). Determination of phthalate esters in samples from the marine environment using gas chromatography mass spectrometry. Chem. in Ecol. 1: 261-277.

Warwick, R.M. (1986). A new method for detecting pollution effects on marine macrobenthic communities. Marine Biology, 92: 557-562

Warwick, R. M., George, C. L., Pope, N.D. and Rowden, A.A (1989). The prediction of post-barrage densities of shorebirds. Volume 3. Invertebrates. Harwell, Department of Energy: 112pp.

Watson, P.G., Frickers, P.E. and Howland, R.J.M. (1993) Benthic fluxes of nutrients and some trace metals in the Tamar estuary, SW England. Netherlands Journal of Aquatic Ecology, 27(2-4):135-146

Webster, P.J., Rowden, A.A., Attrill, M.J. (1998) Effect of shoot density on the infaunal macro-invertebrate community within a *Zostera marina* seagrass bed. Estuarine, Coastal and Shelf Science, 47(3):351-357

West, J. R., Uncles, R.J. and Stephens, J.A. and Shiono, K. (1990). Longitudinal dispersion processes in the upper Tamar Estuary. Estuaries. 13: 118-124.

Wood, R., Gorley, R. and Harris, J. (1996) Estuarine and coastal flux modelling. LOIS. Land-Ocean Interaction Study, (106), 109-110, LOIS Miscellaneous Publications

Woodhead R.J., Law R.J. & Matthiessen P. (1999) Polycyclic aromatic hydrocarbons in surface sediments around England and Wales, and their possible biological significance. Marine Pollution Bulletin 38, 773-790.

Zhou, J.L., Fileman, T.W., Evans, S.V., Donkin, P., Mantoura, R.F.C. and; Rowland, S.J. (1996) Seasonal distribution of dissolved pesticides and polynuclear aromatic hydrocarbons in the Humber Estuary and Humber Coastal Zone. Marine Pollution Bulletin, 32(8/9):599-608

Zieman J.C., Orth, R., Phillips, R.C., Thayer, G.W., Thorhaug, A.T. (1984) The effects of oil on seagrass ecosystems. Restoration of Habitats Impacted by Oil Spills. 36-64

Zinkl, J.G., Lockhart, W.L., Kenny, S.A. and Ward, F.J. (1991) The effects of cholinesterase inhibiting insecticides on fish. In: Mineau, P., (editor). Cholinesterase-inhibiting insecticides. Their impact on wildlife and the environment. .233-254. Elsevier,

12. ANNEXES

## Annex 1. Plymouth Sound and Estuaries cSAC, SPA: Summary of the Interest Features

Summary of the interest (or qualifying) features, and conservation objectives, (adapted from English Nature, 2000)

**Large shallow inlets and bays**

Conservation objective – Maintain in favourable condition re: extent (area), water clarity, density, temperature, salinity

Subfeatures

- Intertidal rock and boulder shore communities
  - maintain relative distribution of biotopes
  - maintain species composition of low shore boulder communities
  - maintain species composition of rock pool communities
- Subtidal rocky reef communities
  - maintain distribution of characteristic biotopes
  - maintain species composition of characteristic biotopes
- Kelp forest communities
  - maintain algal species composition
  - maintain characteristic species population size
  - *Laminari*a spp.
  - *Distomus* (tunicate)
- Subtidal mixed cobble and gravel communities
  - maintain species composition of characteristic biotopes
- Subtidal mud communities
  - maintain species composition of biotopes

**Estuaries**

Conservation objective – Maintain in favourable condition re: extent (area); "morphological equilibrium" * also of saltmarsh/mudflat, nutrient status

Subfeatures

- Intertidal mud communities
  - maintain extent
- Intertidal mixed muddy sediment communities
  - maintain extent
- Subtidal mud communities
  - maintain extent
- Subtidal mixed muddy sediment communities
  - maintain extent and distribution of biotopes
- Estuarine bedrock, boulder and cobble communities
  - maintain extent and distribution of biotopes
- Saltmarsh communities
  - maintain extent, creek patterns, range and distribution of reed bed and saltmarsh communities

* 'morphological equilibrium' = TP/CS ratio - hydrodynamic measurement
TP = m3 water crossing a given profile during flood tide
CS = area at HW springs

(Changes in TP/CS relationship indicate that anthropogenic factors are taking effect)

**Subtidal sandbanks**

Conservation objectives – maintain in favourable condition Re: extent (area), sediment character (granulometry), topography (depth and distribution)

Subfeatures

- Eelgrass bed communities
  - maintain extent
  - maintain water clarity
  - maintain characteristic species density (*Zostera marina,* epiphytic communities)
  - nutrient status(monitor extent of competing green algal mat)
- Gravel and sand communities
  - maintain species composition of characteristic biotopes
- Muddy sand communities
  - maintain species composition of characteristic biotopes

## Annex 1. (cont.) Plymouth Sound And Estuaries cSAC, SPA: Summary Of The Interest Features

Plymouth Sound and Estuaries SPA: Summary of the interest (or qualifying) features, and conservation objectives, (adapted from English Nature, 2000)

**Nationally important Annex 1 bird populations (avocet *Recurcirostra avosetta*)**

- Intertidal mudflat communities and mixed muddy sediment communities
  - maintain extent
  -maintain presence and abundance of prey species <15mm (insects, crustaceans small fish, worms)
- Saltmarch communities
  - maintain extent
  - minimise disturbance in feeding/roosting areas
  - maintain numbers of birds

**Nationally important Annex 1 bird populations (little egret *Egretta garzetta*)**

- Intertidal mudflat communities and mixed muddy sediment communities
  - maintain extent
  -maintain presence and abundance of prey species <15cm (fish, amphibians, large aquatic insects)
- Saltmarch communities
  - maintain extent
  - maintain numbers of birds
  - maintain presence and abundance of prey species <15cm (fish, amphibians, large aquatic insects)
  - minimise disturbance in feeding/roosting areas

## Plymouth Sound and Estuaries cSAC, SPA: Summary of additional interest (or qualifying) features, and conservation objectives, proposed since those described in English Nature, 2000

**Atlantic salt meadows (*Glauca-Puccinellietalia maritimae)***

- **For which the area is considered to be one of the best areas in the UK**

This habitat encompasses saltmarsh vegetation containing perennial flowering plants that are regularly inundated by the sea. The species found in these salt marshes vary according to duration and frequency of flooding with seawater, geographical location and grazing intensity. Salt-tolerant species, such as common salt marsh grass *Puccinellia maritima*, sea aster *Aster tripolium* and sea arrowgrass *Triglochin maritima*, are particularly characteristic of the habitat.

**Reefs**

- **For which the area is considered to be one of the best areas in the UK**

Defined as areas of rock or biological concretions formed by various invertebrate species. Reefs occur in the subtidal zone, but may extend onto the shore. They form the habitat for a variety of biological communities such as those characterised by encrusting animals and attached seaweeds.

## Annex 1. (cont.) Plymouth Sound And Estuaries cSAC, SPA,:Summary Of The Interest Features

Summary of additional interest (or qualifying) features, and conservation objectives, proposed since those described in English Nature, 2000

**Mudflats and sandflats not covered by seawater at low tide**

- **For which the area is considered to support a significant presence**

These are intertidal mud and sand sediments on a shore that are exposed at low tide but submerged at high tide. Many sites are important feeding areas for waders and wildfowl.

***Alosa alosa* (Allis shad)**

- **For which the areais considered to support a significant presence**

The allis shad is a medium-sized fish of coastal waters and estuaries of the western Mediterranean and north-east Atlantic coasts. It spawns in rivers but has beconme rare due to over-fishing, pollution and and obstructions to migration

***Rumex rupestris* (shore dock)**

- **For which this is considered to be one of the best areas in the United Kingdom**

Shore dock grows on rocky and sandy beaches, at the foot of cliffs and infrequently in dune slacks where there is a supply of fresh water. It is thought to be the world's rarest dock and is one of the most rare plants in Europe. In the UK it is found only on a small number of sites in south west England and Wales.

## 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]<br>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]<br>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<br>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]<br>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]<br>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]<br>20 MAC[4] | None mentioned with regard to the annual mean. |
| 4-chloro-3-methyl phenol | µg /l | 40 AA[3]<br>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]<br>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]<br>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]<br>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]<br>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]<br>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]<br>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]<br>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]<br>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]<br>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]<br>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]<br>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]<br>80 MAC[4] | Limited and uncertain chronic data available. |
| Toluene | µg /l | 40 AA[3]<br>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]<br>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]<br>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

| 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

| 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 | µg$C_6H_5OH$ | 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 |

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

| 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 ($\mu gkg^{-1}$)** | | |
| | | |
| 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 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 (e.g. Pipe *et al*, 2000; Raftos & Hutchinson, 1995).

**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 in arising from metals in discharges (e.g. Langston *et al*., 2002).

**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 EROD and metallothionein) 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 Severn biota with those elsewhere to look for signs of adaptation.

**Multivariate Statistical Analysis** of biota 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 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 should 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 Plymouth Sound and Estuaries cSAC

(Information source - EA and SWW)

The 'Clean Sweep' programme is a programme of investment started when the industry was privatised in 1989. Asset Management Plans (AMPs) were instigated (timescale below). Before the coastal improvement programme sewage was discharged directly into the Sound and the lower reaches of the Rivers Tamar and Plym. The project was designed to upgrade the sewerage network and meet the European Waste Water Directive by improving the quality of bathing and amenity waters in the Sound.

The new treatment works is located on the site of the old Cattewater power station beside the River Plym. Waste water is treated to a high standard including UV disinfection before it is returned to the environment via the West Hoe outfall[1].

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

The need for a sewage treatment scheme at Plymouth Central was identified to ensure compliance with the Bathing Water Directive at Plymouth Hoe (East and West) which repeatedly failed Imperative standards before 1990. The scheme, which incorporated secondary treatment and UV disinfection was completed during the 1998 bathing season. However, since completion of this scheme Bathing Water quality at Plymouth Hoe (East and West) continues to fail guideline standards, and Imperitive (Plymouth Hoe, East) standards. As part of this scheme, 19 continuous crude discharges were also transferred to the works for treatment.

At the end of 2001, the primary discharge from Saltash was transferred to Ernesettle where a secondary treatment works with UV had been constructed (previously this works treated to primary standard only). Approximately 35 CSOs (combined sewage outfalls) in the Saltash, Camels Head and Ernesettle catchments have been identified for improvements under the Shellfish Waters Directive in AMP3 – improvements are due by December 2003.

Eight STW discharges on the Lynher and Tamar are due for improvement at the end of the AMP3 period. Six crude discharges to the Hamoaze are also to be transferred to Plymouth Central STW under AMP3. A storm overflow at Plymouth Central STW has been identified for improvement under the Bathing Waters Directive in AMP3 by July 2001.

Four crude discharges impacting on both Kingsand and Cawsand Bathing Waters were removed in May 2001 under AMP3. The foul flows are now pumped to Millbrook STW for treatment. On the Yealm, sanitary standards have been set for the discharge from Newton Ferrers STW and UV disinfection is planned at Brixton STW by 2004. Storm overflows in Brixton and Newton Ferrers were improved in 2001, with another storm discharge at Elburton to follow shortly.

[1] http://www.swwater.co.uk

## Annex 8. Annual load estimates (N) for Fresh Water inputs

Plymouth Sound and Estuaries cSAC

| River | Flow m3/s | NH3 mg/l | TON mg/l | TIN (=NH3+TON) mg/l | N Load g/s |
|---|---|---|---|---|---|
| Yealm | 1.66 | 0.032 | 2.534 | 2.566 | 4.260 |
| Newton Stream | 0.17 | 0.13 | 7.492 | 7.622 | 1.296 |
| | | | | | 5.555 |
| Plym | 3.45 | 0.018 | 1.362 | 1.38 | 4.761 |
| Torry Brook | 0.77 | 0.062 | 1.391 | 1.453 | 1.119 |
| | | | | | 5.880 |
| Tamar | 22.66 | 0.065 | 2.835 | 2.9 | 65.714 |
| Tamerton Stream | 0.23 | 0.022 | 4.432 | 4.454 | 1.024 |
| Tavy | 6.74 | 0.025 | 1.851 | 1.876 | 12.644 |
| | | | | | 79.383 |
| Lynher | 4.51 | 0.072 | 3.238 | 3.31 | 14.928 |
| Tiddy | 0.94 | 0.042 | 5.918 | 5.96 | 5.602 |
| | | | | | 20.531 |

(Based on Annual Mean Chemical Data for 1999 and Annual Mean Flow Data calculated by P.Jonas, EA)

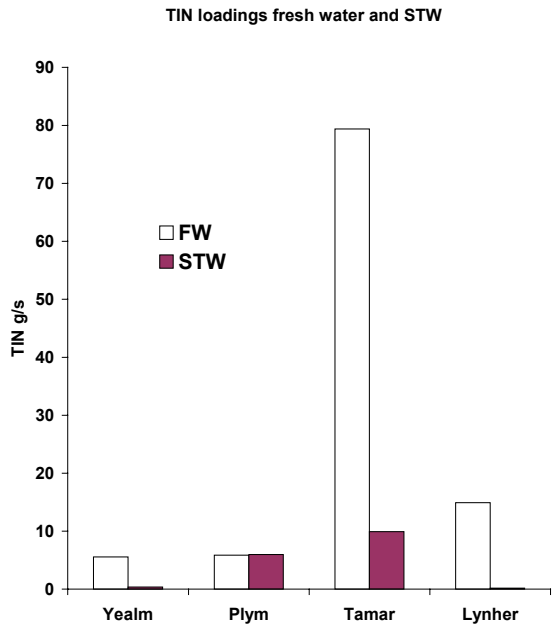
## Annex 9. Annual load estimates (N) for STW

Plymouth Sound and Estuaries cSAC

| Sub-Estuary | STW | DWF m3/d | DWF l/s | Average Flow (1.25xDWF) l/s | $NH_3$ mg/l | TON mg/l | TIN (=$NH_3$+TON) mg/l | TIN Loading g/s |
|---|---|---|---|---|---|---|---|---|
| Yealm | Wembury | 820 | 9.49 | 11.86 | 24.70 | 1.06 | 25.76 | 0.306 |
| | Brixton | *165* | 1.91 | 2.39 | 18.96 | 8.42 | 27.38 | 0.065 |
| | | | | | | | | 0.371 |
| Plym | Marsh Mills | 17266 | 199.84 | 249.80 | *2.33* | *17.07* | *19.40* | 4.846 |
| | Radford | 4501 | 52.09 | 65.12 | 2.16 | 15.28 | 17.44 | 1.136 |
| | | | | | | | | 5.982 |
| Plymouth Sound | Plymouth Central | 22554 | 261.04 | 326.30 | *13.42* | *5.43* | *18.85* | 6.151 |
| Tamar/ | Camels Head | 12000 | 138.89 | 173.61 | *20.13* | *0.66* | *20.79* | 3.609 |
| Tavy | Ernesettle | 17950 | 207.75 | 259.69 | *5.86* | *11.25* | *17.11* | 4.443 |
| | Bere Ferrers | 77 | 0.89 | 1.11 | 3.07 | 20.73 | 23.80 | 0.027 |
| | Bere Alston | 520 | 6.02 | 7.52 | 2.45 | 15.36 | 17.81 | 0.134 |
| | Gunnislake | 330 | 3.82 | 4.77 | 17.31 | 1.35 | 18.66 | 0.089 |
| | Calstock | 259 | 3.00 | 3.75 | 38.65 | 0.73 | 39.38 | 0.148 |
| | St Mellion | *50* | 0.58 | 0.72 | 29.84 | 14.96 | 44.80 | 0.032 |
| | St Dominick | 118 | 1.37 | 1.71 | 32.06 | 1.14 | 33.20 | 0.057 |
| | Cargreen | 100 | 1.16 | 1.45 | 3.50 | 11.18 | 14.68 | 0.021 |
| | Wilcove | *20* | 0.23 | 0.29 | *35.00* | *1* | 36.00 | 0.010 |
| | Torpoint | 4546 | 52.62 | 65.77 | 10.00 | 4.54 | 14.54 | 0.956 |
| | St John | 10 | 0.12 | 0.14 | 32.58 | 0.65 | 33.23 | 0.005 |
| | Millbrook | 2047 | 23.69 | 29.62 | 1.29 | 11.79 | 13.08 | 0.387 |
| | | | | | | | | 9.919 |
| Lynher | Landrake | 150 | 1.74 | 2.17 | 19.85 | 23.58 | 43.43 | 0.094 |
| | Tideford | 37 | 0.43 | 0.54 | *24.22* | *0.5* | *24.72* | 0.013 |
| | St Germans | 165 | 1.91 | 2.39 | *18.52* | *1.62* | *20.14* | 0.048 |
| | Sheviock | 24 | 0.28 | 0.35 | *32.48* | *1.96* | *34.44* | 0.012 |
| | Antony | *40* | 0.46 | 0.58 | *14.89* | *1.3* | *16.19* | 0.009 |
| | | | | | | | | 0.177 |

(The ammonia and Total Oxidised Nitrogen data are mostly based on average data for the period 1995-2000, but some are for the period 2001-2002, and some for the period 1990-1994. Those not 1995-2000 data are in italics. Loadings calculated by P.Jonas, EA)

## Relative loadings TIN (total inorganic nitrogen) from freshwaters and STW




Tamar includes Tavy and Tamerton stream; Plym includes Tory Brook; Yealm includes Newton Stream

## 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)

Plymouth Hoe
Photograph: Steve Johnson, Cyberheritage

**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***