## Characterisation of European Marine Sites

# The Mersey Estuary

## Special Protection Area

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THE MARINE BIOLOGICAL ASSOCIATION

Cover photograph: Eastham, Mersey Estuary. Looking down to Liverpool.
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# Site Characterisation of European Marine Sites

# The Mersey Estuary SPA

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**2006**

A study carried out on behalf of English Nature

By

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It should be noted that the opinions expressed in this report are largely those of the authors and do not necessarily reflect the views of EN or EA.

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# 1. EXECUTIVE SUMMARY

This report provides an overview of water and sediment quality within the Mersey Estuary European Marine Site (EMS) and examines evidence for their influence on biological condition. It is has not been possible to determine adequately whether prevailing conditions in the Mersey impact on the interest features of the site (namely qualifying birds) as studies which address this issue, directly, have not been carried out. It is only possible to review the current level of knowledge regarding the biological and chemical status for the Estuary and extrapolate to risks for the bird populations. Often information relates to sites outside the EMS; where this is the case we have tried to appraise the general status of the Estuary, based on best available knowledge, and make suggestions as to how best to remedy the lack of relevant information.

The study is intended to complement other recent reviews undertaken by the EA and hopefully may assist in appropriate assessment in the Review of Consents process. However, as data on individual consents was not available we are unable to comment on impacts from specific discharges. Site characterisation has therefore been accomplished by review of published literature and unpublished reports, together with interrogation of summary data sets for tidal waters provided by EA. Key findings are as follows:

- There is substantial evidence that the numerous initiatives set up in recent years under the Mersey Basin Campaign, coupled with changing industrial practices, have led to improved water quality. However, given the long-term legacy of pollution in the Mersey, and the repository held in fine sediments, it is not surprising that chemical impacts and resultant biological effects are sometimes detectable. Consequently, the Estuary remains one of the most contaminated in the UK, though establishing precise links between cause and effects is problematic in view of the myriad of chemicals present and their shared gradients.
- The severity of dissolved oxygen sags reduced considerably, and nutrient conditions improved between 1975 and 1995. However, the estuary reportedly still receives an elevated nutrient load, which is reflected in high concentrations of N and P downstream of freshwater and point sources. Recent data indicate DO at mid- and inner estuarine sites may still fall below threshold values. It is not known if these oxygen sags are nutrient- or BOD- related. Concentrations of ammonia in the upper estuary have also been reduced dramatically over recent decades, although there are indications from the EA data supplied (2002-2004) that levels may once again be rising. Again, highest concentrations occur in the inner estuarine areas. Despite improvements, the estuary remains nutrient enriched, but, based on rather sparse evidence, without the attendant symptoms of eutrophication.
- A small number of chemicals approach EQS values at certain sites, or are considered by EA as being at medium or high risk of failure, and should be a priority for further investigation (Hg, Cu, Zn and, to a lesser extent, Cr, Cd, nonylphenol). Concentrations and risks from other measured water-borne contaminants appear to be mostly low, though few sites within the EMS have been monitored comprehensively.
- TBT in tidal waters exceeds the EQS at most sites, sometimes by a considerable margin. Sources include the Manchester Ship Canal, docks and shipyards, and the river Mersey itself: highest levels were at Monks Hall at the head of the tidal waterway. Sediments in docks contain hotspots which are above action limits (for safe disposal). Redistribution of these sediments must be considered a potential threat to the condition of the site. TBT concentrations in biota are not exceptional but are higher than OSPAR ecotoxicological assessment criteria and increase upstream, towards the EMS. Further investigation of sources, trends and impacts is recommended.
- There are elevated concentrations of Hg, Zn and Pb in surface sediments of the mid-upper estuary which sometimes exceed probable effects levels. Because of the high energy conditions in the estuary, contamination arising from discharges, once associated with fines, tends to be dispersed over a large area leading to a degree of homogeneity. The conclusion is that metal distributions may reflect sediment characteristics and dynamics rather than proximity to discharges. PAHs, together with PCBs and DDT residues from historical inputs, are of significance. Enhanced loadings sometimes appear in subsurface layers in sediment cores. These may be only temporarily immobilised. Natural erosion events and dredging can re-expose these layers making them and their associated contaminant burdens available to organisms. There is a need for further biomonitoring of sediments (bioaccumulation and effects) and possible to transfer of contaminants through dietary organisms to bird populations of the SPA.

- Most of the reports available in the literature regarding hydrocarbon oil in the EMS, relate to oil spill incidents, though the relative threat from the petrochemical industry and ship-based oil spills is unknown.
- Bioaccumulation data for invertebrates and fish suggest that residues of organochlorine pesticides, PCBs, Hg, Pb, As and Zn are declining in the region, in response to extensive sewage treatment measures and changing industrial practice. They are still a concern, however, in view of the potential for additive toxicity of such a wide range of chemicals. Furthermore, changing conditions in the sediment (e.g. redox) can sometimes cause a dramatic increase in bioavailability of metals such as Ag, Cu and Hg, with associated deleterious effects on infauna, even though overall loadings may not change. This may be an important issue to consider when making assessing the condition of the EMS, given its legacy of sediment-bound contaminants. There is a strong case for a further bioaccumulation study, using established benthic indicators, to update long-term surveys last undertaken in the late 1990s.
- Vitellogenin induction and intersex levels in male flounder are elevated, raising concerns over links between endocrine disruption and environmental quality. The influence of sewage wastes and the presence of ubiquitous persistent organic compounds are both possible causes. There should be investigations to look for evidence of ED within sedentary invertebrate communities.
- Other forms of biological effects monitoring have been undertaken at a small number of sites outside the EMS– mainly as part of NMMP. Results for many of the 'biomarkers' tested indicate similar trends for a range of responses (EROD, DNA adducts, bile metabolites). The Mersey displays moderate-to-high level responses when compared with other UK estuaries (in line with chemical contamination). Sub-lethal biological-effects in Liverpool Bay biota indicate some influence from contaminants emanating from the Mersey Estuary for a range of responses, from biochemical to ecological levels. This includes moderate-high prevalence of some forms of fish pathology and disease.
- Though abundance is still low in some areas, the diversity of invertebrates is thought to have increased in the post industrial-era and was linked to a dramatic increase in birds in the mid-1990s. This in turn coincided with improved water quality. Occasional deleterious events have been observed (notably bird kills in the late 1970s and early 1980s attributed to alkyl lead bioaccumulation and in 1989/1990 due to oil spills), though because of actions of industry and regulators there was an overall favourable trend in qualifying bird numbers up to the end of the 20$^{th}$ century, attributable to improved water quality. Recently, however the number of species for which BTO Alerts have been issued is increasing, often contrasting with both regional and national trends. Causes of declines in bird numbers, and possible links to changing water quality, require investigation.
- The Mersey fish community has historically been impoverished, but since improvements in water quality, the estuary now hosts a wide range of fish species.
- Concerns over acute toxicity within the EMS as a whole are receding - there are few *known* hotspots in the estuary other than in some docks (n.b. TBT in sediments) - though the estuary remains at risk of accidental acute events. Furthemore, the site remains chronically contaminated over much of its area (generally increasing upstream), and though there is little available data on individual discharges the possibility that combined pressures might impair performance of sensitive species and benthic communities cannot be ruled out. Indirectly this may have potential for impact on designated bird species (through bioaccumulation or changes in prey species). Hence, despite a trend towards 'recovery' of some benthic populations, sub-lethal effects may still be exhibited. A programme of research to measure biological impacts at a variety of levels, *specifically within the SPA,* would help to establish whether deleterious effects are occurring, and help to support or refute conclusions reached by WQ models. Without such information there remains substantial uncertainty over the biological condition of the site. In broad terms, bioassay and biomarker-type studies could provide important contextual information to inform the European Marine site assessment and might be used to investigate individual outfalls. At present, biological response information, and WQ data, tends to be rather sparse and disjointed for sites within the EMS itself. It is therefore recommended that a programme of harmonised chemical and biological effects monitoring be instigated at the earliest opportunity, focusing on priority contaminants and key biota of the EMS, particularly those which are of major dietary significance for bird populations. Links to broader biological consequences should be established by traditional benthic survey. Such a programme would give the Conservation Agencies greater confidence that appropriate and consistent assessments are made and realistic targets set.

# CONTENTS

# 2. INTRODUCTION

This review considers the characteristics of the marine area of the MERSEY ESTUARY EUROPEAN MARINE SITE (EMS) and how the status of the site is influenced by existing permissions and activities, either alone or in combination. Also considered are possible impacts from other factors such as unconsented activities, diffuse sources and natural processes. This includes activities and consents outside the site itself. The purpose is thus to collate and interpret information relevant to the assessment of water quality impacts and risks to the marine component of the EMS, to ensure that EA and EN are fully informed when making decisions in relation to the scope of appropriate assessment. It should be noted that although efforts were made to gather all available relevant data, the authors are aware that the report is not comprehensive but draws on data sets and publications that were readily available at the time. The opinions expressed are made on the basis of available information (up to 2005). We have emphasised areas where information is lacking, or where we see an opportunity to improve implementation and monitoring to comply with the requirements of the Habitats Directive and to provide a better means of establishing the status of the site.

To achieve this goal, specific objectives were:

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

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

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

| Standard list of operations which may cause deterioration or disturbance | Internationally important assemblages of waterfowl |
|---|---|
| **Physical loss** | |
| Removal (e.g. harvesting, coastal development) | ✔ |
| Smothering (e.g. artificial structures, disposal of dredge spoil) | ✔ |
| **Physical damage** | |
| Siltation (e.g. run-off, channel dredging, outfalls) | |
| Abrasion (e.g. boating, anchoring, trampling) | ✔ |
| Selective extraction (e.g. aggregate dredging,) | |
| **Non-physical disturbance** | |
| Noise (e.g. boat activity) | ✔ |
| Visual presence(e.g. recreational activity) | ✔ |
| **Toxic contamination** | |
| Introduction of synthetic compounds (e.g. TBT, PCB's,) | ✔ |
| Introduction of non-synthetic compounds (e.g. heavy metals, hydrocarbons) | ✔ |
| Introduction of radionuclides | |
| **Non-toxic contamination** | |
| Changes in nutrient loading (e.g. agricultural run-off, outfalls) | ✔ |
| Changes in organic loading (e.g. mariculture, outfalls) | ✔ |
| Changes in thermal regime (e.g. power station) | |
| Changes in turbidity (e.g. run-off, dredging ) | |
| Changes in salinity | |
| **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) | ✔ |

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

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

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

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

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

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

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

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

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

**Structure of the report**

In **Section 3** we identify sources of information and the generalised approach used in assessing data to come to an opinion on water and sediment quality. There is also a critical evaluation of the constraints.

**Section 4** of this report describes the main physical, chemical and biological features which shape the character of the site and summarises some of the perceived threats to its favourable status.

Studies which describe the biology and ecology of benthic communities within the site, many of which support the bird populations for which the site is designated, are discussed briefly in **Section 5.** This section also provides a resume of trends in bird populations for SPAs, based on British Trust for Ornithology reports.

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

**Section 7** focuses on evidence for biological impacts within the EMS, including reviews of bioaccumulation and biological effects (from the cellular to community level).

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

Concluding remarks (**section 9**) include a summary of evidence for impact in the Mersey Estuary European Marine Site, together with recommendations for future monitoring and research.

## 3. REFERENCE LISTS AND SOURCES OF INFORMATION

A full list of publications in the open literature has been assembled using the Aquatic Sciences and Fisheries Abstracts (ASFA) and Web of Science information retrieval systems. The National Marine Biological Library in-house data base LIB-WEB has provided additional listings.

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

Information, monitoring data and summary statistics for tidal waters provided by the Environment Agency, 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.

Comparative data for other UK estuaries, including south-west European Marine Sites (e.g. Exe, Severn, Poole, Fal, Plymouth Sound and Estuaries, Chesil and the Fleet) have been used to draw comparisons with the Mersey Estuary European Marine Site, wherever possible.

### Methods: Contaminants and Quality Standards

*Water Quality Data*

In section 6 we examine published and unpublished information on contaminant trends, together with EA data on determinands which may influence the Mersey Estuary European Marine Site (EMS). Summary statistics for tidal water quality have been drawn up by the Agency (based on monitoring between 2002 and 2004, rather than annual averages).

It should be noted that much of the data from EA 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 values reported as below detection limits have usually been included in summary statistics since it allows at least a crude assessment of water quality issues. With these caveats in mind the majority of priority List I and List II (Dangerous Substances) determinands have been screened in the tidal waters data-set, together with other water quality parameters such as nutrients, chlorophyll a and DO. These are compared with Environmental Quality Standards, if applicable. The location of principal tidal water sampling sites is shown in figure 6.

In the absence of extensive site-specific biological effects information, comparisons of water-monitoring results with Environmental Quality Standards (EQS) are used in order to gain a first-order approximation of possible impact on biota. Thus, in the context of the current project, descriptions of ‘threat’ or ‘risk’ to the site from individual contaminants are scaled against the relevant EQS, assuming this to be an appropriate threshold for the protection of aquatic life.

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

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

Data for Harmonised Monitoring Points or the equivalent freshwater site immediately above tidal limits were requested (to characterise riverine inputs) but were not available within the timescale of the current project. The only information on 'riverine' sources into the Estuary on hand were represented by data for the Mersey between Monks Hall (Warrington) and Fiddlers Ferry. However, it should be remembered that this stretch is tidally-influenced brackish water (mean salinities range between <2 and 4.72 psu) as opposed to truly representing the fresh water end-member. As such, contaminants may have been subjected to a degree of estuarine reactivity (removal or enrichment) during transport through this uppermost section of the water-way; i.e. concentrations may be somewhat different from original fresh-water inputs at the head of the estuary (Howley Weir).

Similarly, discharge data for contaminants were requested to gauge the importance of specific industrial and trade effluent point sources. However as the Agency has completed it's own assessment of all the continuous discharges in the upstream catchment under earlier stages of the RoC process, or, in the case of intermittent discharges, is in the process of evaluation of discharges under stage 3[2], their recommendation was that further review was unnecessary. Consideration of biological information was considered a more important priority at this stage.

Some general information on discharges can be found in section 4. Sites of some of the more important outfalls, supplied by the EA, (see annex 7) are also shown in figures 2 and 3 to put the current evaluation in context.

*Sediment Quality Data*

Sediments are not monitored routinely by the Agency as there are no requirements to do so in the context of managing outfalls. Nevertheless they represent important sinks and sources for chemicals in estuaries and coastal areas and can play an important part in determining site condition. In general, levels of contamination in estuarine sediments decrease significantly towards offshore sites, partly due to distance from major inputs, and partly due to changing characteristics of the sediments. The progression from fine silts rich in binding sites in the upper estuaries, to coarser sediments offshore is usually accompanied by decreasing contaminant loading. Thus, distributions will be governed to a large extent by the hydrodynamic regime in the system and the sorting and redistribution of fines. Sieving and normalisation procedures[3] are required to compensate for such granulometric and geochemical effects, to allow meaningful comparison of contamination levels, particularly for metals (Langston *et al*., 1999; MPMMG, 1998). In the current report we have used our own metals data, for sediments sieved at 100µm, to summarise sediment quality in the EMS (partly to ensure comparability with other reviews on SPAs and SACs in this series; listed at the end of this report). Metals discussed are Hg, Cd, As, Cr, Cu, Ni, Pb and Zn. These data are several years old (mainly from 1997) and are therefore only intended as guidelines; nevertheless, changes since then are unlikely to have been substantial. Methodologies have been successfully validated in numerous intercalibration exercises (Langston *et al.,* 1994a). The MBA sediment metals data described here are for the <100µm fraction, without further normalisation (*see footnote for details*), and are in concentrated nitric acid digests. Trends and 'risks' are

[2] Under Stage 2 (the likely significant effect test) all continuous discharges to the Mersey were considered to be of likely significant effect.

[3] 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 metal 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.

briefly compared with a other published and unpublished data on sediment analyses including those of CEFAS, BGS and Astra Zeneca.

In comparison with metals, the information on organic contaminants is very limited at sites within the EMS.

At present there are no statutory standards for sediments in the UK. Several guidelines on sediment quality are emerging, and CEFAS has cautiously recommended the Canadian/US effects-based approach (CCME ,1999; Long *et al*., 1995). Threshold Effects Levels (TELs - affecting the most sensitive species) and Probable Effect Levels (PELs - likely to affect a range of organisms) are derived from published toxicity data for a variety of substances in sediments (laboratory and field exposures). TELs are proposed as an Interim Sediment Quality Guideline (ISQG) value. Their application is discussed further in the Habitats Water Quality TAG document WQTAG078K (EA). 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).

There are a number of further caveats to the application of these guidelines, as discussed by Grimwood and Dixon (1997) in the context of List II metals. Foremost are the possible influences due to fundamental differences in sediment geochemistry (as discussed above) and the use of non-indigenous test species in deriving thresholds. It is stressed that current sediment TELs/PELs are for total fraction (unsieved), therefore MBA data (<100μM) may represent the “worst case” assessment (discussed also in footnote[3]). Nevertheless, in the absence of any UK standards, interim guidelines adopted by Environment Canada (CCME 1999; see Annex 7) serve as a rough indication of the risk to biota from sediment contaminants. Hence, their application will help to identify instances where efforts may need to be made to minimise further inputs of these substances to the SPA. Nevertheless, in the absence of any UK standards, interim guidelines adopted by Environment Canada (CCME 1999; see Annex 5) serve as a rough indication of the risk to biota from sediment contaminants. Hence, their application will help to identify instances where efforts may need to be made to minimise further inputs of these substances to the SPA.

CEFAS and EA data on particulate metals and organic contaminants feed in to the UK National Marine Monitoring Programme (NMMP). Together these provide part of the information gathered under various EC Directives including Dangerous Substances (76/464/EEC); Shellfish Waters (79/923/EEC), Shellfish Hygiene (91/492/EEC), Urban Wastewater Treatment (91/271/EEC) and Nitrates (91/676/EEC). Many requirements will soon fall within the remit of the Water Framework Directive (2000/60/EC).

There are several NMMP monitoring sites in the area including Seacombe in the estuary and a further four sites off the mouth of the estuary, in Liverpool Bay. Locations of NMMP sites are shown on figure 6, together with the EAs tidal waters sampling sites.

*Bioaccumulation and Biological Effects Indicators*

The use of biological samples as indicators of environmental contaminant levels has long been suggested as an essential component of monitoring programmes, in addition to more traditional assessments using water and sediment analyses (Phillips, 1980; Bryan *et al.*, 1985). The incoming water framework directive also places increasing emphasis on biological effects monitoring.

With biological/ecological condition becoming a major driver behind environmental protection the reasons for the inclusion of indicator species (of exposure) are principally two-fold:

1. They accumulate only the biologically available forms of contaminants.
2. They act as temporal integrators of contamination, and average out varying environmental levels during the period of exposure.

In contrast, analyses of water or sediments usually indicate total concentrations of the contaminant, irrespective of whether it is bioavailable or not, and do not define accumulation potential or biological impact. Furthermore, water, and to a lesser extent sediment analyses provide a 'snapshot' of conditions at the time of sampling: they are influenced by tidal and meteorological conditions at that moment, and are not temporally integrated. Since environmental quality targets are most often aimed at the protection of biological resources, the use of organisms which reflect the presence of bioavailable metals is therefore a preferable means of assessing contamination.

Such sampling was been carried out in the Mersey estuary by MBA staff on more than a dozen occasions since 1980, principally as part of a long-term collaborative study with EA to assess spatial and temporal trends in metal and TBT bioavailability, notably in relation to pollution control measures. Objectives also included long-term observations on the distribution of key indicator organisms in relation to contaminant trends. Even in the 'ideal' estuary there is no single universal indicator capable of surviving the extremes of conditions found along its length, or with the ability to accurately reflect contamination for all metals. Furthermore, a range of species must be sampled (e.g. seaweed, suspension feeder, deposit feeder) to assess bioavailable metals in various phases (water, suspended solids, sediments). The choice of indicators in the Mersey estuary is largely limited by availability. Thus, in the upper estuary the choice of practical alternatives is virtually limited to the polychaete *Nereis diversicolor*. However, a much wider variety of species becomes available downstream towards the Narrows. The criteria for selection of *Nereis*, seaweed *Fucus vesiculosus*; gastropods *Littorina littorea*; suspension feeding bivalves *Mytilus edulis*, *Cerastoderma edule*; and deposit feeding clams *Macoma balthica*, *Scrobicularia plana*; and their relative merits as indicators of metal contamination have been described previously (see, for example, Bryan *et al*., 1985; Langston, 1988; Pope *et al* 1998). Because the current synthesis is only intended as general guidance of trends in bioaccumulation, we limit discussion of results in section 7.1 mainly to *Scrobicularia* and *Nereis.*

Protocols for biological effects monitoring are still under development though some effects (as opposed to exposure) biomonitoring has been undertaken at sites near to the Mersey SPA (reviewed in section 7.2). In view of the importance of this emerging field the intention is to highlight links between biological effects and environmental conditions (nb chemistry) where possible, and to establish some of the priorities for the future – perhaps with a view to routine application within the EMS and as an aid to future assessments.

## 4. THE SITE: FEATURES AND THREATS

*Designations*

The Mersey Estuary is hugely important to the economy of the region – but it is also valuable from an environmental perspective. The Estuary has been designated as Special Protection Area (SPA) under the European Commission Directive on the Conservation of Wild Birds (79/409/EEC, article 4.2) for its internationally important numbers of migratory species and waterfowl. The Mersey Estuary SPA covers an area of 5033.14 ha and includes both marine areas (subtidal and intertidal) and land which is not subject to tidal influence. In essence this encompasses the intertidal habitats between Runcorn Bridge downstream to Bromborough, together with some land such as the Ince Banks above the high water mark. The marine element of the SPA is a designated European Marine Site (EMS). The extent of the Mersey Estuary EMS is illustrated in Figure 1. In addition to its status as an EMS and SPA the estuary is also a Ramsar site (wetland of international importance designated under the Ramsar Convention 1971), and parts of the estuary are also designated an SSSI under the Wildlife and Countryside Act 1981 (amended 1985). The SSSI citation describes the special interests for which the site was notified in the British context (although this does not include the sublittoral).

Because of its position, the condition of the site may be influenced by upstream and downstream activities, in addition to any direct impacts.

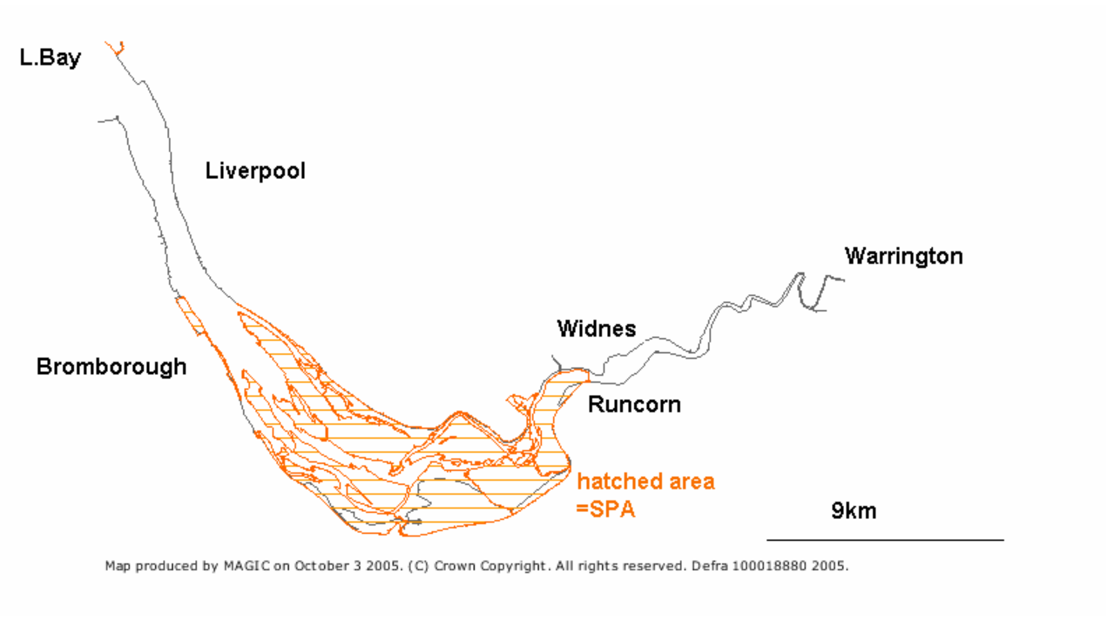



**Figure 1: The Mersey Estuary European marine site showing boundaries of the SPA**

*Physical characteristics*

Situated on the coast of north-west England the Mersey Estuary is one of the largest in the UK and receives drainage from a large catchment area (~5000km$^2$) encompassing the conurbations of Liverpool and Manchester; 46 km in length, its width varies significantly and its precise path changes from year to year. In the upper estuary the main freshwater input is the Mersey river, whilst the principal freshwater input in the inner estuary is the Manchester Ship canal.

The River Mersey itself, which flows through the estuary before discharging into Liverpool Bay on the Irish Sea, is 110km in length and originates in the Peak District at the confluence of the Rivers Tame and Goyt in Stockport, Northwest England. It flows west, towards Liverpool, passing through South Manchester. The river flows into the Manchester Ship Canal at Irlam weir and leaves the canal at Rixton Junction. Abstraction for industrial purposes occurs along much of the lower reaches of the river. At Howley Weir, Warrington the river becomes tidal, Further downstream below Runcorn, run-off from the Weaver enters the estuary via sluice gates in the Ship Canal. Below this point the Mersey widens considerably (up to 5 km) to form the Inner Estuary .

The Manchester Ship Canal was opened in 1894. It was built to connect Manchester directly to the sea, thus bypassing Liverpool Docks with its prohibitive tolls and harbour dues, and negating the need for road and rail transportation of goods. The canal runs from Eastham Locks (10km up the Mersey from Liverpool) to Woden Street Bridge, Manchester. Locks raise ships about 18m over its 58km length, Eastham Locks connect the Ship Canal to the tidal channel of the River Mersey. The canal diverts the course of the River Weaver and reduces direct particulate loadings to the estuary. Dock facilities were constructed at various points along the canal, and some of these are still operational, although nearer to Manchester many have fallen into disuse. However, the lower reaches of the canal are still quite busy today, particularly at the huge Queen Elizabeth II Dock at Eastham, which can accommodate tankers of up to 65,000 tonnes. Larger vessels are handled at the in-river terminal at Tranmere. Both these facilities supply crude oil to the refinery at Stanlow which has its own dock for smaller vessels. These ships mainly transport finished products. During 2004, the canal handled more than 6 million tonnes of cargo, mainly oil and petrochemicals.

The Mersey Estuary is a major trade route leading to important industrial complexes around Ellesmere Port, Runcorn, Widnes and the outskirts of Manchester (via the Ship Canal). Liverpool and Birkenhead were formerly important docks and centres of ship building activity. . The Royal Seaforth Dock is a major international container terminal as is the smaller facility at Garston.

The landscape varies along the estuary; the upper reaches are fringed with urban and industrial development, the mid-estuary (the designated EMS) has a more traditional periphery, whilst the Narrows (a straight narrow channel with depths of up to 30m, driven by a change in geology) are again urban. The outer estuary has a coastal landscape with beaches. Development around the estuary has lead to the reclamation of large areas of saltmarsh and much of the original shoreline has been modified. Alteration to physical habitat has therefore been considerable. Hydrology has also been substantially changed. At around 10 metres, the tidal Mersey has the second highest tidal range in the UK. The strong tides created have resulted in deep channels and sandbanks throughout the estuary. Near the mouth of the estuary in particular, these require considerable attention to maintain shipping access.

The seaward boundary of the EMS is concurrent with that of the SPA; the landward boundary is generally the upper boundary of the SPA, or, where it is above tidal influence, it extends to the limit of the marine habitats. The EMS is a large, sheltered estuary with considerable areas of saltmarsh and extensive intertidal sand- and mud-flats. There are also limited areas of brackish marsh (including an area of reclaimed marshland) rocky shoreline and boulder clay cliffs with freshwater seepages, set within a rural and industrial environment. The intertidal flats and saltmarshes provide feeding and roosting sites for large populations of waterbirds; during the winter, the site supports ducks and waders, and during the spring and autumn migration periods, it is particularly important for wader populations moving along the west coast of Britain. The Manchester Ship Canal forms part of the southern boundary of the site and separates a series of pools from the main estuary. These pools together with the Hale Marsh are important roosting sites for the wildfowl and waders at high tide. Bird populations feed on the rich invertebrate fauna of the intertidal sediments as well as plants and seeds from the salt-marsh and adjacent agricultural land.

*Past and current threats to water quality*

Industrial development through the 18$^{th}$ century led to increased discharge of liquid wastes from textile, tanning, metal processing, chemical, and later, petrochemical industries. Commonly, effluent simply flowed into the nearest watercourse, so that effluents combined in the rivers supplying the Mersey, and ultimately the estuary itself, and coastal waters. In addition, the pollutant effect was increased by the discharge of domestic waste water, sewage and surface runoff from a large populated area. The overall result was a complex mixture of contaminants entering the estuarine environment by a system of spatially diverse and temporally variant sources.

Pollution of the Mersey has therefore been a problem since the last century, but was probably at its worst in the 1960's, although there is limited water quality data prior to that time. One of the fundamental problems was that of the Biological Oxygen Demand (BOD) created by the microbial digestion of the vast excess of organic material entering the estuarine system. Widespread oxygen depletion, particularly in the upper/middle reaches of the estuary meant that 'normal' estuarine fauna including invertebrates and fish were unable to survive.

Modelling studies showed that organic inputs from the non-tidal River Mersey were particularly important in determining dissolved oxygen concentrations due to the magnitude of the load in relation to the relatively small volume of riverine input (NRA, 1995). A further complicating factor is the physical nature of the Mersey estuary itself: a large, mainly inter tidal inner basin separated from the sea by the constricted 'Narrows' channel. The large volume of the estuary, combined with the low volume of riverine input results in a long residence time (up to one month) for contaminants entering the upper estuary. In contrast, inputs into the lower estuary are exposed to stronger tidal flows, and are nearer to the sea, so that flushing times in that area are considerably shorter (in the order of a few days).

Widespread recognition of the state of the Mersey led, in 1976, to North West Water initiating the Mersey Clean Up Scheme, with 2 simple aims:

- that all parts of the estuary should contain dissolved oxygen at all times
- that beaches and foreshores should not be fouled by crude sewage or solid industrial waste.

To achieve these aims, NWW (North West Water) set about reducing discharges of untreated sewage, and in particular, the load to the upper estuary. Thus, by 1985 a major initiative was underway - The Mersey Basin Campaign - to revitalise the River Mersey and its waterfront. A major component of this project included the construction of a primary sewage treatment works for Liverpool, at Sandon Dock, replacing 28 crude sewage discharges, linked by an interceptor sewer reaching from Crosby in the north to Speke in the south. In addition, fine sewage screening plants at Scott's Field, Beaconsfield and Shore Road on the Wirral peninsula eliminated crude sewage discharges on the south bank of the Mersey. Ellesmere Port sewage treatment works was also extended to include secondary treatment, and treatment of effluent from petrochemical complexes, while sewage treatment plants at Widnes and Warrington were upgraded to include secondary treatment as well. Modification to the Davyhulme treatment plant at Manchester to reduce discharged levels of ammonia resulted in a considerable reduction in the BOD of the upper estuary. Key improvements were also carried out in 2000, as required by the UWTTD eg secondary treatment at Birkenhead/Bromborough WwTW

Thus, from the standpoint of organic inputs, and dissolved oxygen levels, there has been improvement in the Mersey, which will hopefully continue as further reductions of organic input are effected.

Although the major improvements so far have focused on reducing the organic load to the estuary, there have been schemes to reduce inputs of many dangerous substances especially heavy metals such as mercury, lead and cadmium.

The major source of mercury in the Mersey has been from chlor-alkali plants at Runcorn and Ellesmere Port which utilised flowing mercury cathode cells in the electrolysis of brine. Thus, waste brine effluent was significantly contaminated with mercury. The installation at Runcorn, on the Mersey, represents the largest point source discharge of Hg in the UK, despite a reduction in discharge from over 70 tonnes per year in the mid 1970s to less than 1.0 tonne/year in 1995 (NRA, 1995) and only 259 kg in 1998 (P.D. Jones, Environment Agency, personal communication). Meanwhile, the plant at Ellesmere Port, which used to discharge ~0.3 tonnes Hg/year into the Manchester Ship Canal has changed to a mercury-free process, further reducing Hg input to the Canal.

The Associated Octel plant at Ellesmere Port also produced tetra-alkyl lead compounds, used as anti-knock agents in petrol, which, in the past have been discharged to the estuary via the Manchester Ship Canal. in the form of stable, soluble and organic, tetra-alkyl lead compounds (now ceased). Organic Pb was implicated in a major mortality of over wintering birds in 1979, when an unusual build up of Pb in the Manchester Ship Canal was flushed to the estuary as a shock load and entered the food chain (Edwards and Hill, 1995; NRA, 1995; Riley and Towner, 1984; Wilson *et al*., 1986).

The implementation of an EC directive in 1985 requiring the regulation of cadmium discharges has lead to an estimated reduction of Cd inputs from 0.282 tonnes/year in 1985 to 0.052 tonnes/year in 1991, primarily from electroplating activities (NRA, 1995). Previously there were 10 such industrial concerns operating in 1985, all with untreated effluents.

Other major changes to discharge practice include the textile finishing industry in north-west England – a major source of pentachlorophenol (PCP), which is used as a rot-proofing agent after the bleaching and dying process. In 1988 an estimated 900 kg/year of PCP entered the Mersey Estuary compared with 180 kg/year in 1992 (Edwards and Hill, 1995; NRA, 1995).

Chlorinated hydrocarbons were common contaminants in the Mersey. Inputs of volatile organics such as trichloromethane (chloroform) to the Mersey Estuary reduced from 26 tonne/year in 1989 to less than 5 tonne/year in 1993, largely due to the cessation of production at the Runcorn plant and the ending of Alloprene (chlorinated rubber) production at ICI plants in Widnes and Lostock (Edwards and Hill, 1995; NRA, 1995). Dichloroethane (DCE), used in the manufacture of vinyl chloride and tetra-alkyl lead compounds, was discharged from ICI Runcorn, Associated Octel at Ellesmere Port and the Halewood sewage treatment works (which receives a trade effluent containing DCE from pesticide production). The Runcorn plant of ICI was also a source of perchloroethylene, trichloroethylene and chloroform. The chlorinated solvents discharged at Runcorn also contained quantities of impurities such as hexachlorobenzene, hexachlorobutadiene and trichlorobenzene. Total inputs of DCE to the Mersey Estuary fell from over 25 tonne/year in 1991 to less than 10 tonne/year in 1993. Similarly, trichloromethane (chloroform) loads have fallen from over 35 tonne/year in 1990 to less than 20 tonne/year in 1992 (Edwards and Hill, 1995; NRA, 1995).

Most other organic contaminants (e.g. pesticides and herbicides) cannot be related directly to point source inputs, although the first production of DDT (now banned) has been attributed by Fox *et al*. (1999) to the region of Trafford Park in Manchester in the mid-1940s. Inputs from the chemical industry (direct and atmospheric) have historically been substantial. Dairy farming is widespread in the River Mersey catchment area; farm effluents affect the upper river system from which residual pesticides are dispersed to the estuary and the Irish Sea (NRA, 1995).

Phthalate esters are thought to come from wastewater discharges in the upper Mersey Estuary (Preston and Alomran, 1986) and atmospheric input, mainly from the burning of fossil fuels, is considered to be a major source of azaarenes and polycyclic aromatic hydrocarbons (PAHs) (Osborne *et al*., 1997). Hydrocarbon contamination is widespread in Mersey Estuary sediments (Davies and Wolff, 1990), but estimates of inputs to the Irish Sea are difficult. The number of oil spills requiring clean-up measures in the Irish Sea averaged around 12 per year for 1985-89, with a total of ca. 8 in 1990 according to figures quoted by DoE (1992). These represent only a proportion of the actual pollution incidents which were recorded in 1989 (32) and 1990 (22) (ACOPS, 1990 reported in; Hamilton Oil Company, 1993).

Camacho-Ibar & McEvoy (1996) consider the main source of polychlorinated biphenyls (PCBs) in Liverpool Bay sediments to be the River Mersey, although input from sewage sludge (now ceased) and dredge spoils might also be important. The ultimate source of the PCBs in the Mersey is likely to be contaminated land in the catchment area. As an example, Edwards & Hill (1995) report that Alvanley tip in Cheshire, where electrical capacitors containing PCBs were disposed of in the 1970s, continues to contaminate a local stream.

Also significant changes have occurred in the 'levelling' operations of the Ship Canal which may have affected the apparent input patterns of a number of contaminants. Water movement from the canal to the estuary is a mixture of lockage and leakage, with the Weaver Sluices acting primarily as a discharge for excess water entering the canal from the river Weaver. In the past, high spring tides meant that excess water could enter the canal at Eastham Locks, and this too was discharged at Weaver sluices as 'levellings'. In 1989 the outer storm gates at Eastham, that were that not functioning, were renewed to reduce inputs of silt-laden estuarine water to the canal, thus eliminating levelling operations, but also reducing the dilution of pollutants discharged into the canal, such that when outflows do occur, they are in effect pulsed discharges of 'concentrated' canal water.

*Priority Consented discharges*

An earlier (1999) but useful indication of the location and size of WWTW inputs to the Mersey Estuary, is shown in figure 2 below (from Allen *et al.*, 2000). These are outfalls which are situated within the EMS itself and does not include discharges into rivers above the tidal limits. Estimated inputs from trade effluents (~650,000 $m^3$/d) represent just over half the amount of sewage effluent (~1,200,000 $m^3$/d). There are few other EMS which have such a high level of discharges (Thames and Solent and Southampton have comparable levels of trade discharge; the former receives higher sewage effluent loadings than the Mersey, the later receives less).

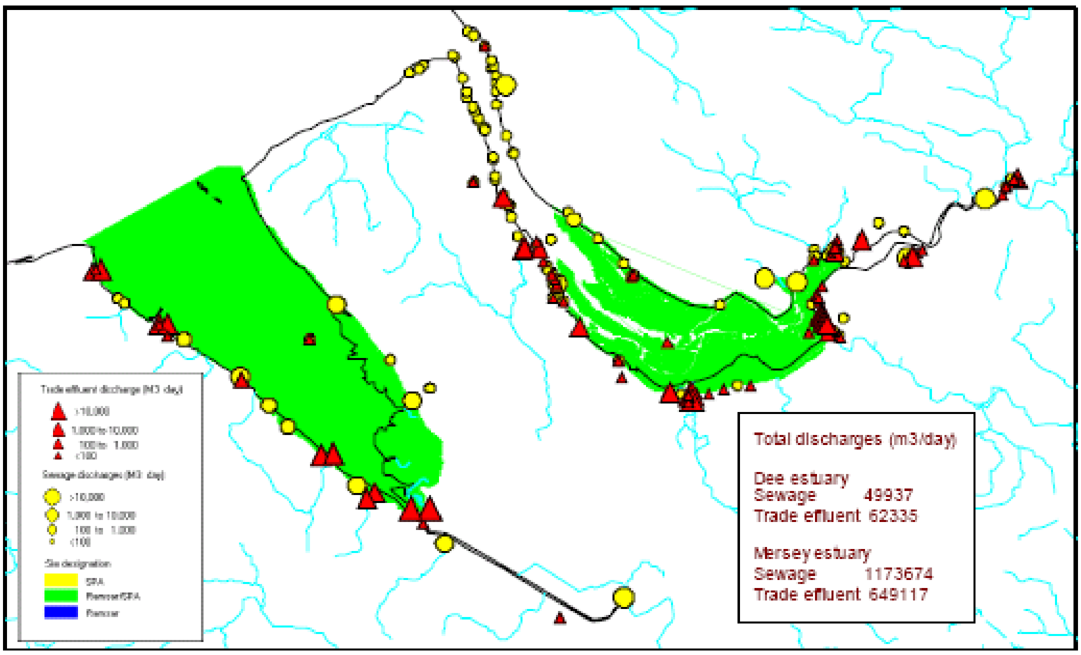


**Figure 2. 1999 data on consented discharges within the boundary of the Mersey Estuary EMS. (Reproduced from Allen *et al*., 2000).**

No data on contaminants in discharges were made available for the current project. In view of the large number of consents this would require a major data retrieval exercise outside the scope of this project. The Agency is understood to be conducting its own review of sources in relation to appropriate assessment (under the Conservation (Natural Habitats &c.) Regulations 1994).

According to a recent EA planning document for the Mersey Estuary ROC (stage 3), all 3,887 permitted water discharges (all discharges in hydrological continuity with the estuary) were identified as being relevant discharges under Stage 1 and taken forward to Stage 2 (Is the discharge likely to have a significant effect?). Of these 3,887 discharges, 919 have passed through to Stage 3 and need to be considered further as part of the appropriate assessment (Simmons 2004). The 919 discharges contain:

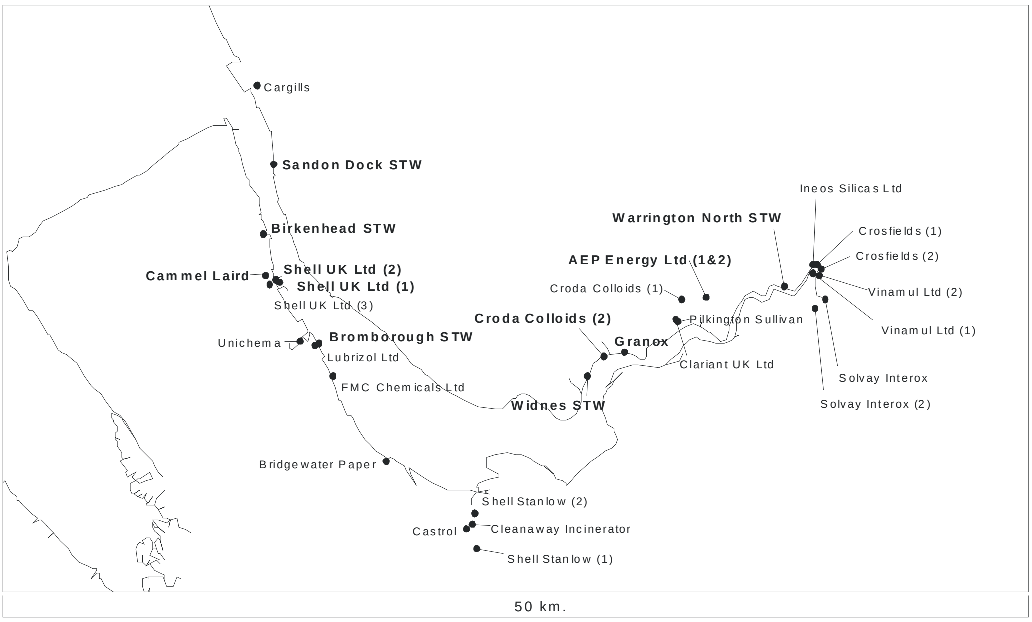
- Those discharges responsible for discharging the top 90% of the nutrient/BOD/ammonia load entering the Mersey Estuary.
- Those discharges discharging directly into the Mersey Estuary.
- Those discharges authorised to discharge a List 1 and/or List 2 Dangerous substance that has been found to be either exceeding or at risk of exceeding the Environmental Quality Standard in the Mersey Estuary.
- All IPC/IPPPC water discharges not already considered under the Directive.

Of the 919 discharges requiring an appropriate assessment only around 380 are continuous discharges. The remainder largely represent intermittent discharges (storm sewage overflows / emergency discharges from pumping stations). Further prioritisation has also been undertaken by the Agency as indicated in figure 3A which also indicates a subset for which a CORMIX near field modelling approach is proposed using the hydrodynamics from the 2D-MARGIS Model (see section 8). Listings of these priority discharges and some of the determinands of concern can be found in Annex 7.

Thus, the Mersey Clean Up Scheme, designed to counteract the years of misuse and neglect, has led to much-heralded improvements in water quality. The Mersey is now reported to support a wide range of fish species, including migratory fish, and there has been an increase in numbers of other animals returning to the estuary including reported sightings of porpoises, grey seals and octopus. In this report we have examined the evidence for improvements in water quality and the links with biological recovery. Hopefully this will be a useful supplement to EN/EA appropriate assessments.

*Dumping*

Dumping of sewage sludge into Liverpool Bay ceased in 1998 (~ 1.2 m tonnes from Davyhulme, Liverpool and Warrington WwTWs) when sea disposal of such material around the UK was halted. Dumping of dredge spoils in to the bay continues at site Y and site Z (~1.8m tonnes in 1998; figure 3B). Because of the hydrodynamics of the system and sediment transport it is likely that fines and their associated contaminant loadings have influenced the Mersey Estuary. There are tidal currents of up to 0.8m $s^{-1}$ whose directions are modified by mobile sand bars, and sediments are strongly influenced by waves generated by NW winds which, coupled with a south easterly residual current, are likely to transport fines towards the mouth of the estuary. Density currents (saline intrusion at depth) subsequently promote the movement of coastal sediments towards the inner estuary. Estimates of accretion rate in the upper estuary vary from ~0.6 cm $yr^{-1}$ at Widnes and 0.8-3.1 cm $yr^{-1}$ on the Ince Banks (Fox *et al*., 1999), but such accretion may be reversed as a result of shifts in channels. Thus the tidal conditions have produced a mixture of sediment types in the estuary ranging from medium sands in the Narrows, fine sands in the inner estuary (grading to very fine sands in places) and large inter-tidal areas of silts and clays along the slow flowing margins.



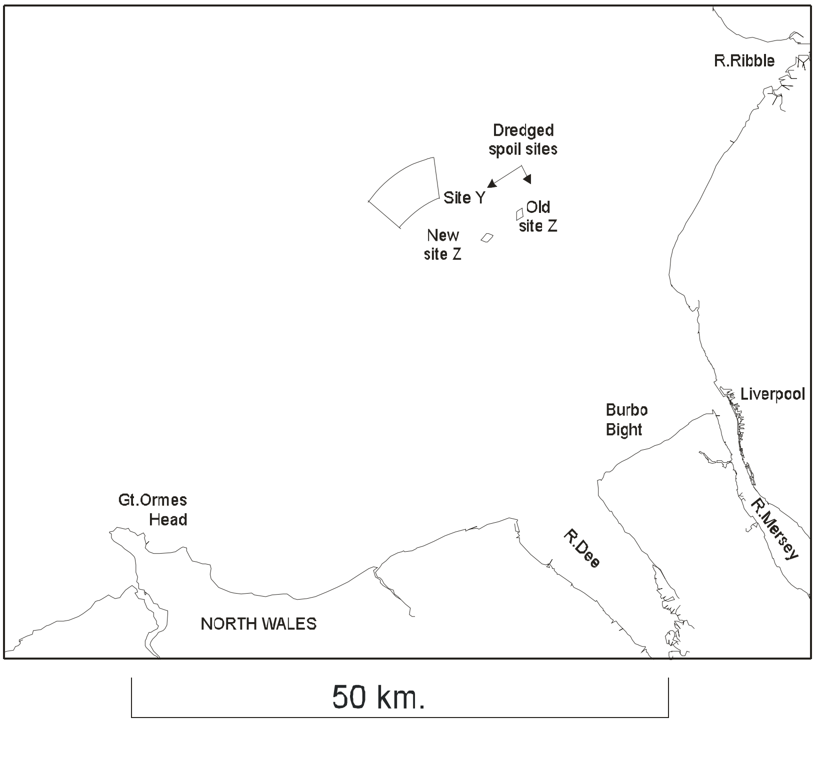



**Figure 3. (A) Mersey Estuary. EAs priority outfalls, including (in bold) those intended for water quality modelling (from report by Simmons, 2004). (B) Liverpool Bay dredge spoil sites.**

## 5. STUDIES ON BIOLOGICAL COMMUNITIES

*Phytoplankton*

Voltalina (1983) provides a list of all the phytoplankton species found during a research project on Liverpool Bay, together with some taxonomic and autoecological notes. 34 species new to British waters were found during this survey. Subsequent studies in Liverpool Bay (Voltolina and Foster, 1985; Voltolina, 1985) established that the seasonal and geographic distributions of the silicoflagellate *Distephanus speculum* were dependent upon ambient concentrations of dissolved inorganic silicon, rather than upon the thermal characteristics of the sea area, and summarised field observations of *Calyptrosphaera* spp.

Concerns that the proposed tidal barrage might result in 'red tide' blooms of dinoflagellates, Henderson (1989) assessed potential effects of a barrage on phytoplankton in the Estuary. In the estuary, three major groups of phytoplankton were identified: A floating colonial form *Phaeocystis pouchetii*, reported to be very abundant in the estuary, this does not cause red tides but is unpalatable to herbivores. *Phaecystis*, is considered to play a major role in the ecology of Liverpool Bay although little is known about its density in the Mersey Estuary. Non-motile diatoms were the second group, and the third, dinoflagellates. The latter include red tide species, and are motile therefore able to select their depth in the water column. Henderson (1989) assessed the requirements of these major groups (nutrients, light availability, water movement) and predicted that in a post-barrage scenario, *Phaeocystis* would be the dominant group as it is able to maintain itself in the photic zone. However it was noted that the distribution, concentration and viability of dinoflagellate cysts in the sediment was unknown, and a post-barrage red tide event could be generated by the synchronised germination of these cysts in the estuary, particularly as the barrage would reduce longitudinal dispersion of sediments (Henderson, 1989).

*Saltmarsh Communities*

Saltmarshes are an important habitat for wintering and migratory waterfowl within the estuary both for feeding and for high tide roosting. A recent survey assessed the saltmarsh and associated communities within the Mersey Estuary (Skelcher, 2003). The total area covered 724 ha, with 99 ha on the northern side of the Estuary and 626 ha on the southern fringes. This may represent a reduction in area, as saltmarsh within the estuary was previously estimated to cover 848.39 ha (Skelcher, 2003).

The most extensive area of marsh at Hale, is dominated by upper marsh communities *Festuca rubra* and *Elymus repens* and transitional grassland *Agrostis stolonifera, Potentilla anserina* with a *Lolium perenne* sub-community.

On the north side of the estuary, part of the coastline is formed by boulder clay cliffs. Portions of the cliff have become exposed by slumping and in these areas a number of unusual species occur including Yellow-wort (*Blackstonia perfoliata*) and Bristly Oxtongue (*Picris echioides*) both of which are at the northern limits of their distribution. Small depressions and old cuttings support *Puccinellia maritima*, *Spergularia marina* and *Puccinellia distans* saltmarsh. Along the remainder of the north coast, saltmarsh occurs primarily as a band of lower marsh and pioneer communities, stretching from Hale westwards to Garston. This comprises mosaics of *Puccinellia maritima* and *Spartina anglica*, with local *Salicornia* and *Suaeda maritima* saltmarsh. Swamp communities of *Phragmites australis* and *Scirpus maritimus* occur frequently as small stands along the strandline.

On the southern side of the Estuary, only accessible by ferry across the Manchester Ship Canal, the vast majority of marsh is characterised by *Puccinellia maritima*, occurring both as relatively stable lower marsh and as pioneer marsh. *Spartina anglica* saltmarsh also occurs frequently as a pioneer community along with more local *Salicornia* and *Suaeda maritima* saltmarsh. The western and central parts of the southern saltmarsh are composed of upper marsh species *Festuca rubra* and *Elymus repens,* swamp communities *Phragmites australis*, *Typha latifolia* and *Scirpus maritimus* occur only as small narrow stands along the bottom of the Ship Canal bank. A more extensive mosaic of species-poor upper marsh occurs at the eastern end along the Frodsham Score, and is dominated by *Festuca rubra* and transitional grassland *Agrostis stolonifera - Potentilla anserina* grassland, with a *Lolium perenne* sub-community.

Skelcher, (2003) found evidence of marsh erosion on the northern side at Hale and at Dungeon Banks and on the south side at Ince Banks. Areas of accretion included Hale Head, Oglet Banks, Stanlow Banks, notably in front of Mount Manisty, and at the western end of Frodsham Score. Comparison with previous surveys suggested that many of the current trends in erosion and accretion were beginning in 1982 (Skelcher, 2003).

Unlike the other salt-marshes in the estuary, Stanlow banks has not been grazed by sheep or cattle and consequently has a more diverse flora. Sea Aster (*Aster tripolium*) and *Hastate Orache* (*Atriplex prostata*) are widespread throughout this area. Sea Plantain (*Plantago maritima*), Annual Seablite (*Sueda maritima*) and Scurvey-grass (*Cochlearia* spp.) also occur. In a number of areas the salt-marsh grades into brackish marsh dominated by Common Reed (*Phragmites australis*) with Sea Arrow-grass (*Triglochin maritima*) and Great Reedmace (*Typha latifolia*) also present in some areas. On the sandy foreshores Sea Sandwort (*Honkenya peploides*) occurs with Sea Milkwort (*Glaux maritima*). Mud Rush (*Juncus gerardi*), Sand Sedge (*Carex arenaria*) and Curled Dock (*Rumex crispus*) grow at the inner edge of the salt-marsh and along the strand-line.

Much of the saltmarsh of the Mersey Estuary is thought to be relatively poor in terms of plant species, perhaps because many areas have been grazed in the past and the diversity associated with long-established ungrazed marsh has not had time to develop. However, withdrawal or depletion of grazing has resulted in a rank sward which is considered less valuable to grazing and roosting birds (Skelcher, 2003).

*Macrofauna and Benthic communities*

Benthic invertebrates are very important food items for fish and birds in the Mersey, particularly in the extensive sand and mudflats in the inner estuary. The large intertidal areas of muddy sands support dense populations of invertebrates notably lugworm *Arenicola marina*, ragworm *Nereis* spp. and bivalve molluscs, including the edible cockle *Cerastoderma edule* and Baltic tellin *Macoma balthica.* The mud snail *Hydrobia ulvae* and sandhopper *Corophium volutator* are also abundant, whilst the outer estuary and the Narrows support generally lower densities of invertebrates (English Nature 2001).

Perhaps one of the most comprehensive descriptions of the intertidal fauna (and to a lesser extent the flora) of the Mersey Estuary can be found in an early publication (Bassindale, 1938). 37 sq.miles of intertidal banks in the outer (Liverpool Bay) and upper estuary (between Warrington and Rock Light) were surveyed and classified according to their nature and fauna. The work includes a general description of the infauna as well as detailed taxonomic listing, therefore would be useful for comparison with contemporary surveys. The principal faunal groups were annelids (relatively numerous polychaetes e.g *Nereis* and *Nephtys* spp., *Arenicola,*and *Lanice*, and one oligochaete *Clitellio arenarius*) and bivalve molluscs (e.g. *Macoma, Mya, Donax*)

One significant observation was that although the mud banks of the upper and outer estuary were inhabited by similar species, a larger number of additional species were recorded in the outer estuary. There was an abundance of burrowing animals throughout the estuary, which comprised large numbers of relatively few species in the upper estuary, notably *Nereis, Macoma*, and *Corophium.* The distribution of species in the Mersey was considered to be similar to that of the River Tees and Tay, with the exception that in the Mersey there was a sharp drop in species numbers at Rock Light (New Brighton). As this could not be attributed to salinity differences, the strong tidal streams in the narrows were considered to be a possible cause (Bassindale, 1938).

Later, Bamber (1988) carried out a survey of the intertidal soft-sediment fauna, in relation to the proposed tidal barrage on the Mersey, and reported a similar faunistic community within the estuary. This study also found the fauna of the upper estuary to be impoverished in comparison to that of the outer sands. Bamber (1988) considered the distinction between upper and outer estuary faunas to be a result of pollution in the upper estuary and noted that there had been a decline in diversity in this area over the previous 40 years. A high biomass of oligochaetes was recorded in the muds at Weaver sluices. These are the principal food source for shelduck in the estuary, although *Hydrobia,* also a preferred food item for shelduck were not found. The most diverse and productive area for wader feeding within the estuary was Stanlow Bank.

Bamber (1988) predicted that the proposed barrier would result the loss of lower littoral sandy sediments, which were anyway unproductive at that time. Littoral infaunal diversity and productivity was predicted to improve as increased sedimentation would lead to finer sediments.

A recent study reviewing the use of environmental biomarkers suggests that the benthos in the Mersey is characterised by coarse sand communities with low productivity and biomass, and muddy sand and mud communities with high productivity (O'Doherty & Leah, 2005). This review also indicates that communities in the inner and upper Estuary, and possibly the Narrows, have been impoverished due to pollution but have improved somewhat since the 1970s. High numbers of oligochaetes were recorded in many areas of the inner and upper Estuary, which is symptomatic of organic enrichment.

Other areas such as the outer estuary, and Oglet and Stanlow Banks, have a more typical estuarine fauna (Scott 2002). Maximum densities of the dominant species *Macoma balthica, Corophium volutator*, *Nereis diversicolor*, *Tubifex costatus* and *Tubificoides benedii* were at the high end of the range of values reported for other UK estuaries. In contrast to early studies, e.g. Bamber (1988), Scott, (2002) recorded the presence of *Hydrobia ulvae*. Early studies had suggested that the absence *Hydrobia* from the estuary in the 1970's was due to pollution, although without long-term data it is difficult to establish the cause of original absence.

Recently, Wilding *et al.,* (2005) provide a synthesis of current information pertaining to benthic communities and seabed habitats in SEA6, a large area which covers the UK territorial waters in the Irish Sea and important industrial estuaries including Liverpool and Mersey. This work was produced as part of the Department of Trade and Industry's offshore energy Strategic Environmental Assessment programme. This is by no means a comprehensive study, but provides useful contextual information as follows:

Much of the Mersey Estuary and foreshore has been modified and is now restrained by concrete banks and surrounded by industrial and urban developments. As a consequence there is a paucity of natural coastal/shore habitat and little literature concerning the benthos in this region. Sand dunes are present to the north of the estuary mouth. Upstream of Liverpool there are extensive mud shores supporting ragworm *Hediste diversicolor* and oligochaete communities (Covey, 1998) typical of low salinity muds.

A range of sediment types make up the seabed of Liverpool Bay and a complex mosaic of community types, related to sediment type, have been found. Towards the north and west a relatively rich fauna is reported whereas in the south the substratum was dominated by relatively sparsely populated, current swept sand. In the southeast of Liverpool Bay, two primary habitat types have been identified, one of muddy sand and the other of clean sand (Eagle, 1973, 1975). Bristleworm *Pectinaria (Lagis) koreni*, sandmason *Lanice conchilega* and bivalve *Abra alba* were numerically dominant across the area although their ratios differed between habitats.

In muddier substrates, differences in species richness and diversity were attributed to destabilisation of sediments, through bioturbatory activity, and subsequent erosion by currents. The benthic infauna has been variously described as highly variable, exhibiting long term shifts in abundance (Rees and Walker, 1984; Rees *et al.,* 1994), and a shallow *Venus* community with the bivalve *Fabulina (Tellina) fabula*, and polychaete *Magelona mirabilis* typically found in the less disturbed areas (Mackie, 1990). In areas subject to higher levels of disturbance, and where coarser material is present, the bivalve *Spisula elliptica* and the polychaete *Nephtys cirrosa* tend to dominate. One of the few epibenthic megafaunal surveys identified several species of starfish, sand star *Astropecten irregularis*, large populations of common starfish *Asteris rubens* and brittlestar *Ophiura ophiura,* from the Liverpool Bay area (Ellis and Rogers, 2000). Brown shrimp *Crangon sp*., Harbour crab *Liocarcinus depurator* and flying crab *L. holsatus* have also been recorded in the area, together with the Thumbnail, or 'polished' crab *Thia scutellata* (Wilson 2005).

There are two designated shellfish harvesting areas within the area, both classed as grade 'B' and both at the mouth of the estuary in Liverpool Bay; North Wirral Moreton/Leasowe (Mussels *Mytilus edulis*) and Meols and Hoylake (cockles *Cardium edule*). The production of bivalves at a further bed in the Mersey at Wallasey is prohibited (due to high bacteriological contamination) (FSA, 2005)[4].

*Fish*

Fish were apparently abundant in the Mersey in the 18th and 19th centuries, and the Mersey was once an important commercial fishery, although by the mid 20th Century fishing activity had been severely reduced due to the effects of industrial development and pollution. At the present time there are still very few commercial fishermen working the inshore waters of Liverpool Bay (Jones, 2005).

It was suspected that migratory salmonids were returning to the Mersey catchment in the mid-1990s and salmon were caught when a fish trap was set at Woolston Weir in 2001. Two of these fish were identified as grilse, having spent 2 years in freshwater and 1 year at sea before returning to spawn. The other fish had spent 1 year in freshwater and 2 at sea. These are multi-migratory fish, only very occasionally observed, which usually run in the spring giving rise to the term 'spring salmon' (Jones, 2005). During October and November 2002, 26 salmon were caught at Woolston along with other species including sea trout and brown trout (*Salmo trutta fario*), dace (*Leuciscus leuciscus*) and the important Annex 2 species, river lamprey (*Lampetra fluviatilis*). These catches were taken as an indication of major improvements in water quality (Jones, 2005).

Fishery investigations over the last few decades initially focussed on the diversity and abundance of fish in the Manchester Ship Canal (e.g. D'Arcy and Pugh-Thomas, 1978, D'Arcy and Wilson, 1978, Taylor, 1983a, 1983b). Both estuarine and freshwater fish were found, as saline water entered the Ship canal during 'levelling' at high spring tides (Wilson *et al.,* 1986). Records of fish entrained on the intake screens at Runcorn (ICI) and Ince (Shell) were taken, and in the two-year period between 1976 and 1978, 25 species were recorded including 6 freshwater fish.

Elliott and Dewailly (1995) compared the structure and components of the Mersey fish assemblage[5] with assemblages from 17 other estuaries in Europe. This study created functional guilds, which described the use made of an estuarine area for each taxon encountered e.g habitat type, feeding type, reproduction type, position in the water column.

Results revealed that in terms of taxonomic assemblage structure, the Mersey and the Elbe showed similarities, although in terms of ecological guilds the Mersey was grouped with the Loire, Tyne, Forth, Aveiro and the German Wadden. When all guilds were considered together, The Mersey fell into a sub-group with the Tyne and

[4] FSA - http://www.food.gov.uk/foodindustry/shellfish/
[5] Complete species list for the Mersey (and other estuaries in this study) can be obtained from the authors)

Elbe, although the overall analyses did not indicate whether the extent of industrialisation or urbanised area within the estuaries could explain differences in fish assemblages (Elliott and Dewailly, 1995). The structure of the Mersey fish assemblage was found to be similar to other comparable estuaries, such as the Humber and Westerschelde, which may indicate that it is now functioning as a typical estuary in terms of types of species present (Jones, 2005). However, it is worth noting that Elliott & Dewailly (1995) made comparisons on the basis of coverage of each habitat type and of the diversity of species present and take no account of the abundance or condition of each species.

JNCC[6] report that the recorded migratory fish fauna of the Mersey Estuary now include sea trout *Salmo trutta*, flounder *Platichthys flesus*, common eels *Anguilla anguilla*, sea and river lampreys *Petromyzon marinus* and *Lampetra fluviatilis,* and Atlantic salmon *Salmo salar*. The latter two are both Annex II species. Over 40 species have been officially recorded as being present in the estuary; the most common include sprat *Sprattus sprattus*, herring *Clupea harengus*, whiting *Merlangius merlangus*, goby *Pomatoschistus spp.*, pipe fish *Syngnathus acus*, flounder *P. flesus* and plaice *Pleuronectes platessa* (Jones 2005).

Eels *A. anguilla* are commonly caught in the Mersey estuary as they migrate upstream, where they remain for many years before returning, as mature adults, to the Sargasso Sea to spawn. The sexes migrate at different ages, with males migrating younger and smaller than the females (Davies *et al.,* 2004). A Europe-wide, sharp decline in populations over recent decades is considered to be due to commercial fishing and habitat loss. The eel is an important prey species for herons, otters and bitterns, but is not well monitored at present (O'Doherty & Leah, 2005).

A recent publication 'Fishes in Estuaries' contains collected studies which concentrate on the status of European Estuaries and brackish habitats in relation to fish and macrocrustaceans (Elliot & Hemingway, 2002). The Mersey is included in several of these studies, notably in relation to the effects to fish (and faunal) communities of various disturbances (Cattrijsse *et al.,*2002), environmental quality (Marchand *et al.,* 2002), and habitat use (Pihl *et al.,*2002).

*Bird Populations*

The Mersey Estuary SPA citation was written in 1993 and the site classified as an SPA in 1995. The intertidal flats and saltmarshes provide feeding and roosting sites for large populations of waterbirds and during the winter, the site is of major importance for ducks and waders. The Estuary is also important during the spring and autumn migration periods, particularly for wader populations moving along the west coast of Britain. Full description of the bird distributions within the Mersey is beyond the scope of the current report. However, accounts of the distributions of individual species can be found in several publications, notably those relating to barrage proposals. These include Clark *et al.*, (1990a) which reviews the literature and data on night- and day-time feeding in relation to barrage impact assessments on feeding waders and wildfowl. This study also assesses the distribution and abundance of wildfowl and waders on the Mersey, and the importance to wildfowl and wader

[6] jncc.co.uk

populations of night feeding on estuaries. To predict how waterfowl populations may be affected by the proposed tidal barrage across the Mersey, Clark *et al.,* (1990b) evaluated the patterns of usage of the intertidal flats of the Mersey estuary by waders and wildfowl. This study also established preferred areas, and identified the places of origin and movement patterns of the populations of waders and wildfowl that visit the Mersey Estuary. Clark *et al.,* (1990b) also considered evidence regarding the capacity of British estuaries to absorb waders and wildfowl populations which might be displaced by a Mersey Barrage. Later, Clark *et al,* (1993) looked at variability in the distribution of waterfowl in relation to sediments and Rehfisch *et al.,* (1994) described waterfowl distribution and diet on the Mersey Estuary and adjacent areas. More recently, Austin (1996) applied a model to predict bird populations on Mersey after barrage construction.

Table 2 lists bird species of International and European importance that use the Mersey Estuary SPA for breeding, roosting or overwintering.

**Table 2. Birds of international and European importance using the Mersey Estuary SPA (**from the SPA Review, Stroud *et al.* 2001 -JNCC.gov.uk)

| **Species** | **Common name** |
|---|---|
| *Podiceps cristatus* | Great Crested Grebe |
| *Tadorna tadorna* | Shelduck |
| *Anas penelope* | Wigeon |
| *Anas crecca* | Teal |
| *Anas acuta* | Pintail |
| *Pluvialis squatarola* | Grey Plover |
| *Calidris alpina alpina* | Dunlin |
| *Numenius arquata* | Curlew |
| *Tringa totanus* | Redshank |
| *Pluvialis apricaria,* | Golden Plover |
| *Vanellus vanellus,* | Lapwing |
| *Limosa limosa islandica* | Black-tailed Godwit |
| *Charadrius hiaticula* | Ringed Plover |

The diversity of invertebrates is thought to have substantially increased in the post industrial-era and was in turn, linked to the dramatic increase in birds in the mid-1990s (table 3). Occasional deleterious events have been observed (notably bird kills in the late 1970s and early 1980s attributed to alkyl lead bioaccumulation and an oil pipeline failure and spillage in 1989/1990) though because of the actions of industry and regulators these have not been sustained sufficiently to affect the overall trend. In the case of alkyl lead poisoning, Dunlin were the most affected species, possibly through ingestion of contaminated prey items such as *Macoma*, though the precise pathways are not fully understood (Wilson *et al*., 1986)

**Table 3. Bird numbers in the Mersey Estuary and qualifying thresholds (fromWeBS surveys - EA, 2002)**

| | | **Qualifying thresholds** | **Abundance at SPA citation (1987/88 – 1991/92)** | **Five-year mean (1994-1999)** |
|---|---|---|---|---|
| | | *Total waterfowl* | | |
| | | 20,000 | 78,015 | 104,784 |
| | **Diet** | *SPA qualifying species* | | |
| **Dunlin** | **Molluscs (*Macoma,Hydrobia*) polychaetes (*Nereis*) and crustaceans (*Crangon, Carcinus*)** | 1500 | 32,528 | 52,181 |
| **Redshank** | **Molluscs (*Macoma,Hydrobia*) polychaetes (*Nereis*) and crustaceans (*Corophium*)** | 1500 | 4,080 | 5,292 |
| **Pintail** | **various plants and invertebrates (*Hydrobia*)** | 600 | 5,925 | 917 |
| **Shelduck** | **Molluscs (*Hydrobia*) polychaetes (*Nereis*) and crustaceans (*Corophium*)** | 3,000 | 4,510 | 10,344 |
| **Teal** | **plant seeds (*Atriplex, Salicornia*), small molluscs (*Hydrobia*)** | 4,000 | 11,705 | 11,002 |
| **Ringed plover** | **polychaetes, crustaceans (Gammarus) and molluscs** | 500 | 1,453 | Not published |

A report to EA by Young Associates described major feeding areas and trends in bird numbers since the submission of baselines for the original SPA designation, up to 2001 (EA, 2002). The major qualifying species had maintained internationally important levels, or have increased. A number of nationally important qualifying species and non-qualifying species also appeared to have increased over the period and these favourable trends were attributed, partly, to improved water quality. Pintail were an exception, though this was part of a European decline. There was an indication that numbers of Pintail had increased, coincidentally, in the adjacent Dee Estuary and this may have represented a regional redistribution of the species. It is possible that the decline in Pintail benefited other species such as Shelduck and Dunlin through reduced competition for *Hydrobia*: the overall improvement in numbers of both Shelduck and Dunlin in the Mersey at that time was contrary to the national picture for these species.

However a decline in Dunlin was observed in 1999-2000 in line with trends observed in a number of other UK sites. A slight decline in Wigeon had been recorded but the Mersey population remained nationally important as in the SPA citation. The Ringed Plover was present in internationally important numbers during autumn passage in 1989 at the time of qualification of the SPA, and in 1996-97 but had not been listed as such in more recent WeBS reviews indicating a downward trend, consistent with the national picture.

Studies conducted by the British Trust for Ornithology (BTO) in the early 1990s compare distributions of six bird species with infaunal characteristics across 18 locations (Rehfisch *et al* 1991; Holloway *et al*., 1992) and established that distributions of Shelduck and Dunlin were statistically related to (transformed) data on total invertebrate biomass and total oligochaete biomass (the dominant taxon). Distribution of Teal was partially correlated with total and oligochaete biomass and *Macoma balthica*. However no such link could be established to account for spatial distributions (or year on year variation in numbers) for Pintail, Grey Plover, Curlew or Redshank.

The BTO carried out a (level 1) review of species trends in SPAs over the 5, 10 and 25 year time periods up to 2000 using data collected as part of the Wetland Bird Survey (WeBS). Armitage *et al* (2002) reviewed the impact of EA permissions and activities on bird populations in SPAs. 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 were 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 10 Evaluated Species in the Mersey Estuary: Great Crested Grebe, **Shelduck,** Wigeon, **Teal, Pintail**, Grey Plover, **Dunlin**, Black-tailed Godwit, Curlew, and **Redshank**[7].

Table 4 lists the species, for which alerts were initially triggered. In total there were 3 high alerts and 1 medium alert for species throughout the SPA.

[7] Species for which a site qualifies under Article 4.1 of the EC Birds Directive (79/409/EEC) by supporting populations of international importance (usually >/= 1% of a species' international flyway population) are highlighted in bold.

**Table 4. Species for which alerts were triggered in the (level 1) review and the level and time span of the alert (from Armitage *et al.,* 2002)**

| Alert Level | Common name | Time span of Alert (years) |
|---|---|---|
| High | Great crested Grebe | 5, 10 |
| | **Pintail** | 5, 10, 25 |
| | Grey Plover | 5 |
| | | |
| Medium | Grey Plover | 10 |

As a result of the level 1 review, Armitage *et al*., (2002) identified the Mersey Estuary SPA, as requiring further investigation. The level 2 investigations reassessed trends in bird numbers (1974/5 – 2000/2001 - summarised in table 5). In total there were 4 high alerts and 4 medium alerts for species throughout the SPA.

**Table 5. Species for which alerts were triggered in the (level 2) review and the level and time span of the alert (from Armitage *et al.,* 2004)**

| Alert Level | Common name | Time span of Alert (years)[8] |
|---|---|---|
| High | Great crested Grebe | 5, 10 |
| | **Teal** | 10 |
| | **Pintail** | 5, 10, 25 |
| | Grey Plover | 5, 10 |
| | | |
| Medium | Great crested Grebe | Max |
| | **Shelduck** | 5,25 |
| | Wigeon | 5 |
| | **Teal** | 5 |

The most recent WeBS report (Maclean *et al*., 2004) has just been published on the BTO website (www//bto.org) and raises even more concern over bird populations in the Mersey. Of the 12 species evaluated (all those in table 2 with the exception of the Ringed Plover), Alerts have been triggered for eight species, including two that occur in internationally important numbers ( Shelduck and Pintail) and one Annex 1 species (Golden Plover) (table 6).

[8] Up to 25 years, or maximum available if less

**Table 6. Species for which alerts were triggered in the 2004 WeBS report and the level and time span of the alert (from Maclean *et al*., 2004)** n = since notification (1995)

| Alert Level | Common name | Time span of Alert (years) |
|---|---|---|
| High | Great crested Grebe | 5, 10, 25,n |
| | **Shelduck** | 25 |
| | Wigeon | 5, 10, n |
| | **Pintail** | 10, 25, n |
| | Grey Plover | 5, 10, n |
| | Black-tailed Godwit | 5 |
| | | |
| Medium | **Shelduck** | 5, 10, n |
| | **Pintail** | 5 |
| | Golden Plover | 5, 10, n |
| | Lapwing | 5, 10, 25 |

It appears that the number of species for which Alerts are issued is increasing since the first BTO WeBS report was published. The latest report states that there is much cause for concern over these declines, as many of these species have not declined in either England or Great Britain as a whole. To summarise findings of this report briefly:

Numbers of Great Crested Grebe increased from a winter average of 10-40 during the late 1970s and 1980s to peak at 120 birds in 1991/92. Since then, numbers have declined to less than 5 birds by 2003/04. The trend contrasts with both regional and national trends, which in general have shown an increase (figure 4) and the site no longer supports nationally important numbers of this species (Pollitt *et al*. 2003). This would suggest that local rather than larger-scale factors are influencing the numbers of Great Crested Grebe over-wintering at the Mersey Estuary SPA.

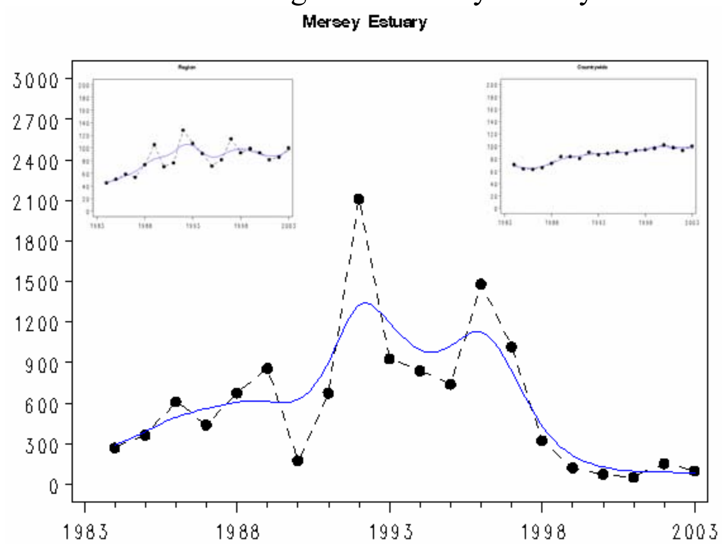



**Figure 4. Annual indices[9] and smoothed trends for numbers of Great Crested Grebe in the Mersey Estuary, North West Region (Region) and Great Britain (Countrywide) (from Maclean *et al*., 2004, reproduced with permission of BTO).**

9 Details of index value calculations in Leech *et al*., (2002)

Winter peaks in numbers of Shelduck have been successively smaller, from a winter average of around 10,000 birds recorded in 1980/81 to around 3,500 in 1990/91, 1995/96 and 1998/99. A recent 5-year decrease in numbers has triggered a Medium-Alert, although this may simply relate to normal fluctuations. The long-term decrease in numbers for Shelduck in the Mersey Estuary is in contrast to largely stable national and regional trends, and the proportion of both the regional and national Shelduck population hosted by this SPA has decreased. This may suggest that despite a redistribution of individuals into the Northwest region that occurred during the 1990s (Austin *et al.* 2003), birds have moved away from the Mersey SPA. For Wigeon wintering on the Mersey Estuary SPA decreases in numbers over 5- and 10-year periods, and since notification, have triggered High-Alerts. The short-term decline could be partly due to natural population fluctuations, as this pattern is broadly similar to regional and national trends, although changes are larger in magnitude and it appears likely that site-problems are at least partially responsible.

Wintering Pintail numbers have decreased from around 12,000 birds in 1984/85, to less than 300 birds in 2003/04 (figure 5 shows trend but uses an index not actual numbers). This downward trend is steeper than the downward trend shown nationally and there has been a marked decrease in the proportions of both the regional and national WeBS totals of this species over-wintering in the Mersey, which at one-time contained almost half the national WeBS total. The decline is therefore of considerable concern, and the authors recommend further investigation to determine the cause.

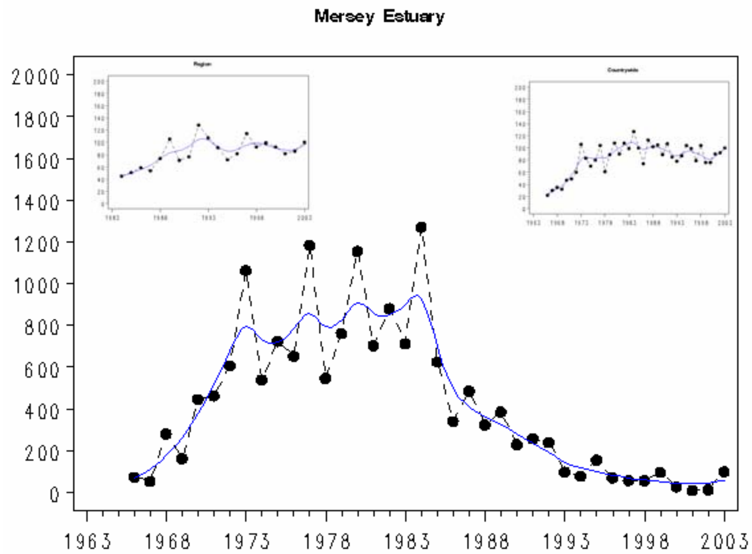



**Figure 5. Annual indices and smoothed trends for numbers of Pintail in the Mersey Estuary, North West Region (Region) and Great Britain (Countrywide). (from Maclean *et al.*, 2004, reproduced with permission of BTO).**

Coupled with the decline in numbers of Golden Plover over-wintering on the Mersey Estuary SPA, which generally mirrors regional and national trends, the high proportion of birds over-wintering on farmland and undergoing seasonal movements, make it difficult to assess whether adverse local factors contribute toward the recent decline.

There have been various fluctuations in numbers of Grey Plover on the Mersey SPA, although there is a general downward trend. Although the pattern is similar to regional and national trends for these birds, the decline has been more severe in the Mersey and an increasingly lower proportion of the regional and national WeBS totals have been overwintering on the estuary. Adverse local conditions are considered to be at least partially responsible. Since the mid-1990s, numbers of Lapwing have decreased, a trend similar but more severe than the regional and national trends. Because a high proportion of birds over-winter on farmland and undergo seasonal movements, it is difficult to assess whether the recent decline is due to adverse local affects. Recent decrease on areas covered by WeBS, could in part be related to a spate of milder winters with a greater proportion of the population wintering inland.

For Black-tailed Godwit, there was a remarkable increase in numbers in the Estuary during the early period covered by WeBS Alerts, although the population has declined significantly since the late-1990s. Elsewhere, both regional and national numbers of Black-tailed Godwit have continued to rise, which suggests that the decline in the Mersey could be due to part of the local population moving away to elsewhere in the region. Given the long-term increases on the site, the decline is thought to be of little immediate concern.

Thus, the decline in numbers of several important bird populations is considered to be partially due to adverse local conditions. Maclean *et al*., (2004) note that although much has been done in recent years to improve the water quality of the Mersey, pollution is still considered a major problem. The site is also threatened by building developments, disturbance, erosion and *Spartina* encroachment.

Armitage *et al.,* (2004) listed possible factors in the decline of these bird populations and also noted that poor water quality is one likely candidate (table 7), either through direct pollution or by altering the biotic environment. A second factor, also related to EA consents, is changes in waste water treatment from the implementation of the UWWTD. Paradoxically, improvements in water quality, notably reductions in organic nutrients, could have negative impacts on bird populations by reducing food abundance and availability.

**Table 7. Factors that may be related to the decline of bird populations in the Mersey Estuary SPA. (**from Armitage *et al.,*, 2004**)**

| Factor | Factors related to EA consents |
|---|---|
| Use of adjacent sites | |
| Saltmarsh accretion | |
| *Spartina* growth | |
| Saltmarsh loss / other erosion | |
| Sediment changes | |
| Dredging | |
| **Effluents / pollution / poor water quality** | √ |
| **Changes to waste water treatment [1]** | √ |
| Other human disturbance | |

[1] wildfowl may be affected by the reduction of directly edible matter from discharges and waders and some wildfowl may also be affected by reduced invertebrate food supplies

Box modelling carried out by Burton *et al*.,(2002) indicated that after BOD fell on the Mersey Estuary following improved treatment to discharges, the numbers of 10, out of 17, species declined (and only one increased). This study reviewed the importance of waste water discharges in providing food for waterbirds and identified species most likely to be at risk from changes to these discharges, which included Shelduck, Wigeon, Teal, Pintail, Grey Plover, Lapwing, Dunlin, Black-tailed Godwit, Curlew and Redshank.

Further investigations sought to establish whether, for individual species, the scale of change in their numbers following improvements to waste water treatment was related to the scale of change in BOD concentration for each site. No significant relationships were found for any species, either using site indices or when taking into account regional change (so as to account for factors not operating at the site-level). Although correlative analyses used in this study could not prove a causal link between waterbird numbers and waste water discharges, the analyses indicated that a significantly greater proportion of species declined following improvements to waste water discharges on sites with the greatest decreases in BOD concentration (Burton *et al.,* 2003 – ENNR 586). The authors recommended specifically designed research programmes within sites, and named the Mersey as one of three possible sites for these studies.

Clearly, bird counts can be variable for a host of reasons not necessarily connected with water quality condition of the site (habitat disturbance, climate, food availability). Attributing causes to changing bird numbers is therefore not possible without detailed study, though a broad-brush qualitative picture of the interactions between bird populations and their environment (including diet) is beginning to emerge. There would seem a strong argument for more quantitative assessments of links between infaunal communities and sediment quality together with bioaccumulation/biomarker studies on representative samples (prey species and birds) from the SPA to assist in appropriate assessments of the Mersey SPA (as with most other European Marine Sites). EN is currently engaged in a project to assess direct toxicity to birds through ingestion of prey (M. Coyle, *pers comm*.)

# 6. TRENDS IN WATER AND SEDIMENT QUALITY

## 6.1 Toxic contaminants

### 6.1.1 Metals

*Water*

Inputs from chemical industries focused much interest on metal contamination in the site in earlier years. Data from the 1970s and 1980s showed that metal concentrations were elevated, and contributed to adverse effects in biota. Chemical plants, numerous light industries and the WwTWs were all considered likely sources.

The Environment Agency have supplied summary statistics for water quality determinands in tidal waters of the Mersey Estuary over the period 2000-2004. The sites sampled are indicated in figure 6. NMMP sites in the region are also shown.

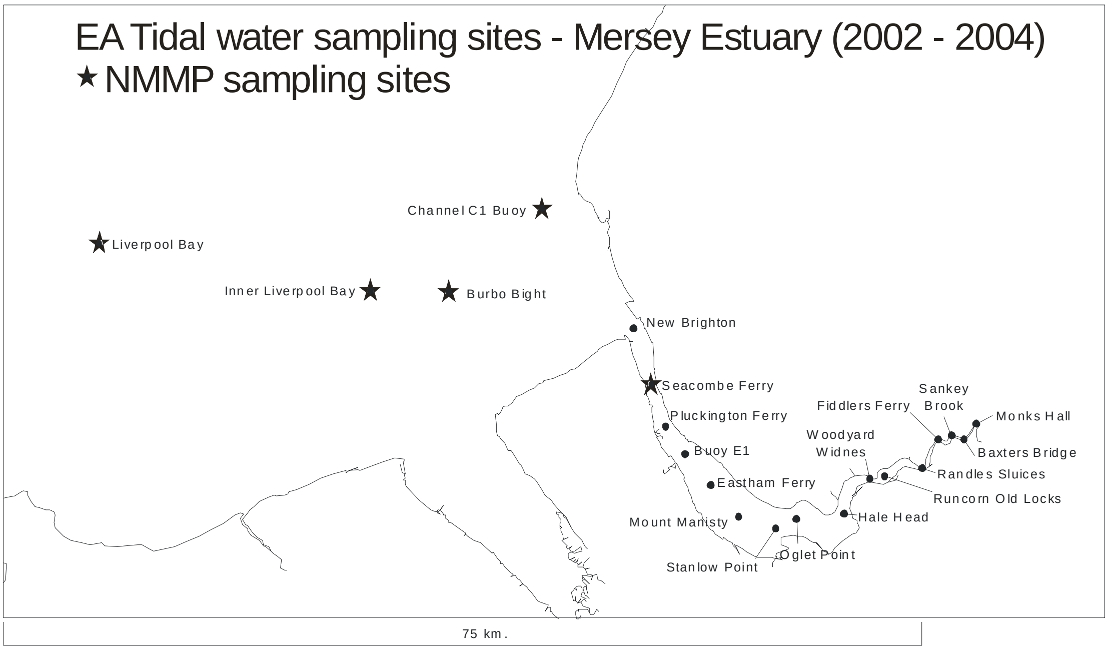



**Figure 6. Tidal waters sampling sites for which summary statistics on water quality (2000-2004) were provided by EA.** Note; Pluckington Ferry is sometimes referred to as Pluckington Buoy.

Results are discussed here on a metal by metal basis, based on EA statistics for estuarine water (2002-2004). As no data for freshwater are supplied we have used upper estuary (low salinity) tidal wters as a proxy for inputs from the River Mersey. It should be noted that freshwater EQS values are not strictly relevant but are included as guidelines only.

Arsenic

The EQS for As in fresh waters is 50µg $l^{-1}$ (AD). The upper tidal section of the Mersey (above Fiddlers Ferry) indicate some enrichment with As (up to 10µg $l^{-1}$)

compared with background values for As in rivers (1-2µg $l^{-1}$), though, clearly, inputs from the river Mersey are unlikely to cause EQS excedence in the Estuary/SPA.

The pattern of dissolved As in tidal waters of the Mersey are plotted in figure 7. Averages were above background and increase consistently upstream but were invariably below the EQS for tidal water (25 µg $l^{-1}$ AD). Highest concentrations were those between Widnes and Fiddlers Ferry, implying inputs here. For the sites monitored dissolved As appears to pose little acute threat (risk of EQS failure low), though contributions to chronic effects cannot be dismissed.

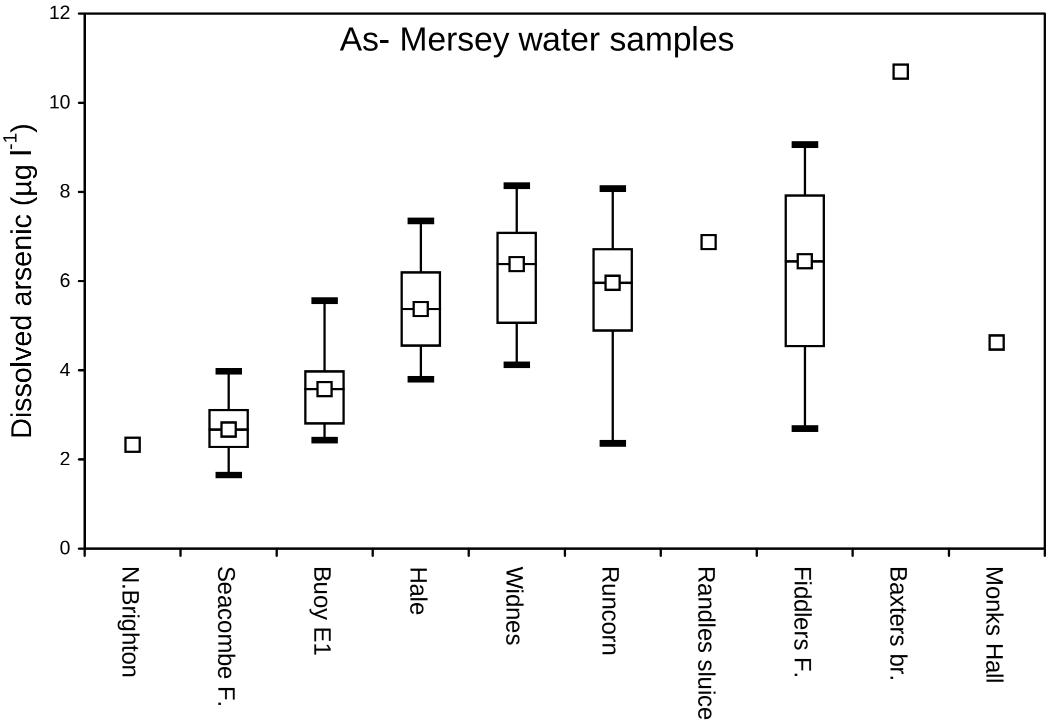



**Figure 7. Concentrations of dissolved As (µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, 25$^{th}$ and 75$^{th}$ percentiles).**

Cadmium

The EQS for Cd in fresh waters is 5µg $l^{-1}$ ('total' Cd). In the upper tidal section of the Mersey (above Fiddlers Ferry) all values for dissolved Cd were below detection (usually <0.1 µg $l^{-1}$) and the river is unlikely to be a cause of excedence in the Estuary, even though the power station at Fiddlers Ferry is identified as a priority outfall for assessment (includes Cd).

The pattern of dissolved Cd in tidal waters of the Mersey are plotted in figure 8. Elevated concentrations were occasionally measured at Buoy E1 and Widnes. However, averages were invariably below the EQS for tidal water (2.5 µg $l^{-1}$ dissolved) and a significant proportion of tidal water values were below DL. For the sites monitored dissolved Cd appears to pose little acute threat despite evidence of some inputs to the estuary: the overall risk of EQS failure is considered low.

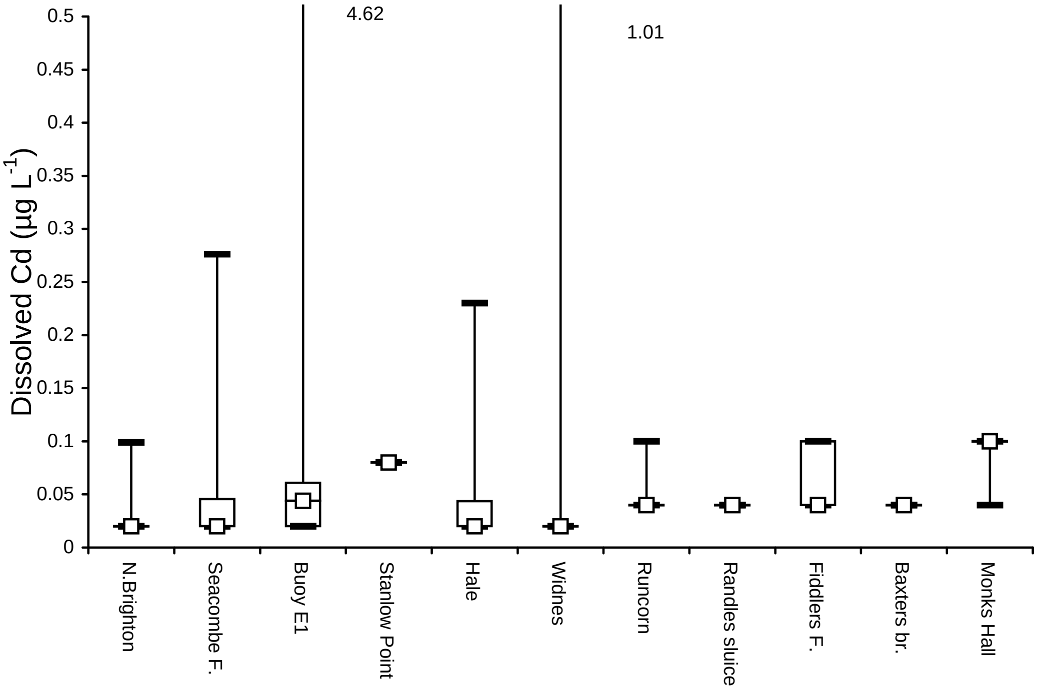



**Figure 8. Concentrations of dissolved Cd (µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, $25^{th}$ and $75^{th}$ percentiles).**

Chromium.

The EQS for Cr in fresh waters suitable for salmonids ranges between 5 and 50µg $l^{-1}$ depending on hardness. Highest median concentrations in tidal waters tend to be those at the upstream limits (figure 9) implying some inputs from the River Mersey. Nevertheless, all the points examined above would comply with even the lowest standard.

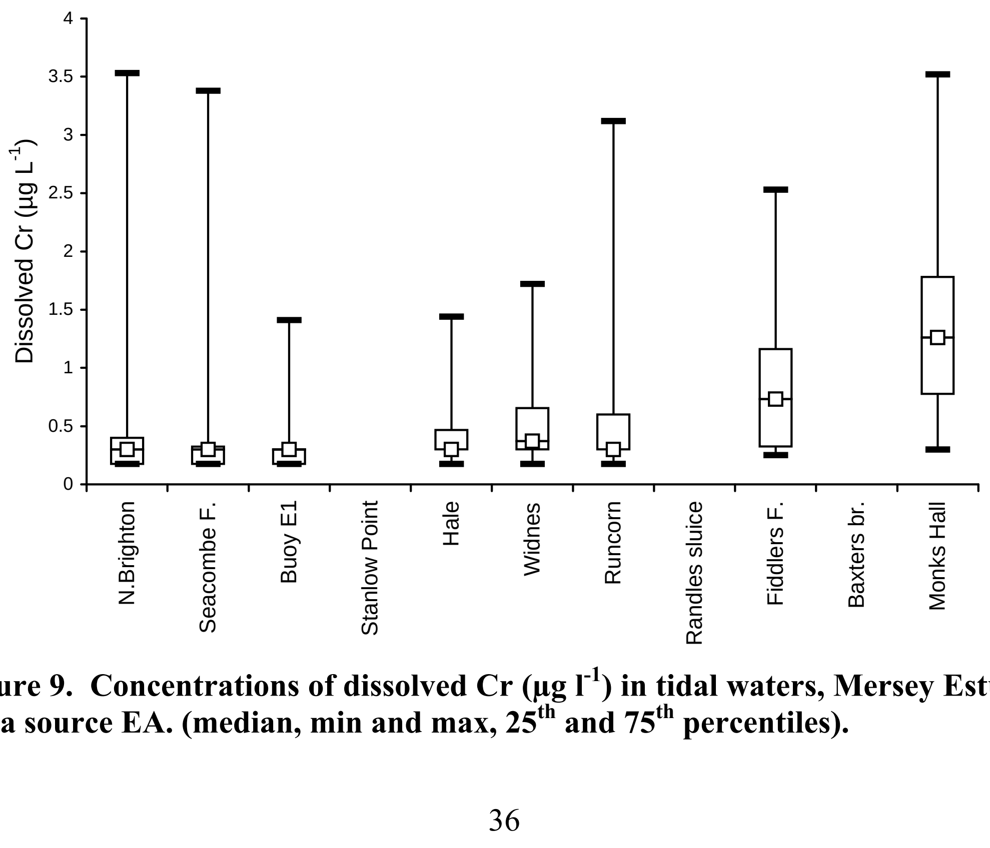



**Figure 9. Concentrations of dissolved Cr (µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, $25^{th}$ and $75^{th}$ percentiles).**

The pattern of Cr distribution in estuarine waters (figure 9) indicates that median values for all sites are lower than the EQS (15 µg $l^{-1}$) by more than an order of magnitude (with a significant proportion of data for tidal waters below DL). There are occasional elevated levels of dissolved Cr at several sites however suggesting perhaps multiple sources including major WwTWs. Croda colloids at Widnes is also identified by EA as a priority outfall for assessment (includes Cr).

At estuarine sites, including the SPA, there is little evidence to suggest there is a risk of failure of the EQS or that Cr concentrations in tidal waters would be acutely toxic; however, some forms of Cr cause deleterious effects in invertebrates and fish at concentrations close to the EQS for saline waters. Cr is also considered genotoxic. More comprehensive data are needed to assess possible sources and sublethal impact on biota.

Copper

The EQS for Cu in freshwater is in the range 1 - 28 µg $l^{-1}$ depending on hardness; that for saline waters is 5 µg $l^{-1}$. At the majority of sampling sites ~2 µg $l^{-1}$ dissolved Cu appears to be typical for the estuary (Figure 10). Elevated levels above the EQS benchmark are occasionally recorded (NB 14 µg $l^{-1}$ at New Brighton). The Agency's assessment suggests medium risk of compliance failure at the majority of tidal waters monitoring sites, though this appears to represent a pessimistic scenario.

More comprehensive discharge data and evaluation are needed to assess possible influences on estuarine water quality and sublethal impact on biota, since Cu is potentially one of the most toxicologically significant metals.

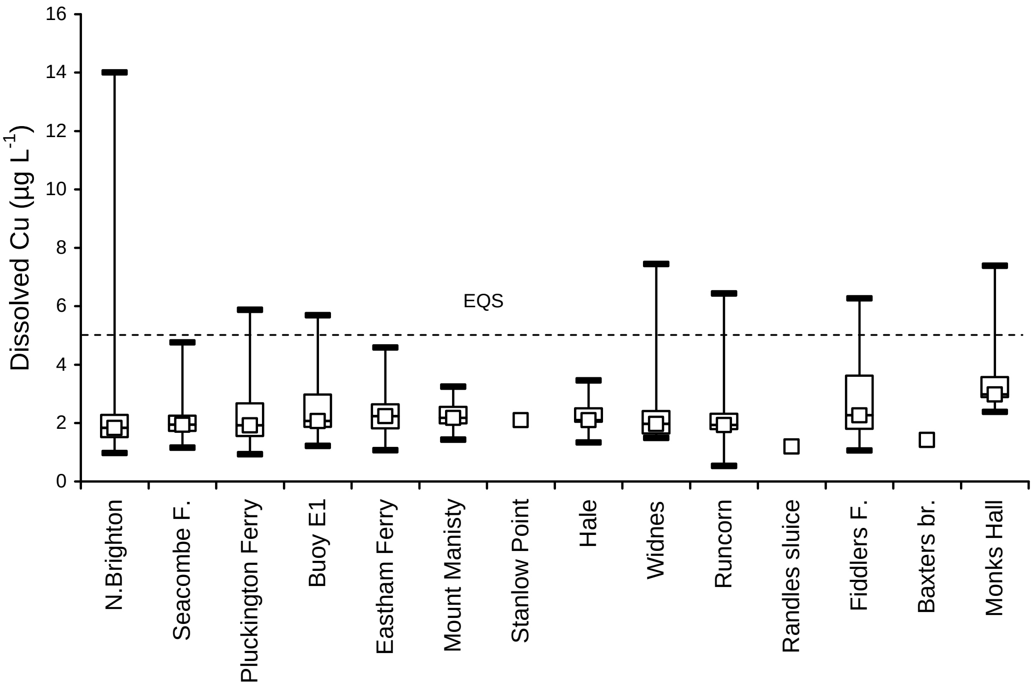



**Figure 10. Concentrations of dissolved Cu (µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, $25^{th}$ and $75^{th}$ percentiles).**

Iron

The EQS for dissolved Fe in fresh and seawater is 1000µg $l^{-1}$.

Because of the relatively small number of data for this parameter, the pattern of dissolved Fe concentrations in tidal waters of the Mersey is difficult to discern (Figure 11). Median values for all sites are well below the EQS (1000 µg $l^{-1}$) and for saline samples are often below detection limits (hence the Agency's assessment of Low Risk of non-compliance). Occasional elevated levels are recorded (NB the single sample Seacombe Ferry). The source of this Fe is not known (no values for Fe in discharges are available). However, it is unlikely that Fe would represent a threat to marine biota at the site.

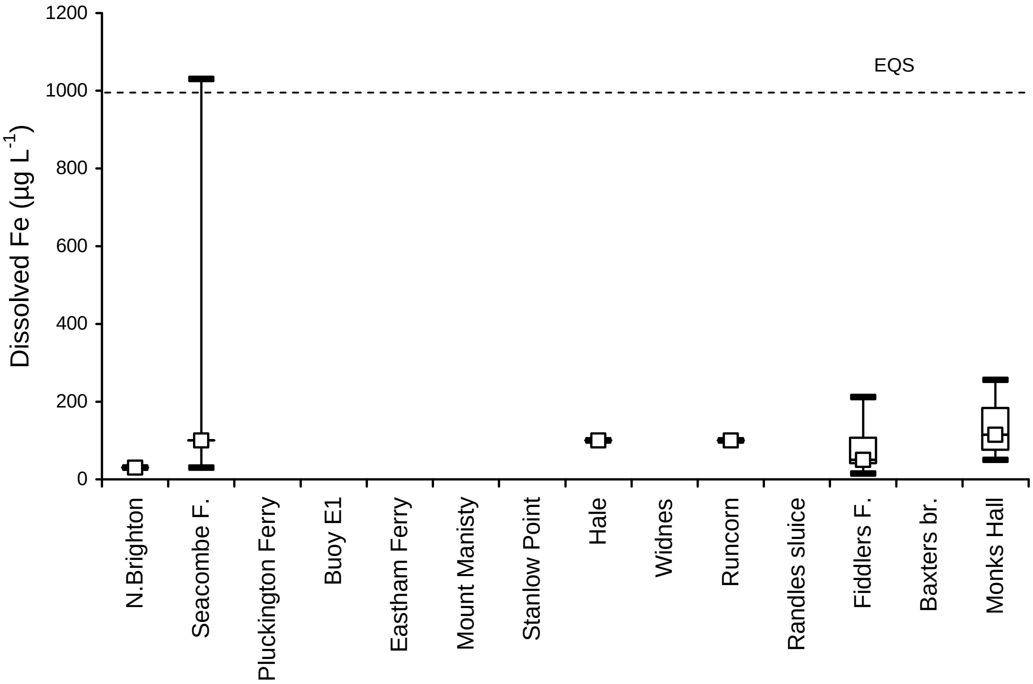



**Figure 11. Concentrations of dissolved Fe (µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, 25$^{th}$ and 75$^{th}$ percentiles).**

Nickel

The distribution of dissolved Ni in tidal waters is dominated by the freshwater loading of the River Mersey (figure 12) with a linear gradient along the estuary. There appears to be little additional anthropogenic contribution to dissolved Ni levels at sites further downstream. Medians do not exceed 6 µg dissolved Ni $l^{-1}$ and are below the EQS both for freshwater (which ranges between 50 and 200 µg $l^{-1}$ depending on hardness) and for saline water (30 µg $l^{-1}$). Maximum values are also well within EQS. The Agency's characterization of risk of non-compliance is Low. Some of the data involve detection limit-derived values.

On this evidence it is unlikely that Ni would represent a threat to marine biota at the site.

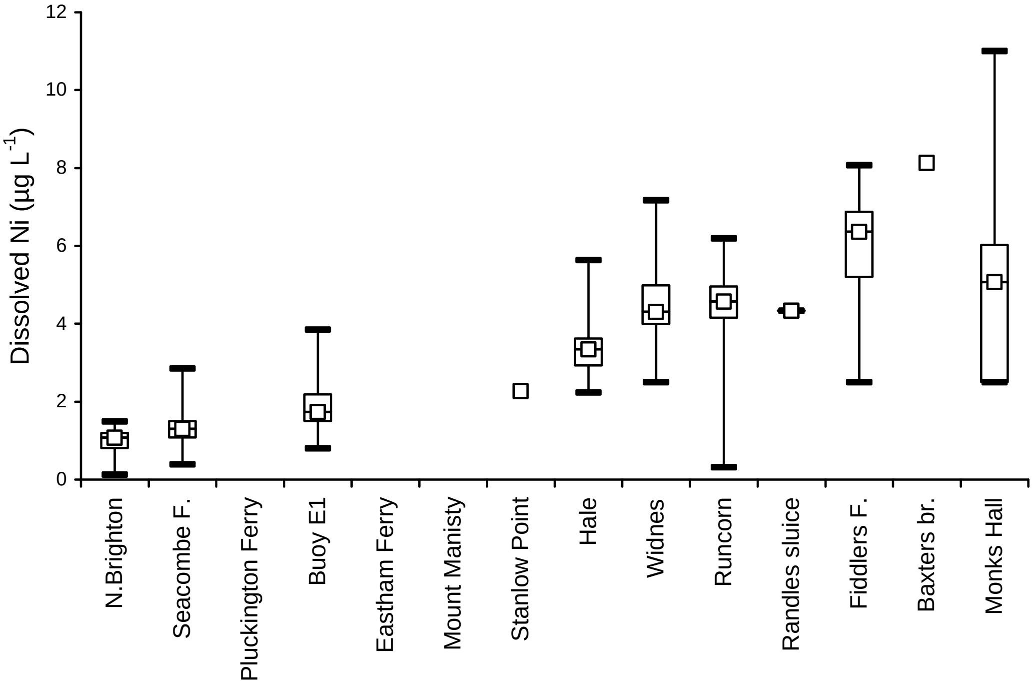



**Figure 12. Concentrations of dissolved Ni (µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, 25th and 75th percentiles).**

Lead

The distribution of dissolved Pb in tidal waters appears to be dominated largely by the freshwater loading of the River Mersey (figure 13) with median values decreasing in a seaward direction along the estuary. Medians do not exceed ~1µg $l^{-1}$ (below the lowest EQS for dissolved Pb which ranges between 4 and 20 µg $l^{-1}$ in freshwater, depending on hardness; and 25 µg $l^{-1}$ in saline waters). There appears to be little consistent anthropogenic contribution in the estuary itself: though occasional ‘outliers’ are observed, they too are within EQS. The Agency’s characterization of risk of non-compliance is ‘low’.

Organic lead analyses (Σ di- and tri-alkyl Pb) conducted at some of these locations are largely (88% of values) below detection limits of ~1 µg $l^{-1}$ (Figure 14) and on this evidence it is unlikely that organolead species would represent a threat to marine biota at the site (though water samples from within the SPA have not been sampled often). Lead levels were a cause for concern following extensive mortality amongst over-wintering estuarine birds during 1979 - 1982. This was attributed to the food-chain magnification and toxicity of tri-alkyl lead compounds, released into the estuary via the Manchester Ship Canal (Wilson *et al.*, 1986). Results of MBA bioaccumulation surveys have indicated that total Pb levels in biota dropped significantly following confirmation and action on the cause of the problem and from ~ 1987 there has been 'steady state' at reduced levels (Langston, 1988). The decline in the use of organolead compounds in petrol, combined with controls on discharges, appears to have removed the threat to wildlife in the vicinity of the SPA.

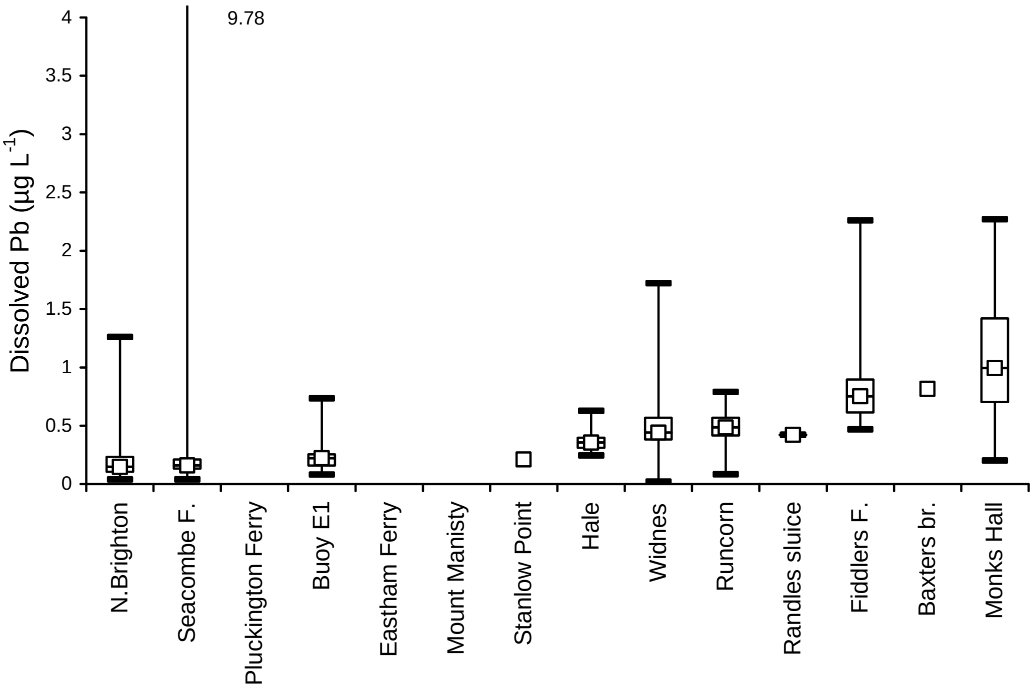



**Figure 13. Concentrations of dissolved Pb (µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, $25^{th}$ and $75^{th}$ percentiles).**

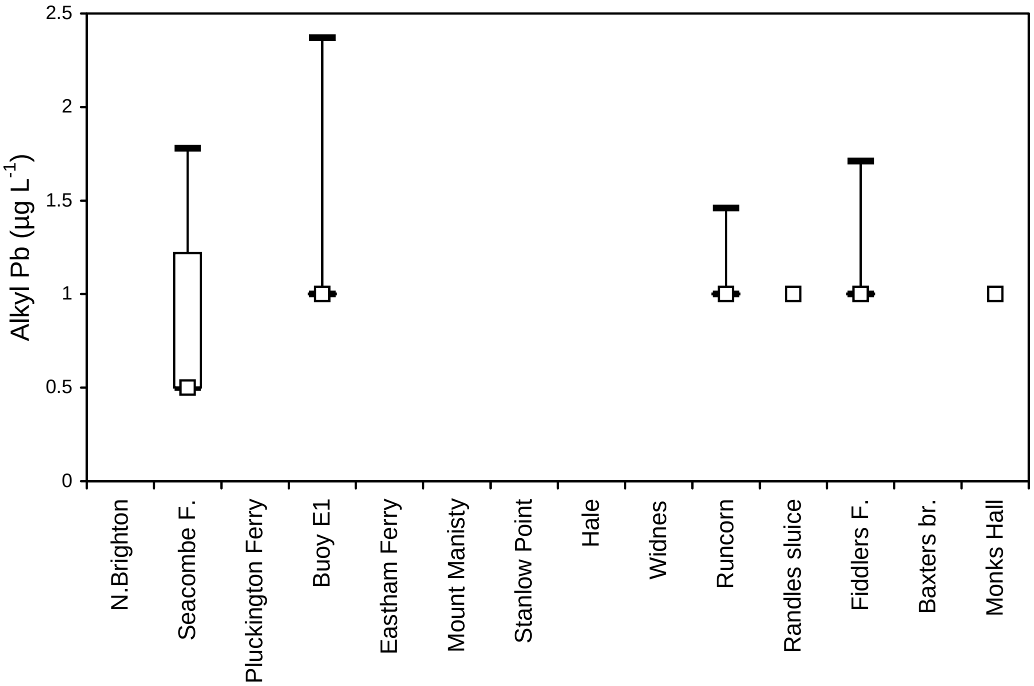



**Figure 14. Concentrations of organolead (Σ di- and tri-alkyl Pb; µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, $25^{th}$ and $75^{th}$ percentiles).**

Zinc

The distribution of dissolved Zn in tidal waters, like several other metals, is dominated largely by the freshwater loading of the River Mersey (Figure 15). Below Widnes, median values decrease from a peak of around 21µg $l^{-1}$ seawards along the estuary towards the mouth. Based on an EQS for saline waters of 40µg $l^{-1}$ (AD) all sites would appear to be compliant, though with a safety factor of only ~ two-fold, with maximum values occasionally approaching the EQS. Correspondingly, the Agency's characterization of risk of non-compliance is 'medium'. It is unlikely that Zn would represent an acute threat to most marine biota at the site. However values at some sites are elevated, and would not meet an earlier proposed[10] revised standard, indicating sources in this region, and a potential threat to sensitive species. It may be useful to look in further detail at possible sources of Zn.

The EQS (based on total Zn) in fresh waters (suitable for salmonid fish), ranges from 8 to 120 µg $l^{-1}$ depending on hardness. Only four 'total' Zn values could be found in the data supplied - all in the upper section of the tideway. Values ranged from 50-400µg $l^{-1}$ implying that a substantial part of the riverine input may be particulate and perhaps re-inforcing the need for further scrutiny of Zn sources (including sediments). Other possible sources of Zn include boating and shipping. Zn pyrrithione is used as booster biocide to replace TBT in antifouling paints. The use of sacrificial anodes on boats and structures, to reduce corrosion, can also be expected to lead to a measurable increase in concentrations of Zn in marinas, docks and adjacent estuarine waters.

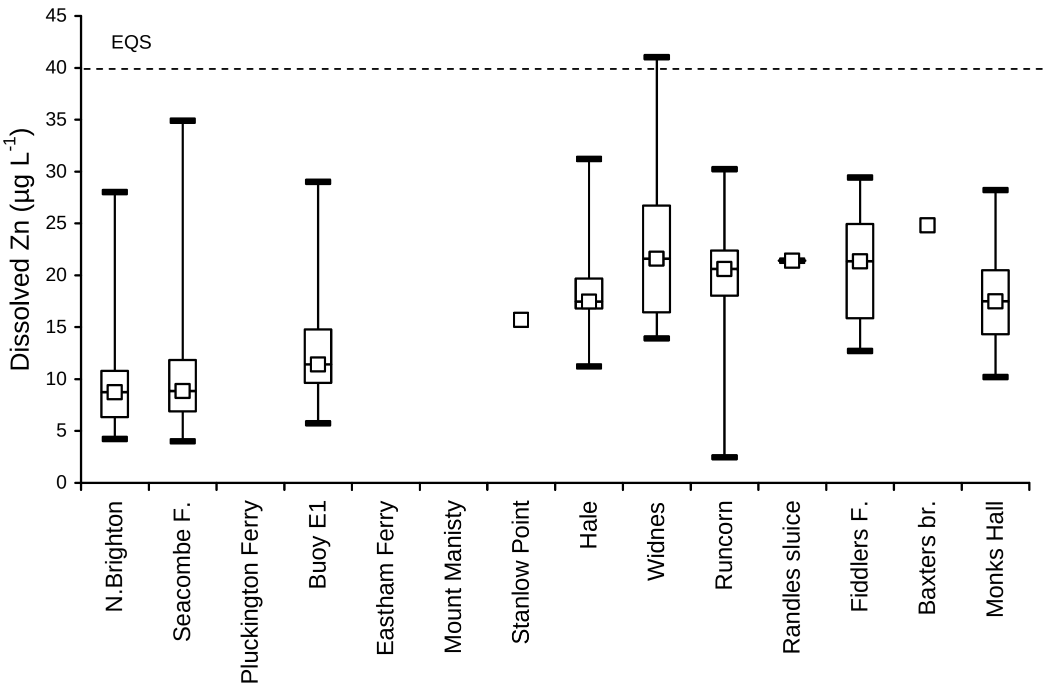



**Figure 15. Concentrations of dissolved Zn (µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, $25^{th}$ and $75^{th}$ percentiles).**

[10] Following a review of 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.

Mercury

The pattern of dissolved Hg in estuarine water along the tideway is plotted in figure 16. Median values are invariably below the EQS (0.3 µg $l^{-1}$) by a considerable margin (hence a low risk of failure categorization by the EA). Median values tend to be highest upstream of Widnes and occasional 'outliers' in this part of the tideway may exceed the benchmark. The outfall at Fiddlers Ferry power station has been prioritized for future assessment by EA (includes Hg)

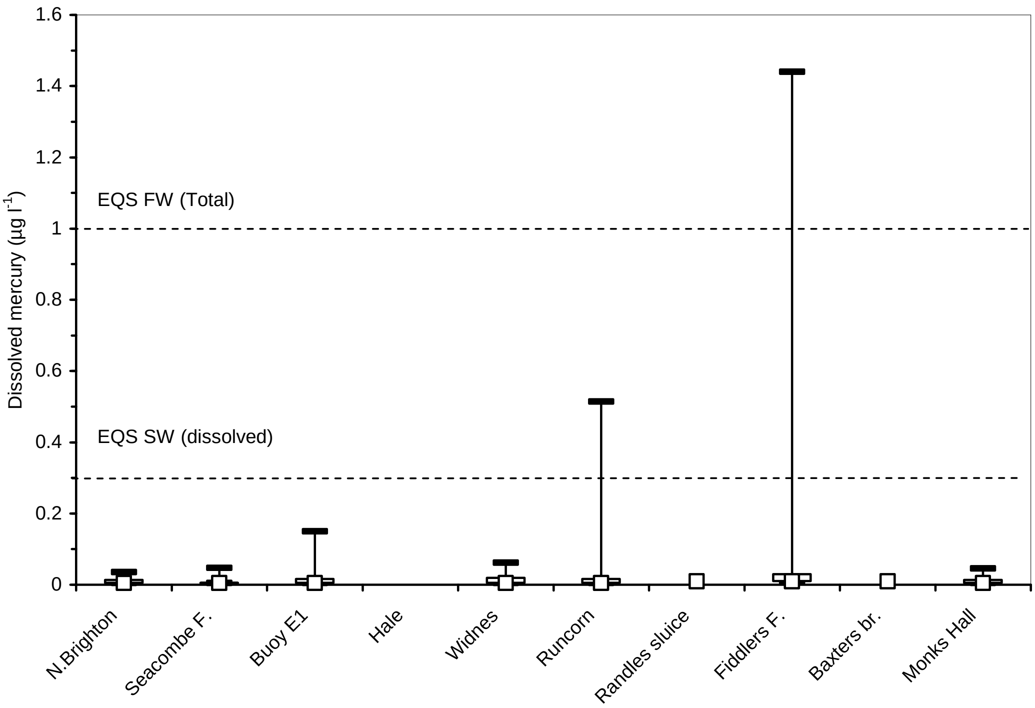



**Figure 16. Concentrations of dissolved Hg (µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, 25th and 75th percentiles).**

For the sites monitored, dissolved Hg is unlikely to pose an acute threat. Hg however has a strong affinity for particulate matter and total Hg concentrations in the water column highlight this affinity (figure 17). At a number of upstream sites (mainly above Fiddlers Ferry) the freshwater EQS of 1 µg $l^{-1}$, as 'total' Hg, is at high risk of failure. This risk declines to 'medium' at Hale and 'low' further seaward according to the EAs assessment, though the freshwater EQS would presumably not be applied here.

Sediment data shown later confirm there are hotspots for this metal in the particulate phase which could be accumulated by deposit feeders and infauna, representing a pathway to waders which feed upon them. As with Pb there have been substantial declines in body burdens in benthic organisms, particularly in the early 1980s following implementation of control measures (Langston, 1988), though surveys in the late 1990s suggest levels may be approaching quasi-steady state, (Pope *et al.*, 1998). Bioaccumulation data is discussed in more detail in section 7.1.

In view of the toxicological and regulatory importance of Hg, further characterization of sources and distributions across the SPA would be useful, together with updated surveys of bioaccumulation and risks to birds.

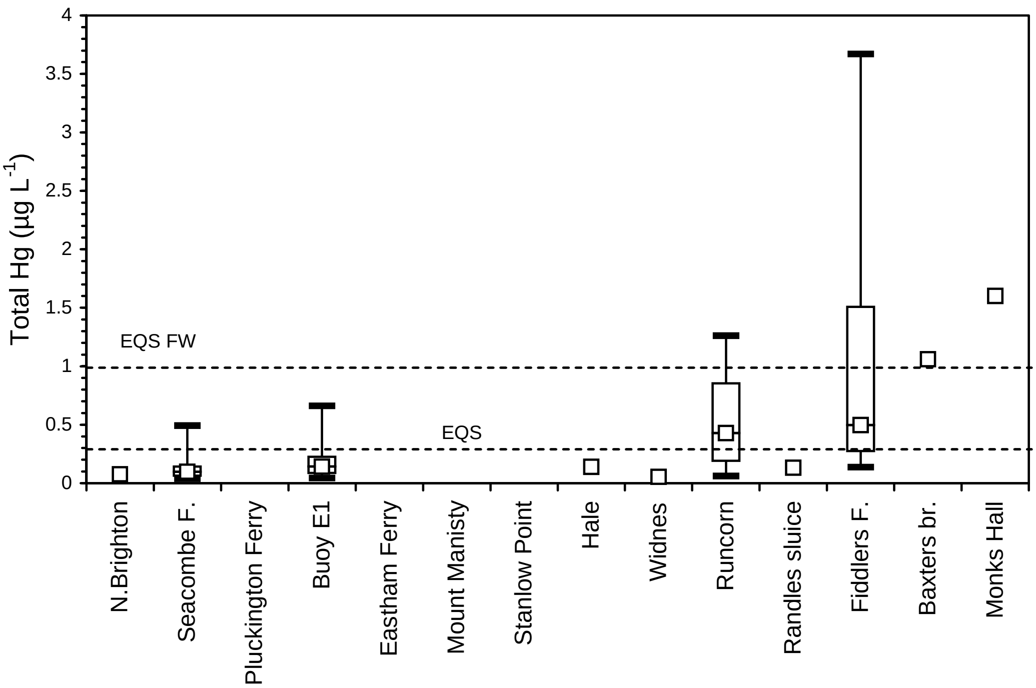



**Figure 17. Concentrations of total Hg (µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, $25^{th}$ and $75^{th}$ percentiles).**

Boron

Boron is used in fire retardants, as a component of enamels, and in the photographic, cosmetic, leather, paint, textile and wood-processing industries. Borax, a major boron compound, is used as a cleaning compound and may occur in domestic and/or industrial effluents. Because of its wide variety of industrial uses, there are many potential pathways for entering the aquatic environment.

The EQS for B in fresh waters is 2000µg $l^{-1}$ (annual average). The coastal and estuarine EQS for boron is 7000 µg $l^{-1}$ (derived by applying an arbitrary factor of 10 to the lowest, rather limited toxicity data). This equates to a level approximating to normal ambient concentrations of boron in seawater. The overall pattern for Boron along the Mersey therefore reflects the mixing of Boron-rich seawater with a much lower level of B towards the freshwater end member (figure 18). At the seaward end of the estuary the risk of excedence is considered low but may reach medium or high risk status in the mid-upper estuary (Buoy E1 and Runcorn respectively). It is considered unlikely that EQS would be exceeded further upstream although isolated values may be higher than the FW EQS. Without further information on discharges it is not possible to comment on sources to the upper- and mid estuary. At Runcorn, high values are not unexpected given the presence of partially saline waters here. At Monks Hall however the presence of the occasional high value does not coincide with high salinity and may reflect riverine discharge. More details for the mid estuarine sites would be welcome to evaluate impact on the SPA.

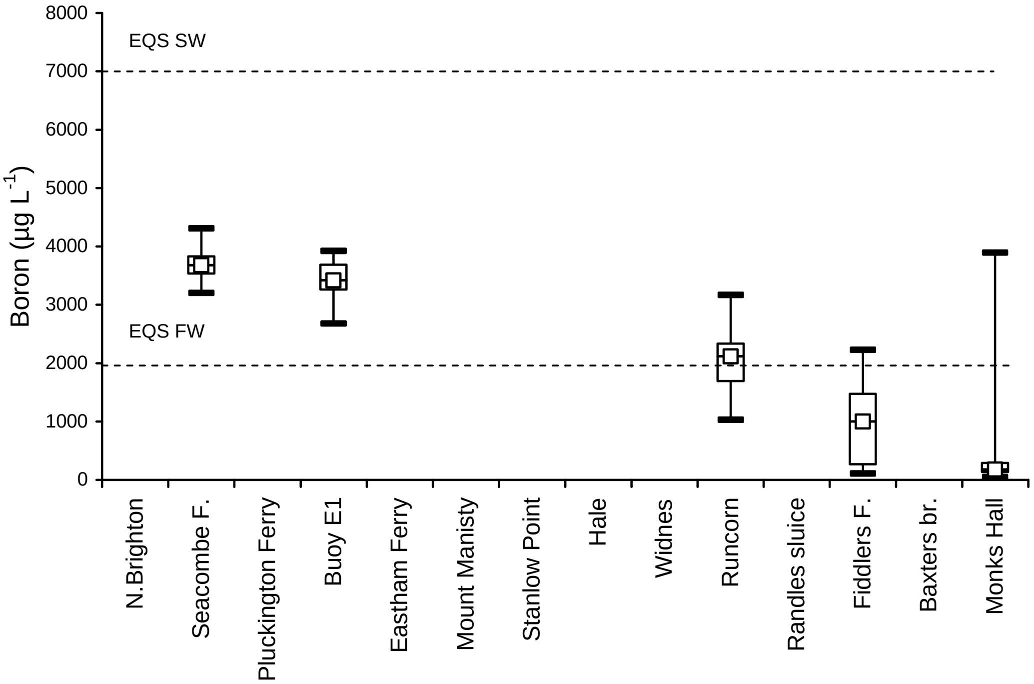



**Figure 18. Concentrations of total B (µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, 25$^{th}$ and 75$^{th}$ percentiles).**

*Sediments*

Particulate metals form an important part of the loading discharged to estuaries. Scavenging of dissolved metals by settling particles also occurs, so that the sediments of the estuary provide an integrated record of contamination history. Because of their larger surface area and greater density of organic and oxyhydroxide binding sites, contamination loadings will be highest in fine fractions and lowest on coarser substrates.

There are various sediment data sets for the Mersey Estuary, all utilising slightly different techniques to compensate for the effects of granulometry (discussed in section 3 and in EA ROC discussion paper on sediments). Provided some sort of normalization procedure is employed however, the trends displayed by each data set are probably similar. For the appraisal of spatial and temporal distributions we shall focus here on the MBA data set (1980-1997) which relates to analysis of inter-tidal surface sediment fines (<100µm, nitric acid digest). The reason for this choice is that contemporary information on bioaccumulation (in invertebrates and macroalgae) is also available for the same sites (section 7.1) - an important consideration given that the emphasis of the current review is on biological issues, particularly those such as bioaccumulation which could affect waders

The distributional profiles for total metals in surface sediments collected in 1997 were generally similar to those seen in earlier MBA surveys, with highest levels in the upper/middle estuary (Figure 19). Only Cd, Cu and Zn concentrations showed a statistically significant decrease seawards through the estuary. A notable ‘outlier’ was the site at Hale, where total sediment concentrations of all metals were consistently low. This may be partly explained by the fact that the sediments at that site appear to be in a state of erosion, rather than deposition and are characterised by a low organic content. The latter also applies to sediments at Blundellsands on the Formby shoreline. The results of correlation analysis confirm that there is a considerable degree of similarity between metal profiles (60 significant correlations out of a total of 78 possible comparisons). Furthermore, the levels of all metals were significantly correlated to the sediment organic content.

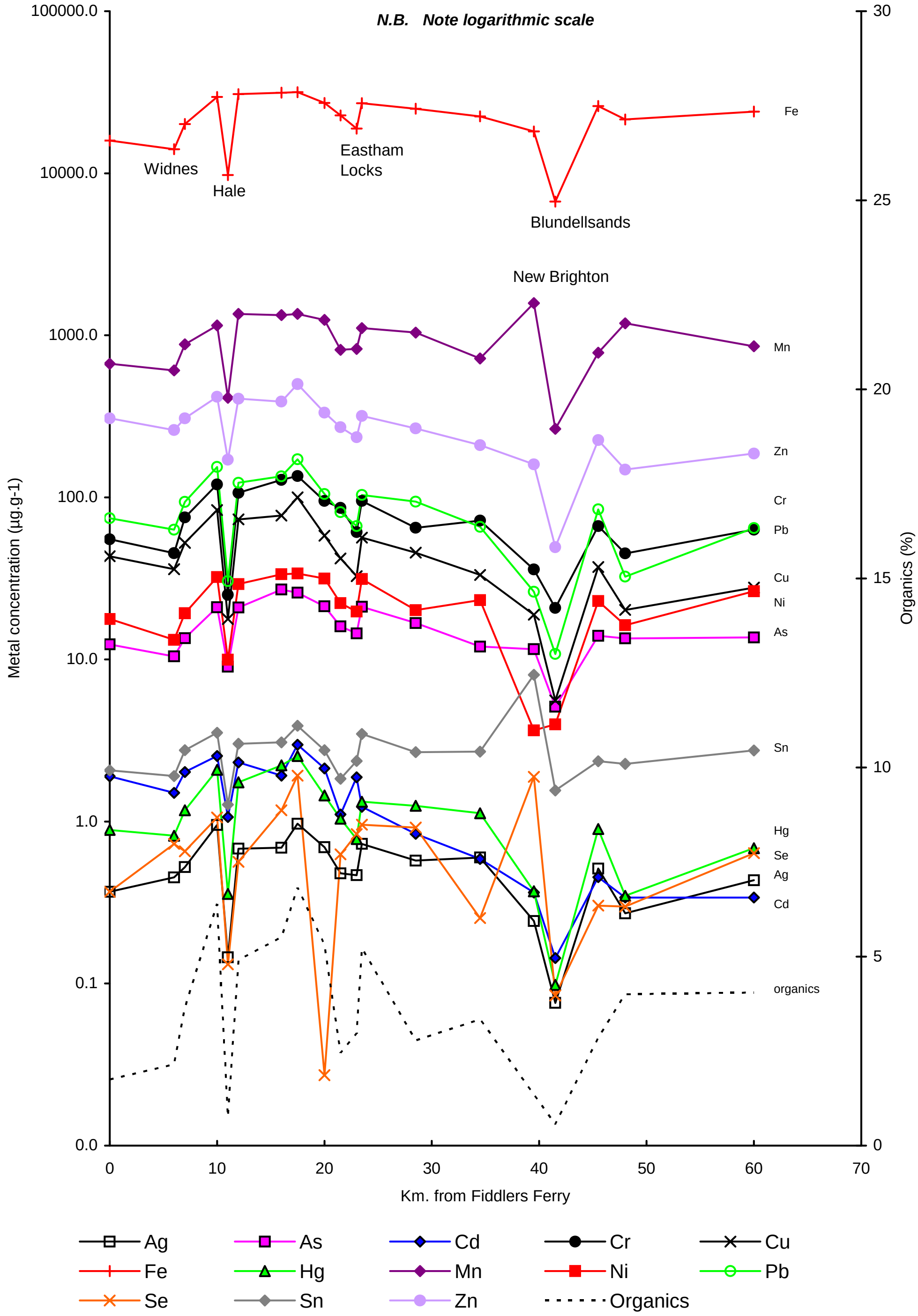



**Figure 19. Mersey Estuary sediments, 1997 (MBA data- surface sediments, <100µm, nitric acid digest). Note logarithmic scales.**

Due to the wide range of concentrations encountered for the different elements a logarithmic scale has been used in figure 19 in order to compress all data onto one diagram for comparative purposes. Unfortunately this tends to flatten the profiles, whose gradients are better interpreted from individual plots (Pope *et al*., 1998). Nevertheless, the treatment of the data in this way illustrates the similarity of distribution patterns between metals, pointing to a common granulometric explanation for the 'fine detail' in metal profiles along the estuary.

Because of the high energy conditions in the estuary, contamination arising from discharges, once associated with fines, tends to be dispersed over a large area leading to the observed homogeneity. In essence, this results in a single population of fines throughout the estuary and the adjacent shores of Liverpool Bay (Rowlatt, 1988). The conclusion is that distributions reflect sediment characteristics and dynamics rather than proximity to discharges.

Such homogeneity makes it difficult to be precise about the origin of metals in sediments. Nevertheless, international agreements (e.g. OSPAR) require that concentrations and bioavailability of metals from anthropogenic sources be distinguished from those originating as a result of natural geological processes. The development of a such a methodology for distinguishing between anthropogenic and natural sources of metals entering the Irish Sea via the Mersey is described in Ridgway *et al*. 2003. Major urban and industrial development in the catchment causes easily recognised departures from the 'background' multi-element geochemical signature. Contributions to Mersey estuary surface sediments arising from human activity are very much in evidence for metals such as Cr, Zn (both >50%) together with As, Pb, Cd, Sn and Hg. Furthermore offshore sediments in Liverpool Bay appear to have comparable 'fingerprints' to those of the estuary, confirming widespread mixing of fines. The balance of evidence suggests, however, that there is some net transport of sediment landwards with a zone of increased winnowing in the inner estuary, close to the tidal limit. This is in keeping with the generally accepted view that the Mersey Estuary is an accretion zone for sediments (Ridgway *et al* 2003).

Related attempts to distinguish the effects of natural vs anthropogenic metal loadings on bioaccumulation in Mersey biota suggest that useful assessments can be made by selective sediment measurements that mimic the 'biologically available' fractions (if validated against appropriate bioindicators). Partial extraction of sediments, using chemical leachates of varying strength, indicate that a significant fraction of the metal loading in Mersey sediments may be labile and thus has potential for remobilisation and bioavailability (Langston, 1982, 1985; Ridgway *et al* 2003). This is particularly so for the anthropogenic/pollutant type elements described above (see also section 7.1). Measurement of 1M-HCl extractable sediment metals were generally the most useful surrogate for bioavailable metal levels.

Although it is rarely possible to apportion metal loadings in sediments to specific sources, one exception arises from a study of Pb isotope ratios from parts of the estuary near the Stanlow oil refinery and MSC; this establishes signatures which are characteristic of inputs from the petrochemical industry (Ridgway *et al* 2003).

*Sediment metals and quality guidelines*

With the possibility of biological effects in mind, data for metals in inter-tidal sediments from the Estuary are represented in map form, classifying sites according to interim sediment guideline criteria for each metal (figures 20A & B). Data used here are for the MBA survey in 1997 (Pope *et al*., 1998). Green bars denote sites where no harm to biota is predicted (below ISQG's / TELs), grey bars denote sites where effects cannot be excluded (between ISQG's/TELs and PEL's) and red bars represent sediment concentrations where harmful effects might be expected (above PEL's).

Chromium levels are moderate throughout the estuary and most values fall between the ISQG/TEL and PEL value (grey bars in figure 20A– biological effects cannot be excluded), though none exceed the PEL value where effects would be expected. Outside the mouth of the estuary and at Hale, where sediments have a low organic content, values fall below ISQG/TEL (effects not expected –green bars in figure 20A). The pattern for Ni, As Cu (figure 20A) and Cd (figure 20B) is very similar, though Cd levels drop most noticeably outside the estuary (reflecting low natural background for this predominantly anthropogenic metal).

Superimposed on this pattern concentrations of Pb and Zn at a number of sites within the mid- and upper sections of the estuary (and within the SPA) exceed PEL values (red bars in figure 20B). For all but the low-organic sample at Hale, Hg values within the estuary, and at Hightown at the mouth of the Alt, are above the PEL, and are at levels where effects might be expected (figure 20B).

It is stressed that these are guideline values only. Where sediments exceed the PEL this is generally by a relatively small margin (usually less than a factor of two), rather than by orders of magnitude. Effects due to these metals, would largely be chronic rather than acute. Furthermore, the data are eight years old and may not be representative of conditions now[11] (though most records suggest that recent changes have been relatively small compared to earlier reductions (see figure 23 and Astra Zeneca data, figure 24). Re-survey, using the same sites/techniques is needed to establish the current status and to re-evaluate temporal trends. This is seen as a particularly important issue in terms of meeting standstill provisions for sediments under the Dangerous Substances Directive, and attainment of Favourable Conservation status (Habitats Directive), and may partially drive the requirement to minimise further inputs via aqueous discharges.

The latest AZ data (2003-2004) suggest fewer PEL exceedences for Pb & Zn and fewer TEL exceedences for Cd and Cr, but perhaps slightly more TEL exceedences for Cu. There are still a significant number of Hg values > PEL (figure 21A, B). It is important to note, however, that these AZ data are 'total' sediment values, with perhaps significant proportions of >100µm (less contaminated?) particles; lower

[11] Later sediment data include Astra Zeneca's annual surveys, BGS, NMMP surveys. As these use different sampling techniques (depth, grain sizes etc) and analytical procedures, some variability between data sets is to be expected. At NMMP sites in the outer estuary (Seacombe and Buoy C1) classifications for sediments (<63µm) are comparable to MBA data i.e. most values between TELs and PELs apart from Hg (mainly >PEL). BGS data are for cores and include some higher values (usually at depth, presumably representing historic contamination); classifications are, however broadly similar to other data-sets

values might therefore to be expected from these ‘totals’ –particularly at sites where coarser particles predominate (an argument for the use of standardised particle sizes). Nevertheless comparisons with TELs and PELs give broadly similar classifications to MBA data.

Although these sediment classifications are guideline values, and do not themselves constitute direct evidence for effects, the results nevertheless indicate that sediments could be of significance for the biota of the SPA.

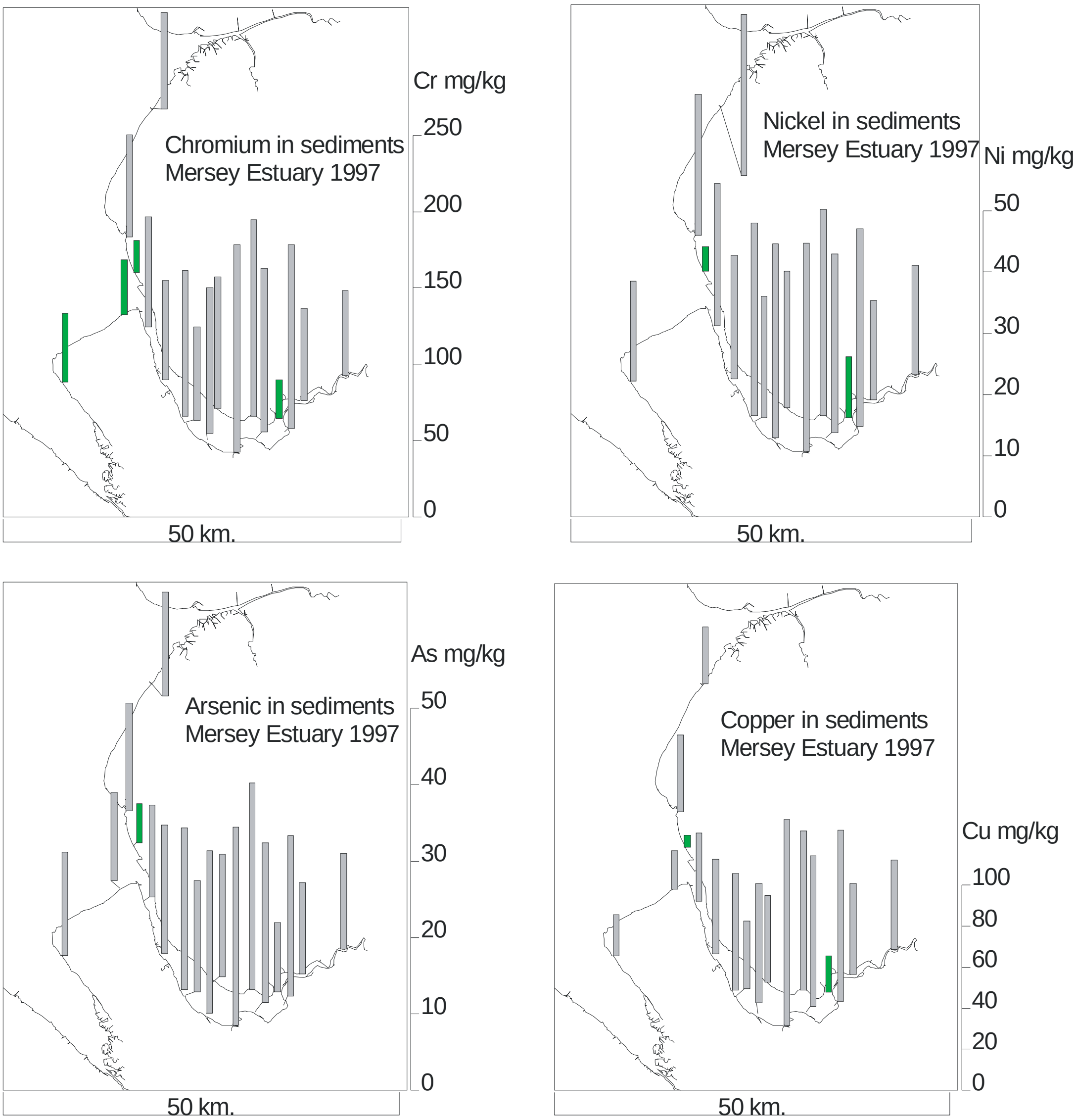



**Figure 20 (A). Chromium, Nickel, Arsenic and Copper in sediment (<100µm fraction). Classification of the Mersey Estuary SPA based on interim marine sediment quality guidelines/Threshold Effect Levels (ISQG/TEL) and probable effect levels (PEL’s) (from CCME 1999).** Red = effects expected; Grey = possible effects cannot be excluded; Green = no harm to the environment expected. (Data Source MBA). Note; PEL and TEL values are set in relation to ‘total (unsieved) sediment. See text for explanation.

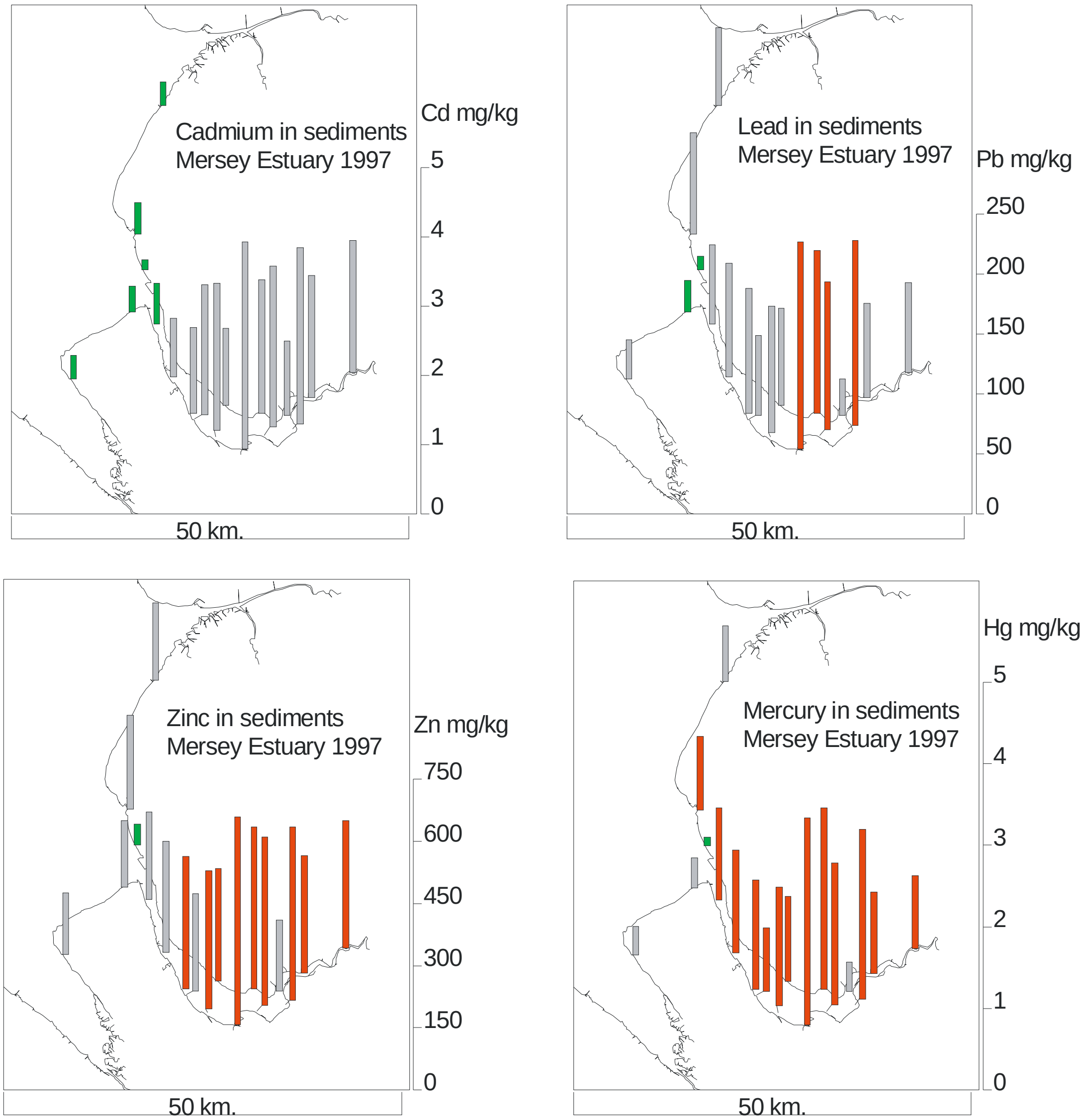



**Figure 20B. Cadmium, Lead, Zinc and Mercury in sediment (<100µm fraction). Classification of the Mersey Estuary SPA based on interim marine sediment quality guidelines/Threshold Effect Levels (ISQG/TEL) and probable effect levels (PEL's) (from CCME 1999).** Red = effects expected; Grey = possible effects cannot be excluded; Green = no harm to the environment expected. (Data Source MBA). Note; PEL and TEL values are set in relation to 'total (unsieved) sediment. See text for explanation.

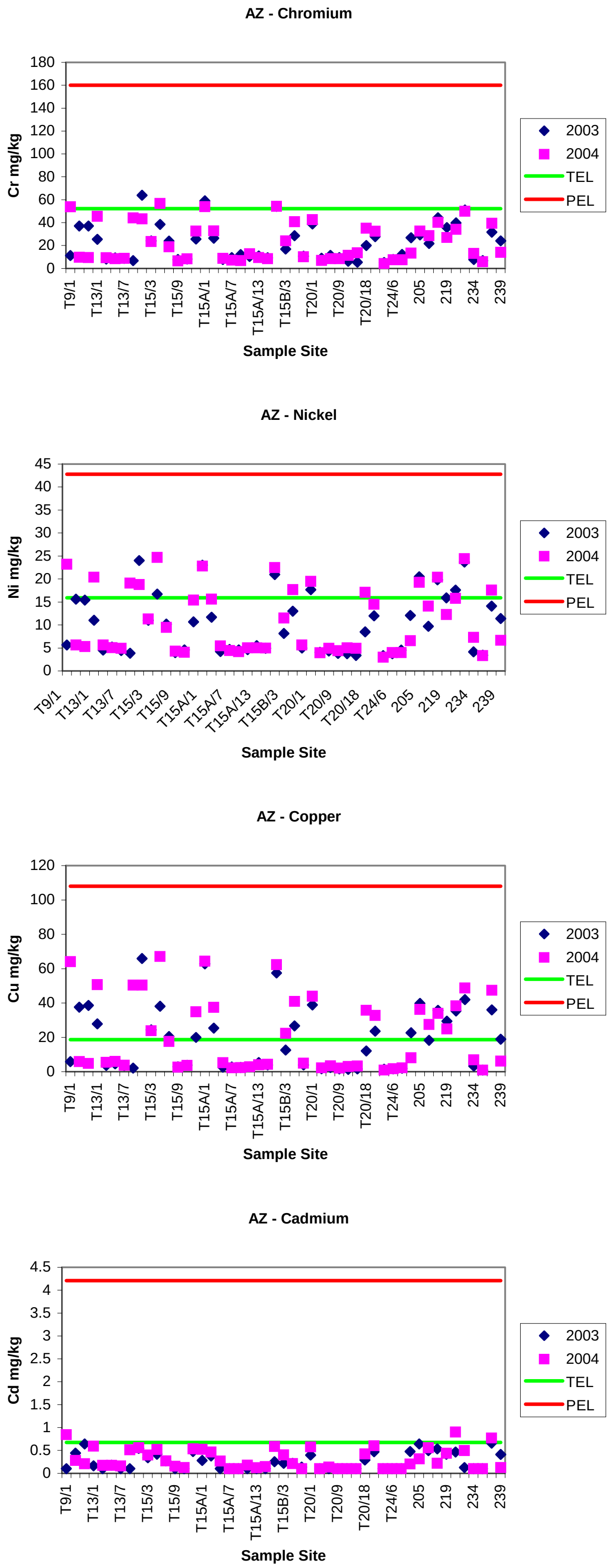
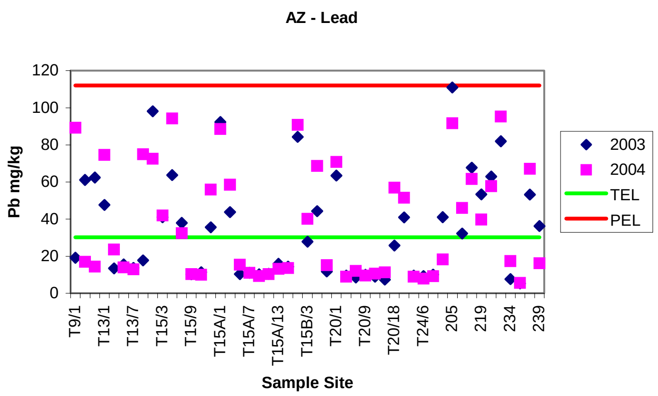
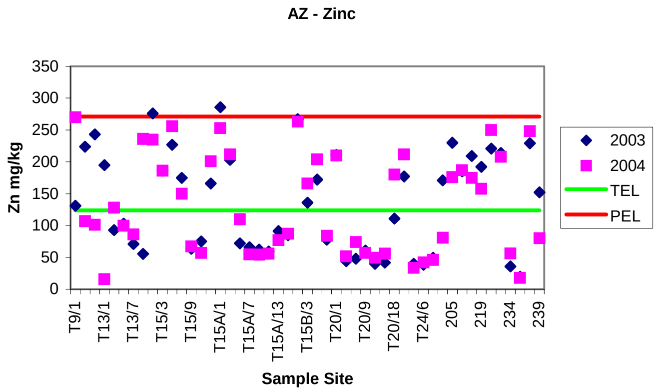



**Figure 21 (A). Cr, Ni, Cu and Cd in sediment (unseived), 2003 and 2004, in relation to TEL and PEL (Data source Astra Zeneca)**



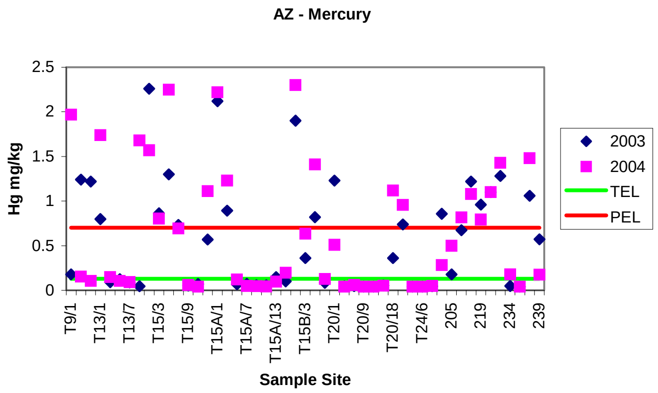




**Figure 21 (B). Pb, Zn and Hg in sediment (unseived), 2003 and 2004, in relation to TEL and PEL (Data source Astra Zeneca)**

BGS data include cores analysed by XRF. Whilst toxicological classifications based on means are broadly similar to other data-sets, they include some higher values (usually at depth, presumably representing historic contamination). These sub-surface hotspots (see for example figure 22) are presumed to be biologically unavailable at present and are not within the RoC remit. However, a point to bear in mind is that dredging or natural remobilisation events could conceivably expose these deposits, with consequences for biota. There is some evidence of erosion events and perturbation of contaminants in the recent past: BGS observations in 2000 suggest that there has been significant displacement of consolidated saltmarsh sediments of the Ince Banks since 1992, together with changes in the position of high water (Ridgway and Shimmield, 2002). This presumably is part of longer-term changes, since some fifty years ago the Ince banks were largely mudflats which have developed in to saltmarsh in the intervening period. Sediment chronologies in cores from Ince and Widnes Warth (an older saltmarsh established at least 120 years ago) clearly demonstrate a sharp rise in metals at depths corresponding to the late 19$^{th}$ /early 20$^{th}$ centuries associated with the advent of major industrial processes such as smelting (As, Cu), production of chlorine (Hg), and galvanising/paint products (Zn) (NRA, 1995; Fox *et al*., 1999).

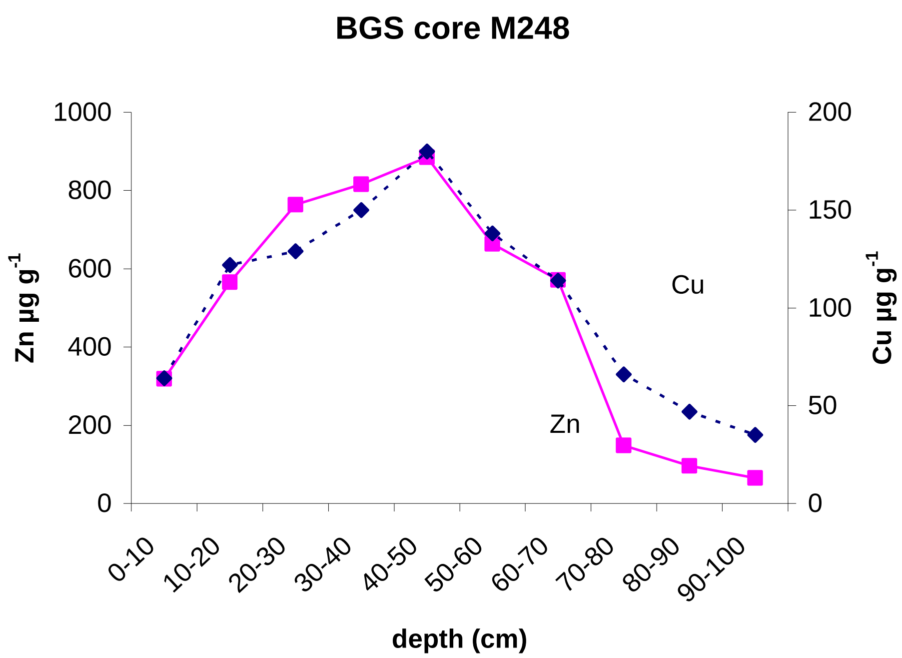



**Figure 22. Cu and Zn profiles in sediment core M246, from the Mersey Estuary near Liverpool Airport, showing subsurface peak in contamination (data source BGS)**

Overall, core data suggest that contamination in the Mersey has decreased with time over recent years, in accord with conclusions for surface sediments reached by Langston (1986), Taylor (1986), Fox *et al.* (1999), Harland *et al.* (2000) and Jones (2000). Examples of temporal trends recorded by repeated sampling of surface sediments during the last three decades are given in figures 23 and 24, based on observations by MBA and Astra Zeneca, respectively.

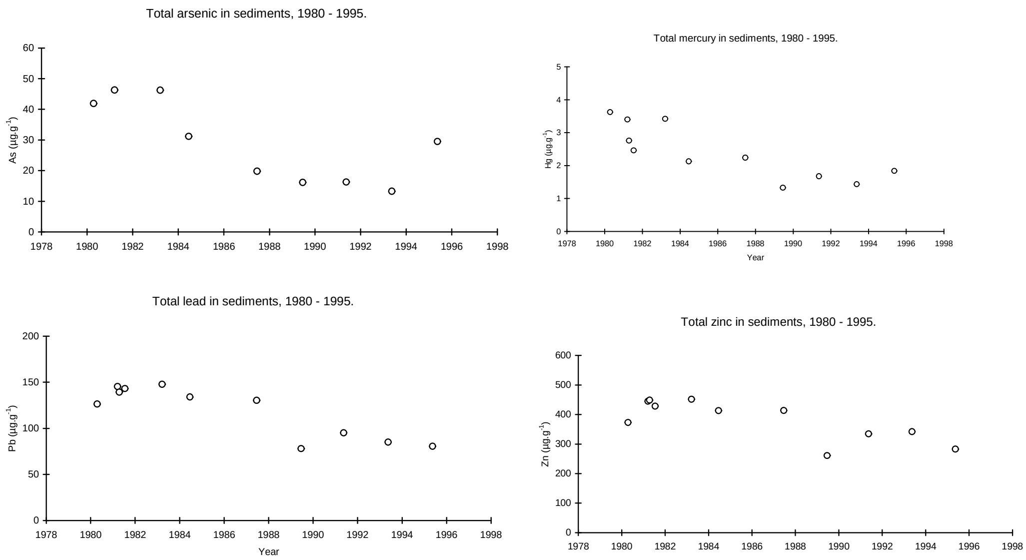



**Figure 23. Trends in mean sediment metals, Mersey Estuary indicating downwards trends in As, Hg, Pb, Zn in line with water quality improvements. (data source: MBA)**

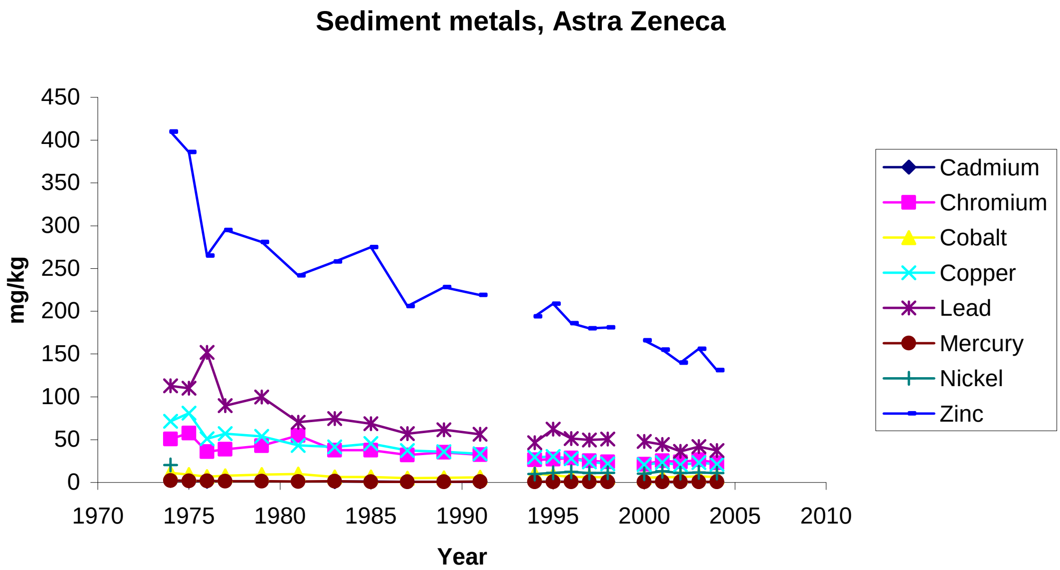



**Figure 24. Trends in metals in Mersey Estuary sediments (data source: Astra Zeneca, normalized to 40% silt)**

Despite these recent improvements it is clear that the Mersey Estuary sediments contain a considerable quantity of buried contamination that has the potential to be remobilised, either physically or chemically.

Parts of the Manchester Ship Canal/Weston Canal system are, because of their proximity to historical sources even more highly contaminated with metals such as Hg; for example four samples from the Weston canal in the early 1990s contained a mean Hg concentration of 11.8 $\mu g\ g^{-1}$ dw (Johnston *et al* 1991)

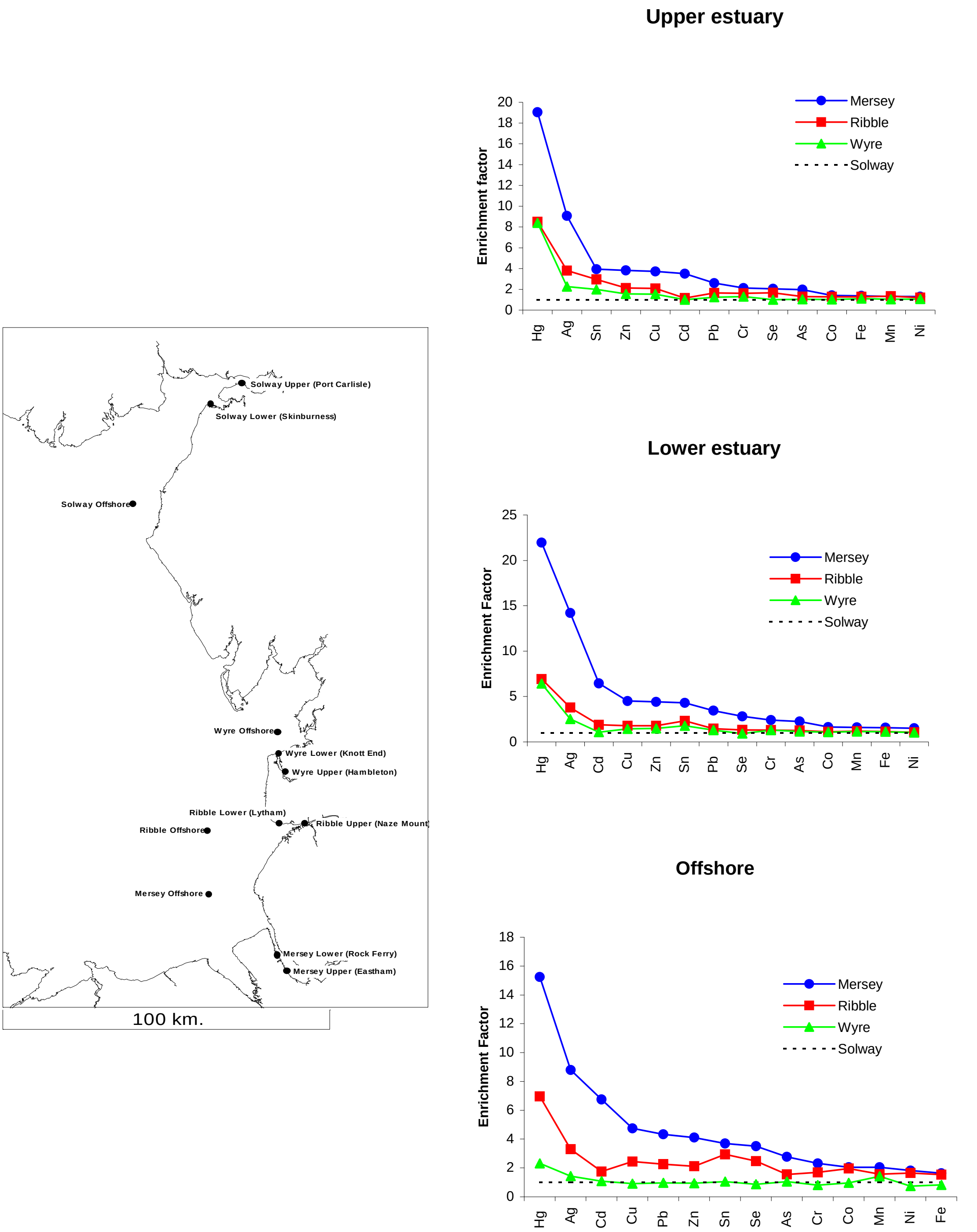



**Figure 25. Comparison of metal enrichment in sediments (totals) from upper, lower estuary and offshore sites, relative to equivalent Solway baseline values (own unpublished data, collected in 1999).**

To put Mersey sediment data into context, figure 25 compares sediment-metal data for the Upper (Eastham) and Lower (Rock Ferry) Mersey and Liverpool Bay (offshore) with comparable sites in other estuaries bordering the Irish Sea including the Ribble, Wyre and Solway (own unpublished data from 1999). Enhancement of each metal in

Mersey, Ribble and Wyre sediment is expressed relative to the Solway (assumed to represent baseline values for the region). Distinctions in size-normalised values (<100µm) between the four Irish Sea estuaries were greatest for 'pollutant' metals (Hg, Ag, Cd, Sn, Zn, Cu, Pb, As, Cr and Se), reflecting their anthropogenic origins, and less so for the more common 'geological' elements such as Fe, Mn, Co and Ni. Mersey sediments were consistently most elevated above baselines, for all pollutant metals (notably for Hg by up to 22-fold).

The ranking of enrichment of metals in each of the estuaries was broadly similar.

Dredging of sediments from the Mersey Estuary and its approaches is carried out to maintain navigational channels. This material is analysed by CEFAS as part of its legislative responsibility to prevent disposal of hazardous materials to sea. Results for 1997 indicate that mean metal concentrations in the dredged materials sometimes exceed TEL (but not PEL), by a small amount (although dredge spoils results would be higher if expressed on a dry weight basis), and are comparable to ranges found in estuarine sediments, above. Variation may be considerable due to the heterogeneity of sediment characteristics. Nevertheless, these concentrations are largely considered by CEFAS to fall within accepted OSPAR guidelines that the metal component should pose little direct toxic threat following disposal (table 8). Occasionally higher levels are encountered (for example Hg in some 1996 samples were >1.5 µg $g^{-1}$ wet wt) and such hotspots are, presumably, given further consideration before disposal licenses are granted.

**Table 8. Metals in dredged materials (µg $g^{-1}$ wet wt), Mersey Estuary, 1997 (Data source CEFAS, 2000)**

| site | n | As | Cd | Cr | Cu | Hg | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| **River Mersey** | 4 | 6.73 | 0.27 | 26.3 | 19.8 | 0.42 | 10.6 | 38.3 | 135 |
| **Wallasey** | 3 | 10.2 | 0.37 | 48.0 | 31.0 | 0.66 | 18.7 | 51 | 158 |
| **River Mersey** | 1 | 5.2 | 0.4 | 5.0 | 1.2 | 0.01 | 2.9 | 6.7 | 29 |
| **Bootle** | 6 | 8.72 | 0.34 | 37.5 | 33.5 | 0.56 | 15.0 | 60.8 | 138 |

Exceeds threshold effects level (expressed as dry weight)
n = number of measurements

**Organic pollutants – Organotins, PCBs, pesticides, herbicides, PAHs, alkylphenols, VOCs**

### 6.1.2 TBT

Use of tributyltin (TBT) antifouling on boats less than 25m in length was prohibited in 1987, though larger vessels (essentially the commercial fleet and Navy) were still entitled to use them unhindered, at least until 2003, when recommendations from IMO for a total ban were implemented in the EU by Council directive 2002/62/EC. By 2008 TBT paints should have been phased out.

Results of TBT analyses from the Mersey Estuary in recent years indicate there may still be threats to the condition of the site from these compounds.

There are probably a number of point-source and diffuse inputs of organotins in the catchment, including from various docks, the MSC, WwTWs, landfill leachates, and widespread contamination of sediments. EA has identified the Cammel Laird shipyard (downstream of the EMS) as a priority for further investigation under the stage 3 review of consents partly because of its organotin burdens. Past uses of triorganotins have included various biocidal applications and wood preservation; diorganotins have been used as stabilizers in plastics and as catalysts.

Hence, from the mid 1990s TBT was included in the EA monthly monitoring program, though it was not until1999 that detection limits were lowered from 10 ng $l^{-1}$ to 2 ng $l^{-1}$ (the EQS for TBT). In June 2000 a one-off spatial survey of water and sediments was conducted at  sites from Liverpool Bay to the head of the Estuary (Environment Agency, 2001); the majority of samples outside the mouth were below the EQS whilst those upstream in the Estuary generally exceeded the EQS, with highest concentrations (up to 40 ng $l^{-1}$) measured at Runcorn. Similarities with the distribution of alkylead compounds in the 1980s lead EA to suggest the MSC could be an important source.

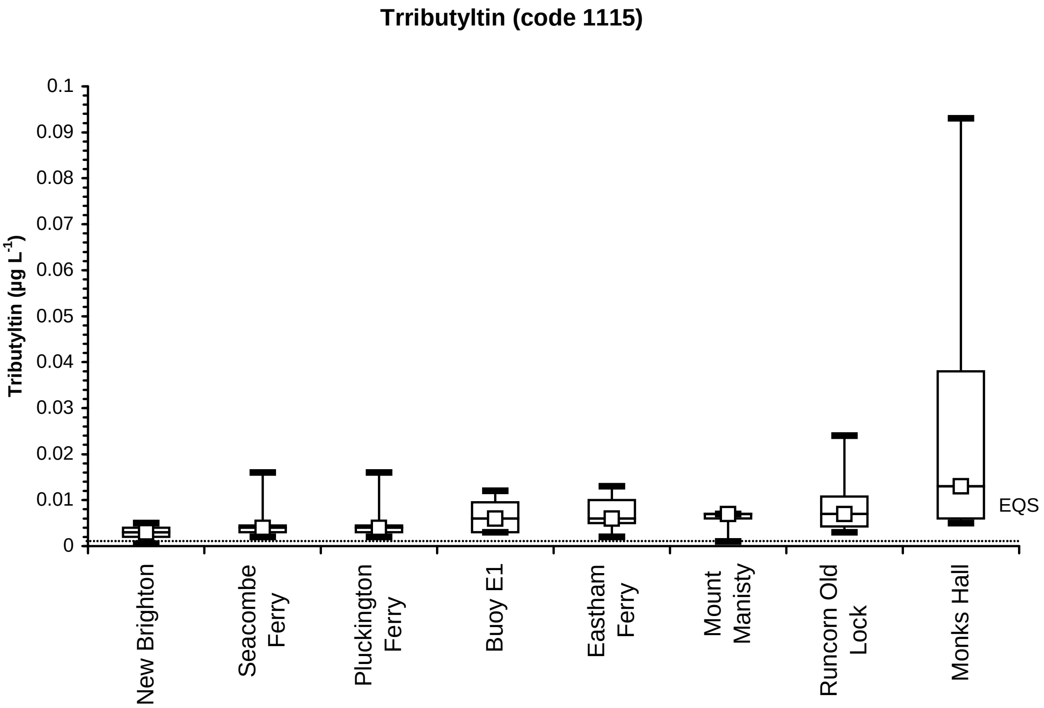
EA TBT data in water between 2002 and 2004 consists of a small number of samples shown in figure 26. The upper figure is for determinand code 1115 (tributyltin) and the lower figure for 9719 (tributyltin) compounds. Both indicate similar distributions. The EQS benchmark for tidal waters (2 ng $l^{-1}$), set as a Maximum Allowable Concentration, is exceeded at all sites. Highest values were recorded upstream at Monks Hall, at the head of the tidal waterway, implying inputs from the river Mersey itself; however, elevated values are indicated at a number of sites on different occasions. The freshwater EQS of 20 ng $l^{-1}$ would also be exceeded if this were applied at Monks Hall.

On this basis the risk of non compliance with EQS for TBT is deemed high.

DBT has only been determined consistently at Monks Hall. Between 2002 and 2004 the median concentration was 6 ng $l^{-1}$ and the maximum 84 ng $l^{-1}$. These represent elevated levels but DBT is considered far less toxic than TBT and no EQS has been put forward.

At the estuarine sites monitored, samples of triphenyltin compounds were below the detection limit of 1ng $l^{-1}$ and thus below the EQS of 8ng $l^{-1}$ in marine waters.

In a (1998) water sample from Liverpool Bay (NMP site 715), TBT (along with the booster biocide Irgarol 1051) was not detectable (<1 ng $l^{-1}$), and presumed to be of low risk (CEFAS, 2001). Diuron, another booster biocide, was present at relatively low levels (3 ng $l^{-1}$) - well below the proposed EQS of 2 µg $l^{-1}$. These results are in agreement with EA data which imply that in the open waters of the Bay the risk of non-compliance is low.



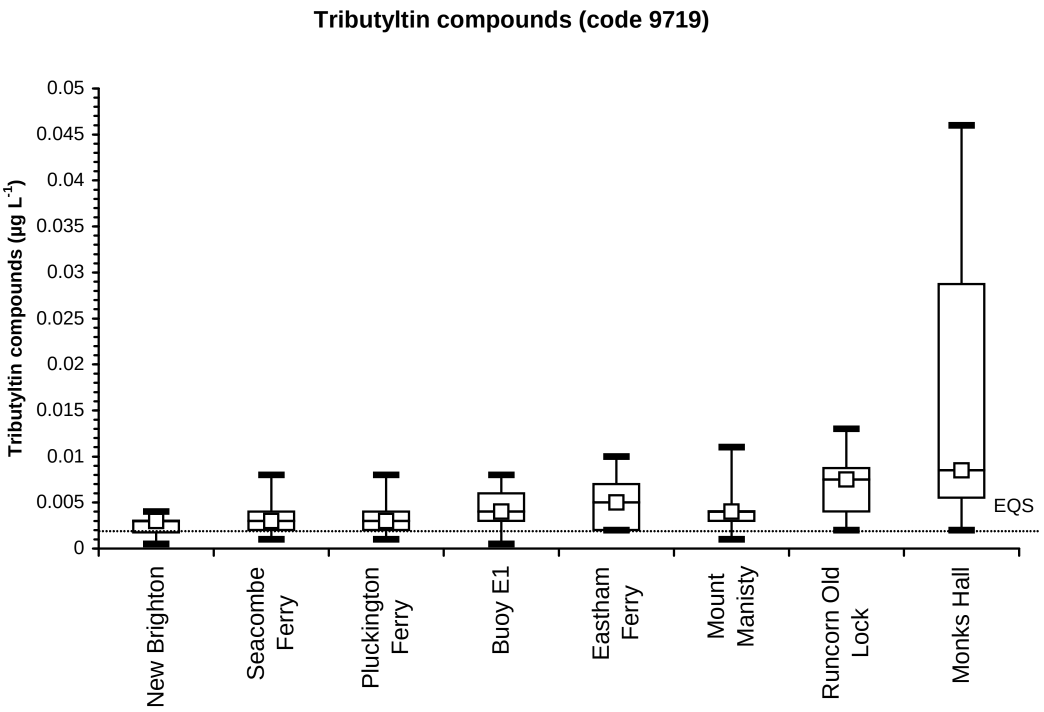
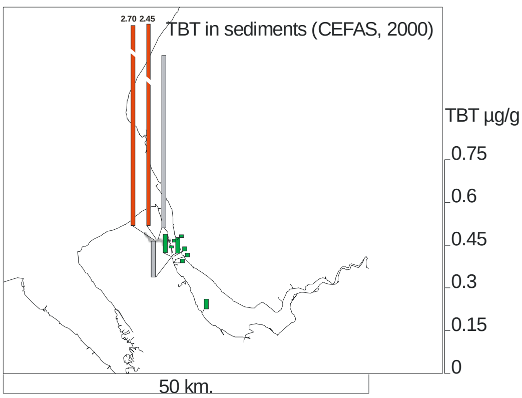




**Figure 26. TBT in tidal waters of the Mersey Estuary, 2002-2004 (data source EA)**

The threat from TBT may be receding, slowly, at least in terms of acutely toxic levels in water, but clearly has not disappeared in the Mersey Estuary The persistence of sediment-bound TBT is potentially a serious concern in terms of long-term chronic impact in poorly flushed areas, and could be exacerbated by dredging activities.

Sediments: There are no CCME guidelines for TBT, though OSPARCOM (1994;2000) has set a provisional ecotoxicological guideline value of 0.00005μg $g^{-1}$ which is exceeded by many samples in the Mersey/Liverpool Bay. It is felt however that this guideline (which has no legal significance and is intended as a guide for further work) may be set too low. Other, perhaps more realistic TBT 'guidelines' are set for dredge spoil samples as part of the procedure for licensing for disposal at sea (CEFAS, 2000, 2005); at concentrations above 0.1 μg $g^{-1}$ dry weight (Action Limit 1) disposal will be condoned only if conditions and amounts are considered to be of low concern. Above 1μg $g^{-1}$ dry weight (Action Limit 2) it is unlikely that disposal at sea would be permitted. These may be more appropriate toxicity guidelines for the assessment of estuarine sediments and are applied in figure27 to 2000 and 2001 data supplied by the Agency. The 2000 data illustrate the presence of some very high levels in dock sediments (Birkenhead). In 2001, data indicate continuing widespread TBT contamination throughout much of the estuary – at levels where toxicological impacts cannot be ruled out. It is possible that the large variation in concentrations between some sites is due to grain size effects, and/or the presence of TBT-rich paint particles.



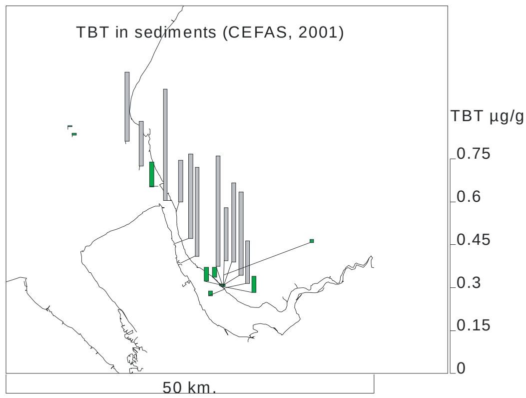




**Figure 27. Tributyltin (TBT) in sediment (<100μm fraction). Classification based on TBT 'guidelines' set for dredge spoil samples: Green bars - concentrations below 0.1 μg $g^{-1}$ dry weight, effects unlikely. Grey - Above 0.1 μg $g^{-1}$ (Action Limit 1) effects possible; disposal will be condoned only if conditions and amounts are considered to be of low concern. Red - Above 1μg $g^{-1}$ (Action Limit 2) effects expected; is unlikely that disposal at sea would be permitted. (Data Source EA)**

An earlier (1997) survey of organotin speciation in inter-tidal Mersey Estuary sediments by Harino *et al.*(2003) showed that TBT concentrations ranged from 0.007 – 0.173 μg $g^{-1}$ dry wt., increasing from Fiddlers Ferry, downstream, towards the middle section of the estuary, and were highest at Stanlow, perhaps indicative of sources from the Manchester Ship Canal (MSC). Concentrations subsequently decreased seawards, though a further peak in TBT concentrations occurred at New Brighton, opposite Liverpool Docks (figure 28). The composition of other butyltin species (MBT and DBT) in sediments, is also shown in figure 28. MBT was the most common species at upstream sites. The proportion of TBT increased dramatically towards Stanlow (60%), and thereafter remained the dominant species except at the most seaward station (Southport). The high TBT content at Blundellsands (70 %), may be due to the influence of paint particles from nearby docks at Liverpool; there are also indications of inputs of TBT from the Alt (EA, 2001). The fact that proportions of TBT were highest in the mid- and lower estuary, and lowest upstream, seems to infer that inputs of TBT to the Mersey Estuary (from shipping activity and, possibly, wastes introduced via the MSC) were still new or ongoing, or that degradation was slower here compared with upstream sites.

No clear patterns were observed for DBT, other than perhaps a trend towards slightly lower proportions at the more seaward sites. Overall, TBT was the predominant butyltin (BT) species in sediments (approximately 50%). Despite the fact that BTs represented only 4% of the total ($HNO_3$-extractable) tin in sediments there was a linear relationship between these two tin compartments. The only phenyltin detectable was TPT, present at 0.359 µg $g^{-1}$ dry wt in the sediment sample from New Brighton (perhaps due to the presence of paint particles originating from nearby docks).

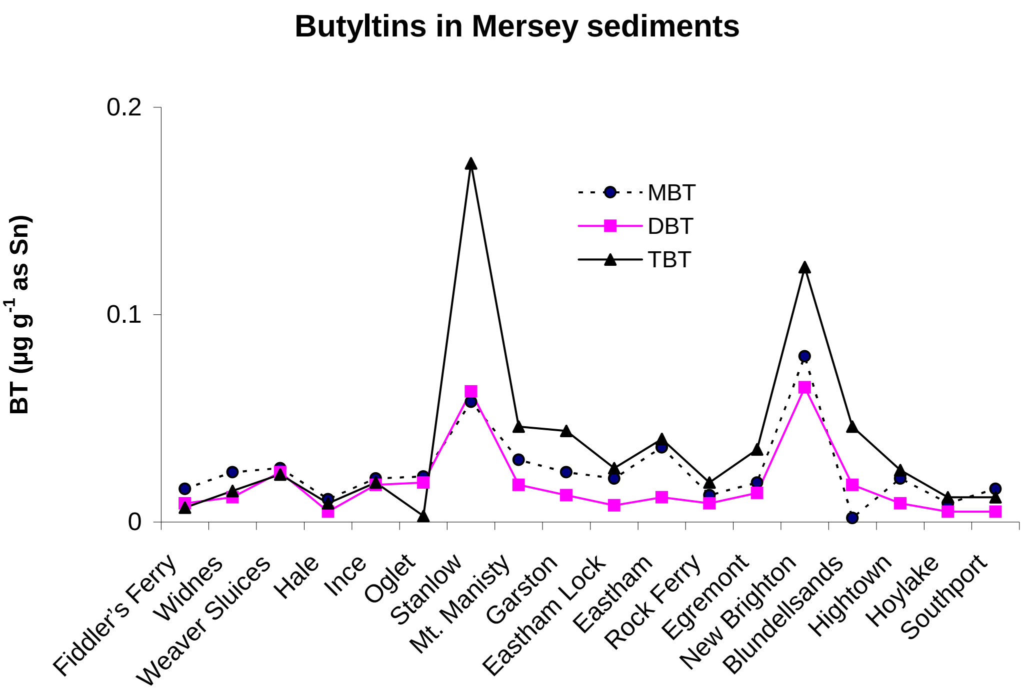



**Figure 28. Organotins in Mersey sediments, May 1997 (from Harino *et al* 2003)**

Thus, both sediment and water monitoring suggest the presence of multiple sources of TBT. The presence of high levels in some docks causes the most serious management problem because many sediments (e.g. parts of Birkenhead Docks) cannot be licensed for disposal at sea. Some examples of TBT distributions in dock sediments are shown in figure 29, colour coded with respect to CEFAS Action Levels. The CEFAS monitoring of dredge spoil materials also confirms the considerable heterogeneity in the system, and the influence of sediment characteristics (CEFAS, 2000). In 1995, for example, mean TBT values in samples from approaches to the MSC were 0.78 µg $g^{-1}$ (*wet weight*); at other Mersey sites mean values ranged from 0.17 µg $g^{-1}$ to 8.84 µg $g^{-1}$ – the latter clearly being unacceptable from a disposal at sea perspective.

There appears to be a higher proportion of TBT:DBT in dock sediments (compared to the estuary) perhaps indicating the presence of fresh inputs, paint particles and a slower rate of metabolism and release.

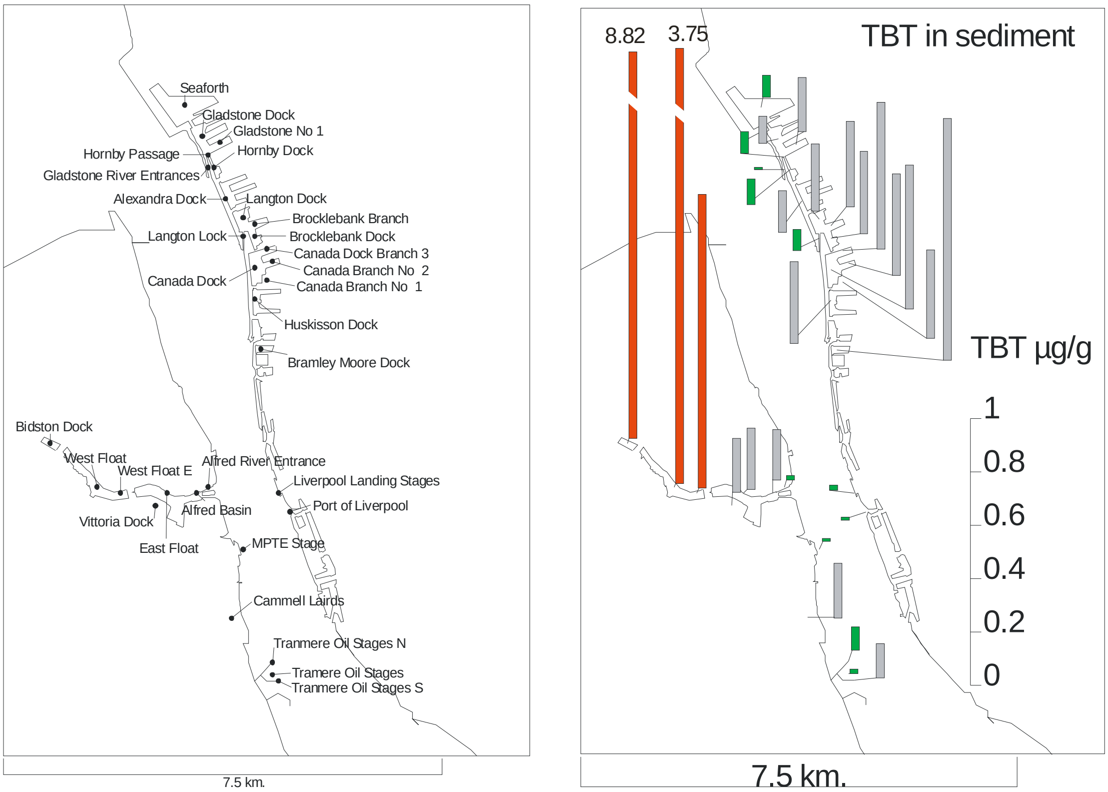



**Figure 29. TBT in sediments from Liverpool and Birkenhead docks area, 1994-2000. Green bars - concentrations below 0.1 µg $g^{-1}$ dry weight, effects unlikely. Grey - Above 0.1 µg $g^{-1}$ (Action Limit 1) effects possible; disposal will be condoned only if conditions and amounts are considered to be of low concern. Red - Above 1µg $g^{-1}$ (Action Limit 2) effects expected; is unlikely that disposal at sea would be permitted. (Data Source CEFAS)**

*TBT at disposal sites in Liverpool Bay*

Sediment quality in Liverpool Bay is monitored in National Monitoring Programme surveys (e.g. MPMMG, 1998) and from analysis of dredge spoil samples as part of the procedure for licensing for disposal at sea (CEFAS, 2000, 2005).

TBT concentrations in sediments from Mostyn Deep, collected between 1998 and 2004 were all below the DL of 0.001µg $g^{-1}$ (n=3), whilst those from disposal site Z in Liverpool Bay had a maximum of 0.004 µg $g^{-1}$ (mean 0.001 µg $g^{-1}$, n=10). The latter were well below 'Action Levels' but were above the (over?)precautionary ecotoxicological guidelines recommended by OSPAR. It is possible that these concentrations *may* be relevant, ecologically, though this is unlikely – except, perhaps, to highly sensitive molluscs. It should be noted that TBT concentrations in dredged sediments can be variable, even over a small area depending on granulometry. Nevertheless, compared to disposal sites off the NE coast, TBT values in Liverpool Bay appear comparatively low. Net transport of these offshore fines into the estuary is unlikely to impact the Mersey SPA.

To summarise, there may be substantial reservoirs of TBT in sediments of the Mersey Estuary system (e.g. docks and the MSC) which should raise caution, particularly if they are to be dredged. Processes including physical resuspension and bioturbation could remobilise these sinks. Furthermore, TBT in such contaminated sediments is likely to be available and potentially harmful to deposit-feeders and infauna (Langston and Burt, 1991).

The classic TBT indicator *Nucella lapillus* is not a native of the Mersey Estuary, though imposex has been observed in the past in dog-whelks from Hilbre Island in Liverpool Bay. The current status of this population is not known but would be a useful indication of conditions. It may also be worth survey of additional areas to look for evidence of colonisation, for example the concrete sea-defences along the N Wirral foreshore.

### 6.1.3 Pesticides and herbicides

Historically, DDT, HCB and HCH pesticides have been manufactured in the Mersey catchment, starting in the 1930s and 1940s; application of other compounds in the agricultural catchment will have been widespread.

Because of the controls on organochlorines, there are now very few values for such pesticides (or later alternatives) in Mersey water samples which exceed the detection limits. Table 9 summarises some of these in relation to EQS values and the EAs subsequent assessment of risk which is predominantly ‘low’. Thus although some of the values in the table may exceed the benchmark, the majority of samples for that determinand are below the EQS (see table 9 for numbers of samples analysed and the proportion below EQS). The risk from Endosulphan is not classifiable, because the detection limit for this compound is above the EQS (though by less than a factor of 2 - hence risk is probably low).

**Table 9. Detectable pesticide concentrations in tidal waters of the Mersey (EA data 2002-2004)**

| | site | concentration (µg/l) | EQS (µg/l) | n | comment |
|---|---|---|---|---|---|
| **HCH Gamma** | Buoy E1 | 0.0048 | 0.02 AT (s/w) 0.1 AT (f/w) | 1 | risk low |
| **Dieldrin** | Buoy E1 | 0.0025 | 0.01 AT | 21 | risk low; values probably < |
| **Malathion** | Seacombe Ferry | 0.0466* | 0.02 AT (s/w) 0.01 AT (f/w) | 1 | risk low |
| **TDE (pp)** | Buoy E1 | 0.0046 | 0.025 AT | 1 | sum DDE(pp),DDT(op),DDT(pp),TDE(pp) |
| | Hale Head | 0.0021-0.0047 | | 3 | |
| | Runcorn Old Lock | 0.0058 | | 1 | risk low all sites |
| | Fiddlers Ferry | 0.02 | | 1 | |
| **TDE (op)** | Monks Hall | 0.0041 | | 1 | |
| | Runcorn Old Lock | 0.0021 | | 1 | |
| **Endosulphan a** | Runcorn Old Lock | 0.0066* | 0.003 AD | 1 | unknown risk - DL above EQS |
| **Diazinon** | Runcorn Old Lock | 0.0758* | 0.015 AA , 0.15 MAC (s/w); 0.01 AA , 0.1MAC (f/w) | 1 | risk low |
| | Seacombe Ferry | 0.0018-0.0711* | | 2 | risk low |
| **Simazine** | Runcorn Old Lock | 0.042 | 2 AT (+atrazine) | 1 | risk low |
| **Atrazine** | Fiddlers Ferry | 0.0594 | 2 AT (+simazine) | 1 | risk low |
| | Runcorn Old Lock | 0.0417-0.054 | | 2 | risk low |
| **Dichlobenil** | Fiddlers Ferry | 0.0312 | | 1 | |

*individual values above EQS

**Table 10. Summary of total numbers of samples analysed for pesticides and proportions below detection limits (EA data, 2002-2004).**

| Determinand | No. samples | Detection limit | % of values <DL | EQS |
|---|---|---|---|---|
| ALDRIN | 104 | 0.0025 | 100% | 0.01 AT |
| HCH ALPHA | 105 | 0.001 | 100% | 0.02 AT (s/w) 0.1 AT (f/w) |
| HCH BETA | 102 | 0.005 | 100% | 0.02 AT (s/w) 0.1 AT (f/w) |
| HCH DELTA | 84 | 0.001 | 100% | 0.02 AT (s/w) 0.1 AT (f/w) |
| HCH GAMMA | 105 | 0.001 | 99% | 0.02 AT (s/w) 0.1 AT (f/w) |
| CHLORFENVINPHOS | 58 | 0.001 | 100% | 0.01 AA 0.1 MAC |
| DICHLORVOS | 57 | 0.0005 | 100% | 0.04 AT (s/w) 0.001 AT (f/w) |
| DIELDRIN | 102 | 0.0025 | 79.4% | 0.01 AT |
| MALATHION | 62 | 0.001 | 98.4% | 0.02 AT (s/w) 0.01 AT (f/w) |
| PARATHION {PARATHION ETHYL} | 62 | 0.01 | 100% | |
| PHORATE | 58 | 0.01 | 100% | |
| DDT (OP) | 105 | 0.0015 | 100% | |
| DDE (PP) | 105 | 0.0015 | 100% | |
| DDT (PP) | 90 | 0.0015 | 100% | 0.025 AT |
| TDE (PP) | 104 | 0.0015 | 94.2% | |
| ENDRIN | 100 | 0.0025 | 100% | 0.005 AT |
| ENDOSULPHAN ALPHA | 84 | 0.005 | 98.8% | 0.003 AD |
| ENDOSULPHAN BETA | 82 | 0.005 | 100% | 0.003 AD |
| TDE (OP) | 86 | 0.002 | 97.7% | |
| DDE (OP) | 86 | 0.002 | 100% | |
| DIAZINON | 61 | 0.001 | | 0.015 AA , 0.15 MAC (s/w); 0.01 AA , 0.1MAC (f/w) |
| FENTHION | 59 | 0.01 | 100% | |
| PARATHION-METHYL | 62 | 0.015 | 100% | |
| SIMAZINE | 77 | 0.03 | 98.7 | 2 AT |
| ATRAZINE | 82 | 0.03 | 96.3 | Sum of compounds |
| TRIAZOPHOS | 58 | 0.0005 | | 0.005 AT |
| COUMAPHOS | 62 | 0.001 | 100% | 0.04 AA, 0.4 MAC (s/w); 0.01 AA, 0.1 MAC (f/w) |
| DICHLOBENIL | 74 | 0.02 | 98.6% | |
| MEVINPHOS | 55 | 0.005 | 100% | 0.02 MT (f/w) |
| ISODRIN | 86 | 0.0025 | 100% | 0.005 AT |
| CARBOPHENOTHION | 59 | 0.01 | 100% | |
| PROPETAMPHOS | 62 | 0.001 | 100% | 0.01 AA 0.1 MAC |
| PROPAZINE | 82 | 0.014 | 100% | |
| AZINPHOS-METHYL | 59 | 0.001 | 100% | 0.01 AD |
| FENITROTHION | 62 | 0.001 | 100% | 0.01 AT |
| AZINPHOS-ETHYL | 61 | 0.02 | 100% | |
| TRIFLURALIN | 86 | 0.01 | 100% | 0.1 AD |

Because of the limited number of real pesticide values in the database (table 10) it is not possible to discuss spatial or temporal trends. The only information is for op TDE which, as expected, increases upstream (figure 30)

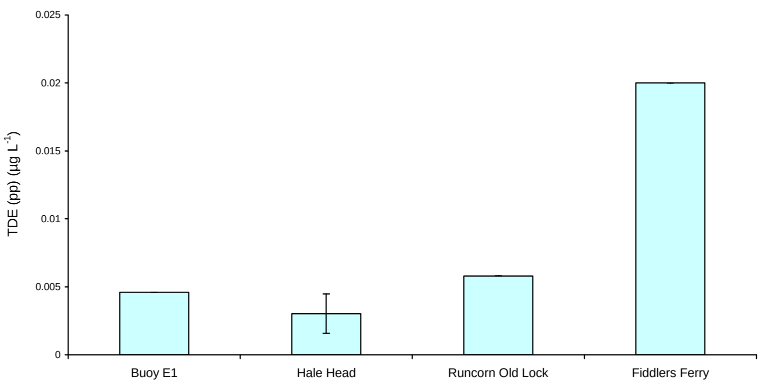



**Figure 30. Spatial Trends in ppTDE in tidal waters of the Mersey Estuary (EA data 2002-2004).**

Work on the chronologies of selected pesticides in a small number of sediment cores is described along with PCBs in the next section (6.1.4) and levels buried at depth could clearly be an issue if exposed through dredging or erosion. Unfortunately recent data sets contain insufficient information on pesticides in surface sediments to give a realistic impression of distribution and sources of contamination for benthic fauna of the Mersey Estuary. If no such data exists it is recommended that a sampling programme be conducted incorporating some of the priority compounds such as lindane (γ-HCH), DDT isomers, 'drins', and perhaps others from the lists in tables 9 and 10.

### 6.1.4 PCBs

Of some 70-80 EA analyses performed on tidal water samples for PCB congeners between 2002-2004, the vast majority were below detection limits of 0.001 $\mu g\ l^{-1}$ (congeners measured included 8, 20, 28, 35, 52, 101, 118, 138, 153, 180). Exceptions were single values for PCB28 (0.0017$\mu g\ l^{-1}$ at Fiddlers Ferry) and PCB52 (0.0014 and 0.0018$\mu g\ l^{-1}$ at Fiddlers Ferry and Seacombe, respectively). Low values reflect the hydrophilic nature of PCBs. Analysis of suspended particulates in samples from Seacombe (figure 31) indicates how the occurrence and affinity for the solid phase increases with increasing chlorination (up to PCB 153). The low solubility and availability of the very highly chlorinated congeners, eg PCB 180, probably accounts for lower concentrations.

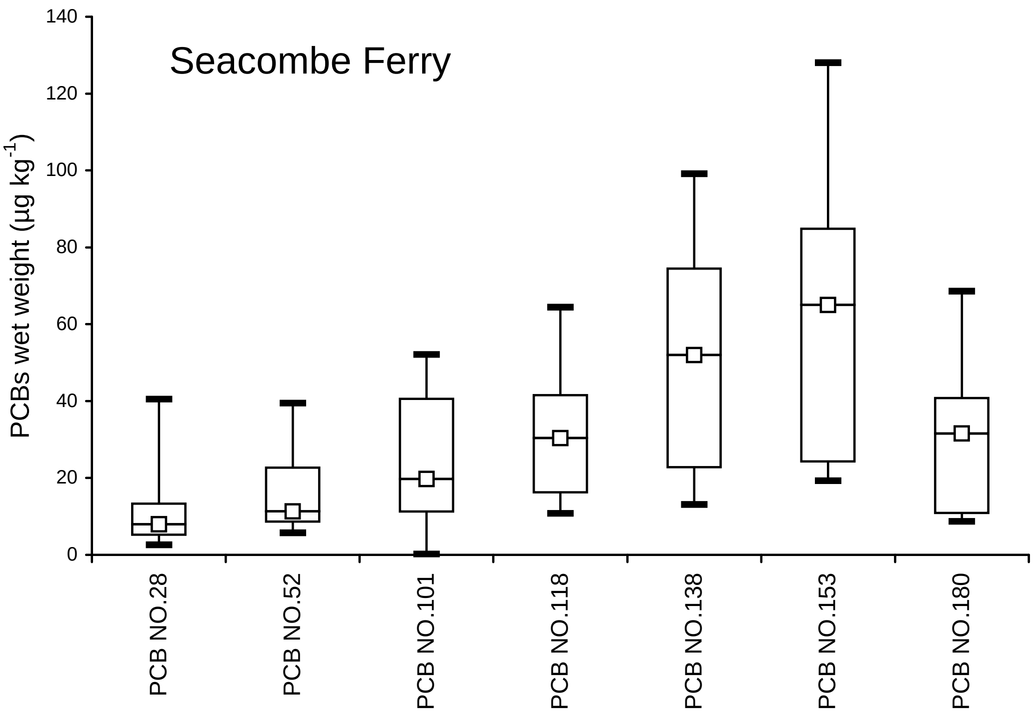



**Figure 31. PCB congeners in suspended solids, Seacombe, Mersey Estuary (2002-2004; data source EA)**

Total PCB concentrations in superficial sediment samples (< 500 µm) from Liverpool Bay in the early 1990s ranged from 0.082 – 37.9 µg $kg^{-1}$ (mean 3.9 µg $kg^{-1}$) and were significantly correlated with the amount of fine particles and with the organic carbon content (Camacho-Ibar & McEvoy, 1996). Lowest concentrations were found in the sandy southern area towards the North Wales coast and highest values in muddy deposits where spoil particles are likely to accumulate, particularly near the River Mersey in the Burbo Bight area, implying the estuary is a net exporter of PCBs, both directly and via dumping activities. The quality guideline (TEL) for total PCB (21.5 µg $kg^{-1}$) was sometimes exceeded though not the probable effect level (PEL 189µg $kg^{-1}$) and ranges of sediment values were consistent with other industrialized areas.

In later NMMP surveys of sediments at 56 UK sites in 1999-2001, Mersey samples (15 µg $kg^{-1}$) were second highest to the Thames (24.6 µg $kg^{-1}$) based on CB 153.

Figure 32 depicts trends in sediment PCBs at two NMMP sites since 2000 (Seacombe, inside the Estuary and Buoy C1 outside the Mouth). Considerable variation was seen at Seacombe in 2001 during which time average values exceeded the TEL, though not the PEL. Since then, however, values appear to have declined to below the TEL at both of these sites. However, these sediments represent a <2mm sieved sample and could include varying quantities of sand (low in contaminants) which might lead to variability of the type seen in figure 32.

CEFAS sediment data (2001 and 2002) also include PCBs at sites along a transect from Liverpool Bay in to the Narrows section of the Estuary (Rock Ferry, approximately). Only one value exceeded the TEL (by a very small margin). The situation for sediments in the SPA is not known since sites were not sampled here, though, on the evidence presented, impact is not expected.

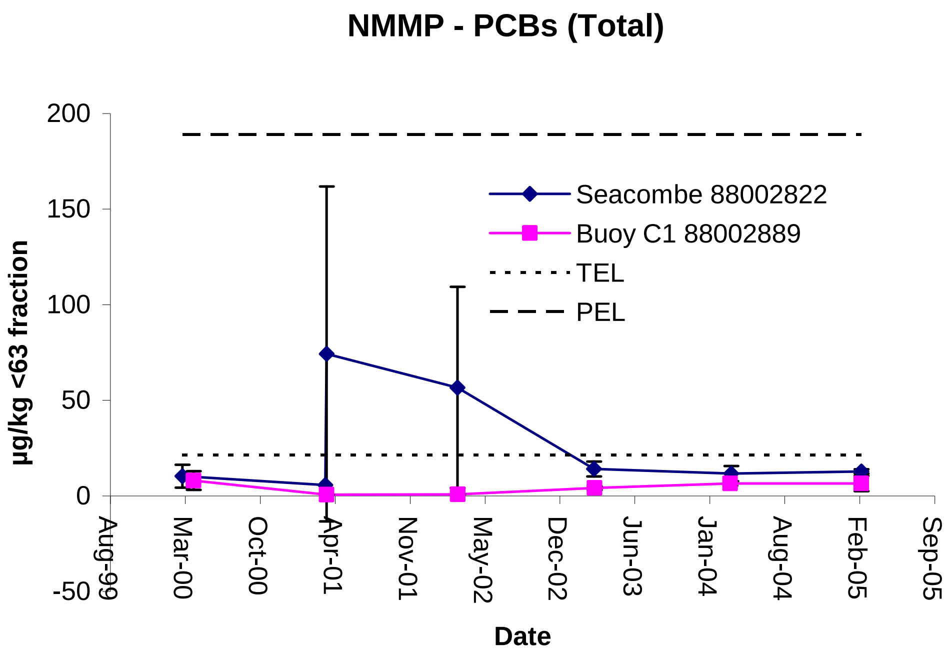



**Figure 32. PCB concentrations in sediments from two NMMP sites, Seacombe and Buoy C1, 2000-2005**

A further, longer-term, perspective of temporal trends in PCBs in Mersey sediments may be gained by analysing trends in dredge spoils from the river since 1990. These results, for a standard suite of 25 congeners, have been generated by CEFAS as a requirement under FEPA. Samples include some of the more contaminated sites in the estuary (exceeding TELs and PELs on occasions) - which are on a par with the more highly contaminated estuaries in the UK such as Blyth, Tyne, Tees, and parts of the Severn Estuary (CEFAS, 2001). Temporal trends for Mersey samples imply significant reductions in recent years (figure 33), although again this may be artefactual due to variable sediment characteristics.

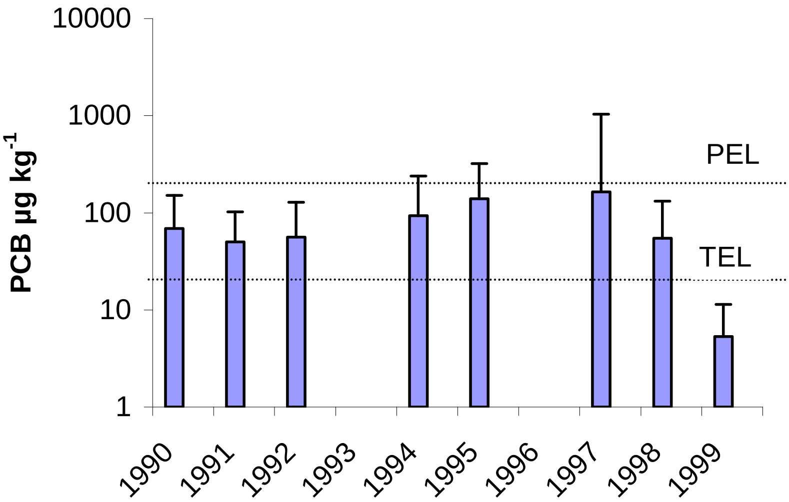



**Figure 33. PCBS (Σ25 congeners) in dredge sediment from the Mersey Estuary (plotted from data in CEFAS, 2001).**

Sediment chronologies in cores from Ince Banks and Widnes show that ΣDDT concentrations start to increase in ~1945, reflecting the start of local production (Manchester) at that time, peaking in the 1960s, and subsequently declining to low levels in surface sediments in response to legislation (Fox *et al*., 2001). Residues are composed mainly of the anoxic degradation product DDD. PCBs start to appear ~1940, coinciding with the start of production (not on Merseyside), peak ~1970 and then start to decline, but at relatively slow rates - presumably because of persistence and residual inputs. A peak for HCH is observed ~1950. Patterns for HCB are less easily interpreted due to multiple sources, whilst levels of dieldrin are consistently low (Fox *et al*., 2001). Clearly however, as with metals, possible historical deposits of organic contaminants, could become an issue during periods of erosion.

Comparisons of surface values and subsurface maximum for PCB (ICES7), HCH, DDT and Dieldrin, together with estimates of quantities buried underneath these marsh sediments (Fox *et al.,* 2001) are illustrated in figure 34. Subsurface maximum levels of both DDT and HCH in give some cause for concern based on comparisons with quality standards and guidelines (TELs and PELs).

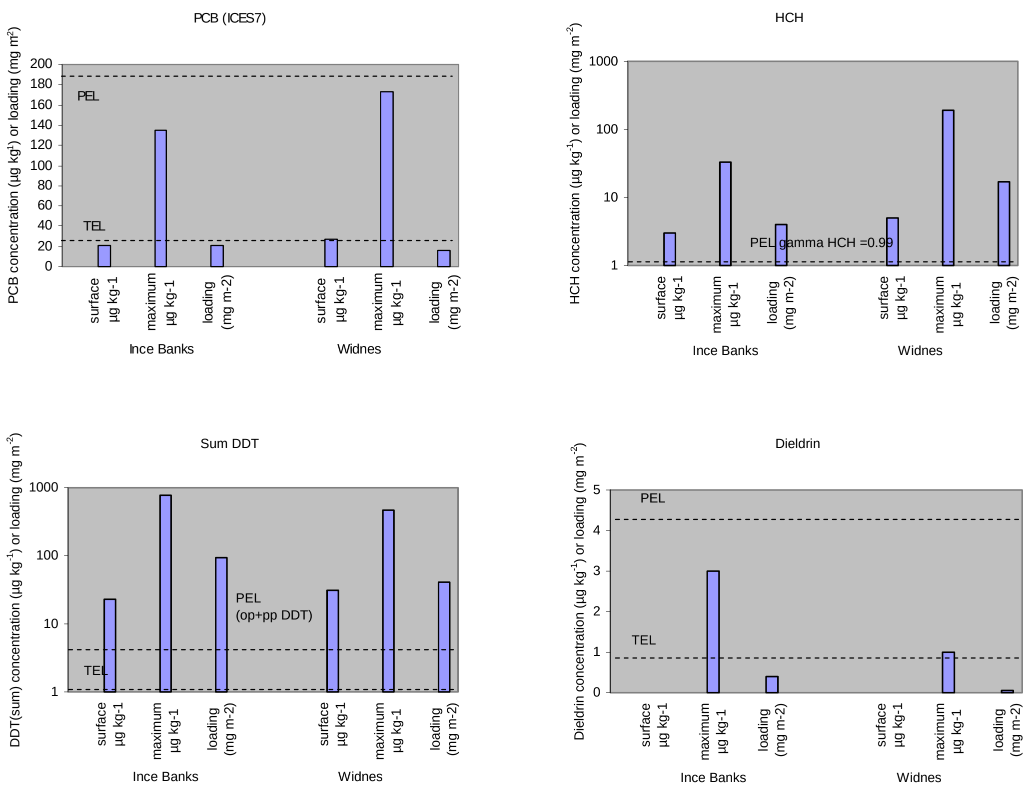



**Figure 34. Subsurface maxima, surface concentrations and loadings by area of ΣPCBs, ΣHCH, ΣDDT and dieldrin in core samples from Ince Banks and Widnes Warth (plotted from data in Fox *et al*., 2001).**

### 6.1.5 Alkylphenols and other endocrine disruptors

*Alkylphenols*

Alkylphenol polyethoxylates (APEs), based mainly on nonyl- and to a lesser extent, octyl-phenols, are non-ionic surfactants which have been used for domestic and industrial purposes for more than half a century (review by Langston *et al.,* 2005). Some 6000 tonnes of APEs enter UK rivers and estuaries annually from various sources including sewage outfalls, industrial discharge and agricultural run-off (Blackburn *et al.,* 1999). Currently this broad group of compounds are utilized in paper and pulp mills, textile processing, resin and paint manufacture and other chemical applications. Up until 1996 they were also a component of waste discharged in to the sea from off-shore oil/gas production platforms, where they were used in lubricant and surfactant formulations (Olsgard & Gray, 1995). About 33% of APEOs are (or were, until recent voluntary EU restrictions) employed as ingredients in household and industrial detergents which are mainly disposed of into the sewer system and are biodegraded in the environment or in sewage treatment works, via stepwise loss of ethoxy groups to more hydrophobic, recalcitrant metabolites including nonylphenol (NP), octylphenol (OP), as well as alkylphenol mon- di- and tri-ethoxylates[12]. Thus, alkylphenols (AP) based on NP and OP accumulate in the aquatic environment as complex mixtures of isomers containing branched alkyl groups with a formula of $C_9H_{19}$ and $C_8H_{17}$, respectively.

Alkylphenols are common contaminants in WwTWs and may be present in µg $l^{-1}$ concentrations in effluent samples and mg $g^{-1}$ quantities in sludges and sediment. For example, concentrations up to 45 µg $l^{-1}$ NPE (3 µg $l^{-1}$ NP) have been measured in an outfall on the Tyne Estuary (Lye *et al.,* 1999). In the vicinity of discharges (particularly in rivers) concentrations may reach several hundred µg $l^{-1}$ – levels sufficient to threaten native organisms (Blackburn and Waldock, 1995). During the mid-1990s total extractable alkylphenols in the tidal River Mersey (Widnes and Warrington) were in the range 6-11 µg $l^{-1}$ (Blackburn *et al.,* 1999).

In a survey of UK estuarine waters, which included the Mersey and six other estuaries (Wear, Tees, Tyne, Blythe, Poole, Southampton), APs in the form of NP were measured in the Tees and Mersey Estuaries at concentrations of 5.2 µg $l^{-1}$ and 0.32 µg $l^{-1}$. Octylphenol was only detected in the Tees Estuary – at 13 µg $l^{-1}$ (Blackburn & Waldock, 1995). Table 11 summarises data from these earlier Mersey surveys illustrating that concentrations in the outer estuary were much lower than those nearer the tidal limit. Data for water samples from two sites in Liverpool Bay collected in 1998 ( CEFAS, 2001) are also shown in table 11 and are comparatively low.

At highly contaminated sites such as the lower Tees estuary, total extractable APE (intermittently >80µg $l^{-1}$) are implicated as contributing to poor water quality in acute toxicity bioassays with marine copepods *Tisbe battagliai* and oyster embryo *Crassostrea gigas* (Thomas *et al*., 1999, 2001). At the sublethal level, though having less strong oestrogenic properties than natural hormones, APs have been shown to induce vitellogenin (VTG) synthesis and testicular abnormalities in male eelpout (Christiansen *et al*., 1998) and inhibit the settlement of barnacle larvae (Billinghurst *et al*., 1998), together with other effects (see review by Langston *et al.,* 2005) . These sublethal effects occur at levels of ~1 µg $l^{-1}$ i.e. at concentrations sometimes observed in the field, including the upper reaches of the tidal Mersey. Both OP and NP have been included in Water Framework Directive lists of priority substances. An Environmental Quality Standard (EQS) of 1 µg $l^{-1}$ (as annual average; maximum allowable concentration 2.5 µg $l^{-1}$) has been set for NP and OP to control these substances in European waters.

The most recent tidal waters data for NP supplied by EA (2002-2004) indicate that at upstream sites -Monks Hall, Baxters Bridge, Sankey - the risk of EGS excedence is high. In fact the upper value at Monks Hall (2.99 µg $l^{-1}$) exceeds the maximum allowable concentration of 2.5 µg $l^{-1}$ (see figure 35). Risk declines to 'medium' at Randalls Sluices and thereafter to 'low' at more seaward sites. These results imply that sources of NP to the Mersey require further investigation. Without further

[12] Note: Alkylphenol ethoxylates themselves are considered less significant, environmentally, than their corresponding transformation products due to their lower persistence, toxicity and oestrogenic activity. MACs of 3.3 and 4.3 µg $l^{-1}$ have been proposed for nonylphenol mono- and di-ethoxylates respectively.

information on freshwater inputs and discharges it is not possible to comment on possible sources.

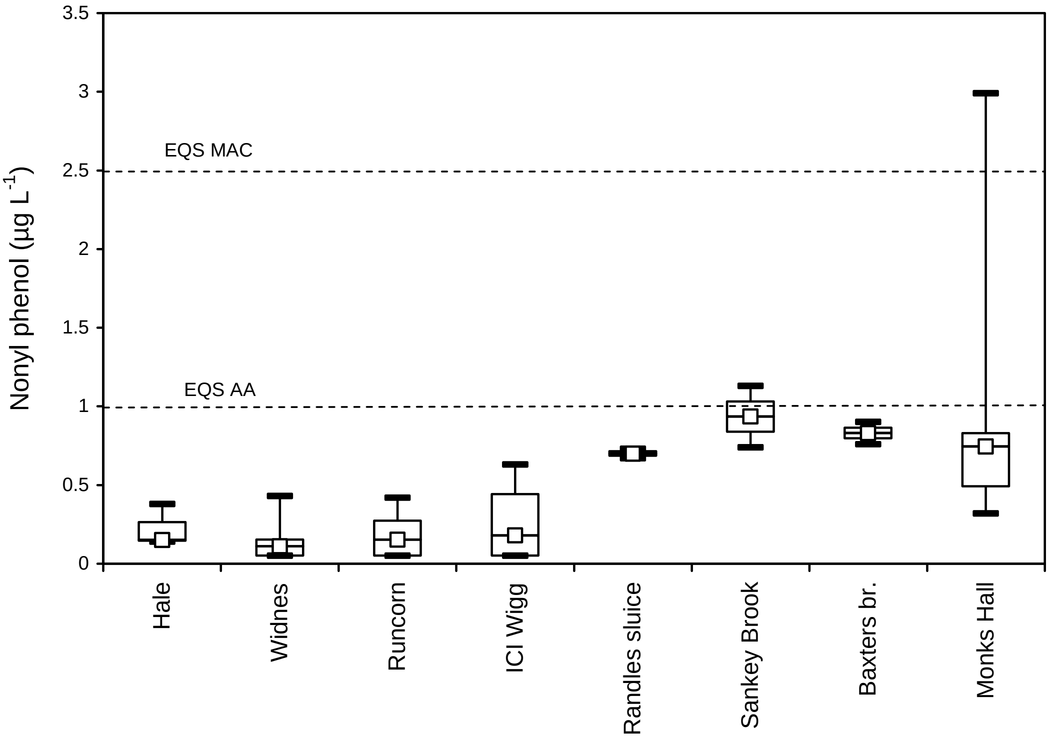



**Figure 35. Concentrations of nonylphenol (µg $l^{-1}$) in tidal waters, Mersey Estuary. Data source EA. (median, min and max, 25th and 75th percentiles).**

**Table 11. Alkylphenols in the Mersey Estuary and Liverpool Bay (from [a]CEFAS, 2001; [b]Blackburn *et al.*, 1999; [c]Blackburn & Waldock, 1995)**

| site | n | Octyl phenol | | nonylphenol | | Nonylphenol mono- and di-ethoxylates | |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| | | total | dissolved | total | dissolved | total | dissolved |
| | | | | | | | |
| *Water(µg $l^{-1}$)* | | | | | | | |
| Warrington,July 1994[b] | 1 | <0.5 | <0.5 | 6.2 | 2.6 | 4.5 | 3.5 |
| Widnes July 1994[b] | 1 | <0.5 | <0.5 | 3.3 | 2.9 | 3.2 | 0.5 |
| Seacombe, July 1995[b] | 1 | <0.5 | <0.5 | 0.4 | <0.2 | <0.6 | <0.6 |
| Eastham (1993)[c] | 1 | | | 0.32 | <0.08 | | |
| Tranmere (1993)[c] | 1 | | | 0.17 | <0.08 | | |
| Seacombe (1993)[c] | 1 | | | <0.08 | <0.08 | | |
| Canada Buoy (1993)[c] | 1 | | | 0.13 | <0.08 | | |
| C1 Buoy(July 1995)[b] | 1 | <0.5 | <0.5 | <0.2 | <0.2 | <0.6 | <0.6 |
| C20 Buoy(July 1995)[b] | 1 | <0.5 | <0.5 | <0.2 | <0.2 | <0.6 | <0.6 |
| Liverpool Bay (1998)[a] | 2 | 0.11-0.22 | 0.04-0.48 | 0.49-0.92 | 0.23-0.28 | 1.1-2.8 | 0.47-0.8 |
| | | | | | | | |
| *Sediment (µg $g^{-1}$)* | | | | | | | |
| Warrington,July 1994[b] (mud/silt) | | | | 5.2 | | 9.2 | |
| Widnes July 1994[b] (mud) | | | | 2.6 | | 7.2 | |
| Seacombe 1995[b] (sand) | | | | <0.1 | | <0.5 | |
| C20 Buoy 1995[b] (sand) | | | | <0.1 | | <0.5 | |
| Liverpool Bay (1998)[a] (<2mm) | 2 | <0.01 | | <0.19 | | <1.0 | |
| | | | | | | | |

The potential for effects from AP-contaminated sediments has been demonstrated for crustacea (Zulkosky *et al.,* 2002) and molluscs: Duft *et al.* (2003) showed that embryo production in the gastropod *Potamopyrgus antipodium* was stimulated in response to long-term exposure to sediments spiked with environmentally realistic concentrations of endocrine disrupting compounds which included OP, NP and BPA. The lowest observed effect concentration (LOEC) was 1 μg $kg^{-1}$ for all test compounds. PNECs for sediments have been suggested from sub-lethal tests to be as low as 0.039 μg $g^{-1}$ and 0.0065 μg $g^{-1}$ for NP and OP, respectively, though Environment Canada propose a values of 2 μg $g^{-1}$ for NP.

Survey of nonylphenol concentrations measured in 27 UK river sediments varied from <0.1 up to 15 μg $g^{-1}$ dry wt (Blackburn *et al*., 1999). Of the waterways sampled, detectable levels of NP were only observed in sediments from the (tidal) River Mersey (table 11) and River Aire - at concentrations higher than most proposed PNECs. In the majority of 'riverine' sediments NP was below the limits of detection. Of 33 estuarine samples analysed in the same study, concentrations of NP ranged from <100 μg $kg^{-1}$ to 1700 μg $kg^{-1}$ dry wt with most samples below the limit of detection (median value of <100 ng $g^{-1}$ dry wt; Blackburn *et al*., 1999). Highest detectable levels of NP were generally those in siltier sediments from the Tees Estuary. As indicated in table 11, NP was not quantifiable in sediments at the mouth of the Mersey estuary (Seacombe, C20 Buoy). However, the latter sediments were sand, and, as with metals, granulometry and organic content are likely to be a major influence controlling concentrations.

Similarly, alkylphenols in the <2mm sediment fraction (includes sand) from Liverpool Bay were below detection limits (table 11), (CEFAS, 2001). Since detection limits were greater than the proposed PNECs, further sampling and detailed analysis may be advisable to confirm that risks to biota from this source are acceptable. Also, in view of the danger of EQS exceedence in Mersey waters, further data is needed for sediments within the estuary (NB within the SPA and upstream).

*Pharmaceutical compounds*

Pharmaceutical compounds measured in water samples from six sites in the Mersey Estuary included Mefenamic acid, Diclofenac, Propranolol, Dextropropoxyphene, Tamoxiphen, Ibuprophen, Trimethoprim and Clotrimazole (CEFAS, 2005). Highest concentrations (usually in the range of tens to hundreds of ng/l) tended to occur near the dock at Seaforth and are presumed to be from WwTWs, largely. Similar concentrations can be found in other major urbanised/industrialised estuaries including the Tyne, Tees and Thames. There are currently no EQSs or other thresholds for these pharmaceutical compounds, and as yet there is little understanding of impacts on aquatic life or concentrations in sediments.

Recently, the Swedish Medical Products Agency performed assessments on the environmental effects of several pharmaceuticals (based on available data) and concluded that Diclofenac and Ibuprofen, amongst others, are 'toxic for water-dwelling organisms and capable of causing harmful long-term effects in an aquatic environment' (there was no information for many substances, thus rendering a complete environmental classification impossible).

Acute and chronic ecotoxicological data for diclofenac and propranolol showed no acute toxic effects to the green alga *Selenastrum capricornutum*, although there were chronic exposure effects (96 hours) at concentrations of over 2 mg $l^{-1}$. The blue/green alga *Synechococcus leopolensis* was particularly sensitive to antibiotics, which inhibited its growth at concentrations of 10 µg $l^{-1}$. For propranolol the NOEC (No Observable Effect Concentration) on reproduction in crustacean *Ceriodaphnia dubia* was 9 µg $l^{-1}$. The report also notes that that the toxicity of mixtures e.g. Diclofenac + Ibuprofen was higher than for the individual substances (Swedish Medical Products Agency, 2004).

However, until more information is forthcoming risks from this group of contaminants are difficult to quantify.

### 6.1.6 Hydrocarbons (Oil, Petrochemicals, PAHs) and VOCs

**Recent published information on hydrocarbon oil and PAHs in the Mersey EMS**

*Oil*

Oil pollution is a continual threat to all inshore marine habitats, and is particularly pronounced in the Mersey Estuary due to its enclosed and sheltered nature. Risks include small leaks, spills and discharges, as well as the possibility of a major accident.

There are a number of ways in which oil could potentially impact on the interest features of the SPA. Inter-tidal habitats are under greatest threat from the physical effects of oil pollution: the most vulnerable of these are inter-tidal sand and mudflats and salt-marshes of the 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. For shellfish beds, the direct effects of oil are potentially serious; in the event of even moderate spillages, significant mortalities of bivalves would be expected. Birds would be affected by consumption of contaminated food and damage to plumage.

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

Sensitivity of *Zostera* beds to chronic exposure to oil (refinery effluent) may not be very high (Hiscock, 1987). The likely impact of acute exposure (oil spillage) will be influenced by the type of oil, the degree of weathering and the nature of the habitat 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.

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

The hydrocarbons present in crude oil can range from aliphatic (straight chain) compounds to more complex aromatic (containing a benzene ring) and polynuclear aromatic (containing two or more benzene rings) compounds. Processed products include petrol and diesel and a range of petrochemicals, e.g. propylene, acetylene, benzene, toluene and naphthalene. In addition to shipping, sources also include river-borne discharges, (including road runoff and licensed and unlicensed discharge to sewers) diffuse discharges from industrialised municipal areas, oil production sites (e.g. accidental release from the Stanlow site) and the atmosphere (PAH's).

Most of the reports available in the literature regarding hydrocarbon oil in the EMS, relate to oil spill incidents such as that which occurred in 1989, when a fractured pipeline spilled over 150t of crude oil into the Mersey at Ellesmere Port. Apart from these, reports of hydrocarbon levels in the Mersey tend to be part of larger studies, involving several estuaries. One such study (Kirby *et al.,* 1998) analysed raw water samples from several estuaries and found total hydrocarbon concentrations (THC) in the Mersey to be amongst the most elevated in the UK (figure 36). In the mouths of the estuaries sampled (including Liverpool Bay for the Mersey), highest THC levels occurred at low tide, reflecting respective dominant flows of more highly contaminated water from upstream. A variety of sources were suggested including industrial discharges and spillages from shipping and land-based sources. The lowest concentrations ($<1 \mu g\ l^{-1}$) were recorded at offshore sites most removed from contaminant inputs.

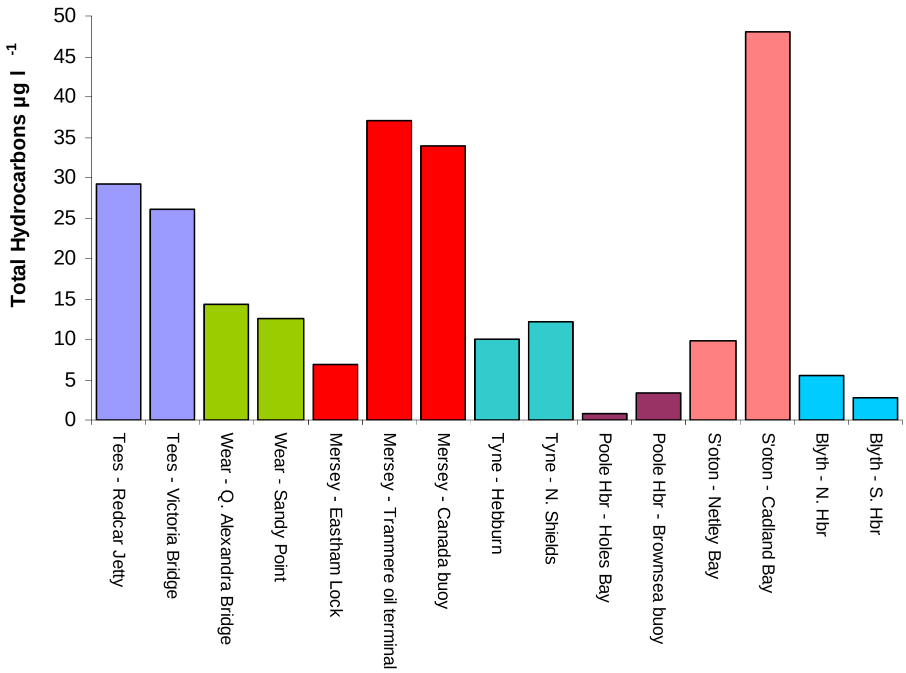



**Figure 36. Total hydrocarbon concentrations (µg $l^{-1}$) in raw water from UK estuaries (drawn from data in Kirby *et al.*, 1998)**

In the Irish Sea, as is the case with many sea areas, total hydrocarbons (THCs) in surface waters away from estuaries and industrialised areas are generally low. In 1991, THCs (expressed as Ekofisk crude oil equivalents) were recorded as 0.4-0.7µg/l in offshore waters, whereas the surface waters of the Mersey estuary contained up to 11µg/l (MAFF, 1993). These levels are lower than reported for the late 1970s when offshore waters were found to contain 6.4-12µg/l and a site the Mersey estuary 74µg/l (Law, 1980). Chromatograms of the Mersey HC's revealed that these were not fresh but were derived from chronic low-level inputs rather than episodic spillages (MAFF, 1993). However, spillages have occurred in the Mersey estuary; in 1989 accidental loss of 150t of crude oil from a refinery raised concerns but effects on HC levels in sediments were found to be minimal due to the elevated background levels already present (Davies and Wolff, 1990).

THC levels in sediments are also lower at offshore sites. Samples of sediment taken from Morecambe Bay in 1979 were found to contain THC concentrations of 12-29µg/g (dry weight) whilst in the Mersey estuary 340µg/g was recorded (Law, 1980) THCs were measured in sea bed sediments collected from the eastern Irish Sea and Cardigan Bay in 1990 by MAFF. Concentrations ranged from 1.1 µg/g in sandy sediment to 240 µg/g in mud, both samples coming from the Mersey illustrating the importance of grain size characteristics. Samples from Cardigan Bay, Morecambe Bay, Liverpool Bay, the Ribble and east of the Isle of Man all had sub-µg/g concentrations (MAFF, 1992).

For estuarine sediments, Readman *et al* (1986) analysed hydrocarbon mixtures isolated from three estuaries, the Mersey (sediments collected from Eastham Ferry), the Dee, and the Tamar. HPLC chromatograms showed a dominance of unsubstituted parent PAHs indicative of a combustion origin in all three estuaries. The 'hump' on the chromatograms 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 12, below, for comparison.

**Table 12. Concentrations (μg $g^{-1}$ dw) of Unresolved Complex Mixture (UCM) in sediments from three UK estuaries (from Readman *et al.*,1986)**

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

Three years after this study, a fractured pipeline spilled over 150t of crude oil into the Mersey at Ellesmere Port, prompting environmental concerns. However, shortly after the incident, analysis of sediment core samples showed that the effect of the spilled oil on levels of hydrocarbons was minimal due to the exceptionally high background levels of hydrocarbon contamination already present in the sediment (up to 400 μg $g^{-1}$ dw total aliphatic hydrocarbons at 10cm depth) (Davies & Wolff, 1990).

More recently, a total ion chromatogram of hydrocarbon mixtures (isolated from sediment collected opposite Canada Dock on the Mersey Estuary) showed a high UCM comparable to that found in 1986 by Readman and co-workers (Thomas *et al.,* 2002). Although actual concentrations of UCM were not quantified in the more recent study, its presence indicates the chronic nature of oil contamination in the estuary.

*Polycyclic aromatic hydrocarbons (PAH's)*

PAH's are ubiquitous environmental contaminants, estimated to constitute some 8% by weight of the total hydrocarbon composition (Kirby *et al*., 1998). Although they can be formed naturally (e.g. oil seeps, forest fires) the predominant source of PAHs is often anthropogenic emissions, and the highest concentrations are generally found around urban centres (Cole *et al*., 1999). They are of particular concern in the marine environment as the lower molecular weight PAHs are toxic to marine organisms, and metabolites of the higher molecular weight PAH's are carcinogenic (Law *et al*., 1997). Elevated levels have been linked to liver neoplasms and other abnormalities in demersal fish (Malins *et al.,* 1988). Some PAHs have also been identified as endocrine disruptors (Anderson *et al*., 1996a,b; Kocan *et al.,* 1996).

Based on observed environmental behaviour, physical and chemical properties, microbial degradation rates and statistical analyses, PAHs are divisible into two groups: *Group 1* or low molecular weight (≤200) PAHs (including naphthalene, phenanthrene and anthracene) have a low affinity for particulates and are subject to microbial degradation. Their solubility and vapour pressure is higher than group 2 PAHs, and photo-oxidation and air-water exchange are important in estuaries.

Consequently group 1 PAHs tend to have comparatively shorter residence times and often exhibit a complex distribution pattern. In contrast, *group 2* or high molecular weight (≥200) homologues (including benzo(a)pyrene, fluoranthrene, pyrene and chrysene), are readily adsorbed onto particulates. They are often correlated with suspended solids along estuaries and, due to the high particulate affinity and microbial refractivity, the principal fate of group 2 PAHs is sediment burial.

As part of the national monitoring programme survey of UK coastal waters, the Marine Pollution Monitoring Management Group – MPMMG, (1998) reported ΣPAH (sum of 15 PAHs) concentrations of up to 0.57 µg $l^{-1}$ in tidal waters of the Mersey. Law *et al*, (1997) carried out a more comprehensive survey of PAHs in tidal waters around England; 177 stations were sampled, including some of the MPMMG sites. The latter study found high levels of ΣPAHs in unfiltered water at some of the Mersey sites, e.g. 1.37 µg $l^{-1}$ at Eastham Lock, reducing with distance out into the estuary to 0.028 µg $l^{-1}$ at Burbo Bight and undetectable offshore in Liverpool Bay (figure 37 ).

Although low molecular weight PAHs (e.g. naphthalene, pyrene, fluorene, fluoranthene) were dominant, significant levels of high molecular weight PAHs (e.g. benzo-[ghi]-perylene, benzo-[a]-pyrene and benzo-[p]-fluoranthene) were also present.

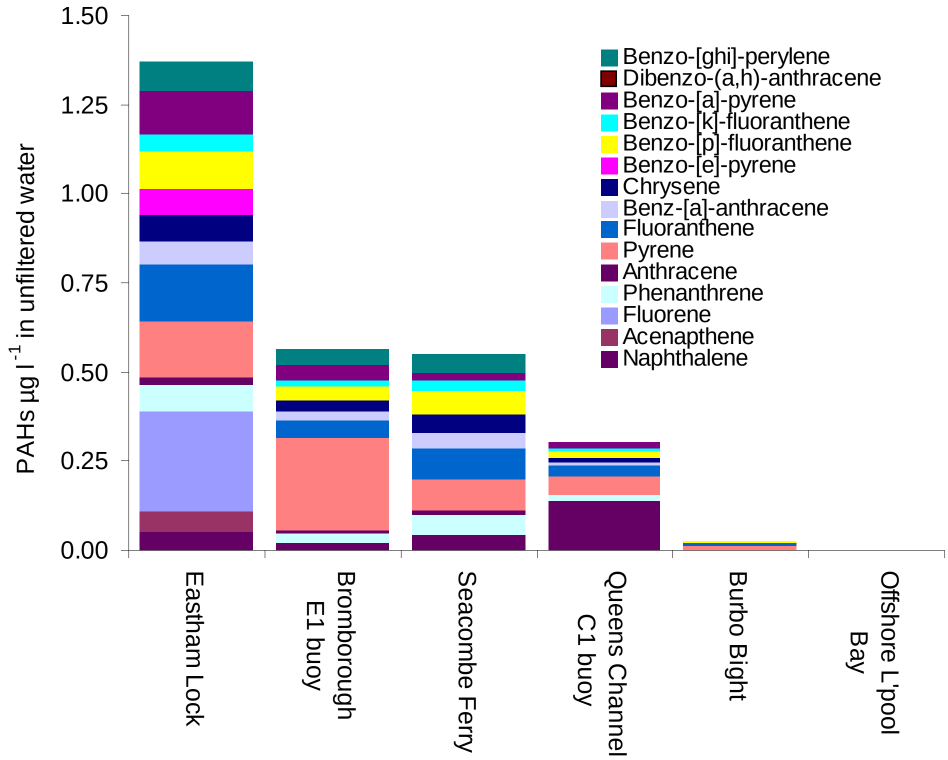



**Figure 37. Total ΣPAH concentrations (µg $l^{-1}$), subdivided into 15 individual PAHs, in unfiltered water from sites along the Mersey Estuary (drawn from data in Law *et al.*, 1997)**

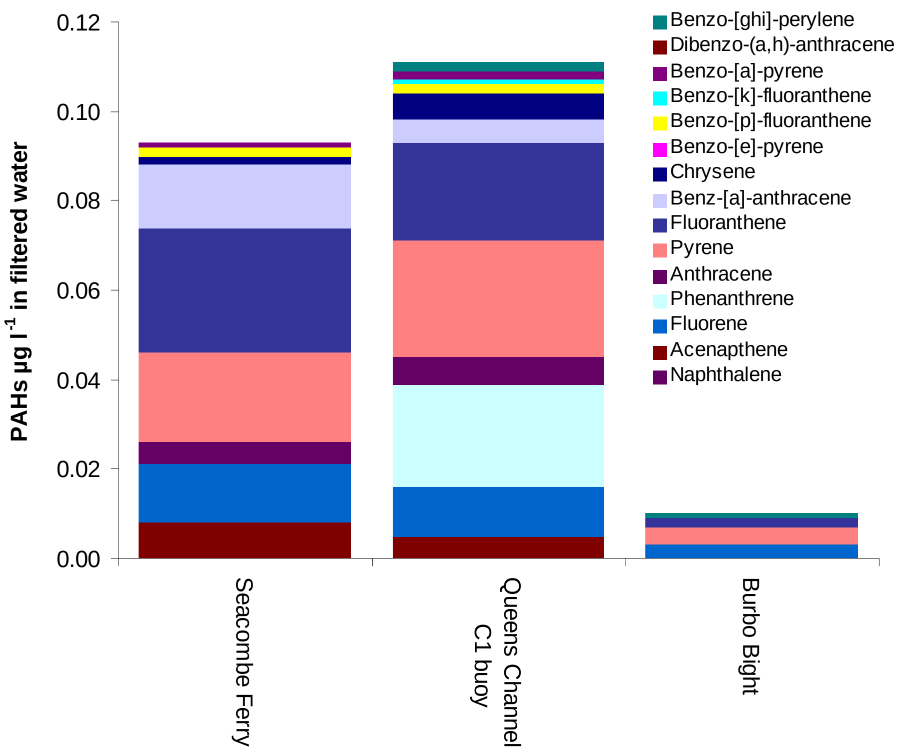



**Figure 38. Total ΣPAH concentrations (µg l$^{-1}$), subdivided into 15 individual PAHs, in filtered water from sites along the Mersey Estuary (drawn from data in Law *et al.*, 1997)**

In comparison with concentrations in some industrialised estuaries (e.g River Tees at Redcar Jetty, ΣPAHs = 10.7 µg l$^{-1}$), such concentrations may be unexceptional, however, ΣPAH concentrations found at Eastham Lock fall above the threshold of 1 µg l$^{-1}$ considered by Cole *et al*., (1999) to be environmentally important. Though there is no environmental quality standard for the protection of aquatic life based on ΣPAH levels in marine waters, some of the values reported in waters of the Mersey Estuary are high compared to the EU drinking water standard which allows a maximum of 0.2 µg l$^{-1}$ and the (same) EU maximum admissible concentration (set to protect human consumers of aquatic life collected from PAH contaminated water). They are also well above the equivalent US criteria of 0.03 µg l$^{-1}$.

With the exception of benzo[a]pyrene at Eastham Locks, individual PAHs found in tidal waters in this study, fall within tentative upper 'safe-levels' based on OSPARCOM guideline ecotoxicological assessment criteria (Oslo and Paris Commissions, 1994).

For three sites along the Mersey, samples were also analysed after filtration and the concentrations of 'dissolved' PAHs determined. These ranged from 'not detected' to 0.028 µg l$^{-1}$ (for fluoranthene) (Law *et al.*, 1997) and are represented in figure 38. Perhaps not surprisingly, the majority of high molecular weight PAHs had been removed (adsorbed to particulate material) and were below detection limits or present only in extremely low concentrations (figure38).

In sediments, PAH concentrations may be persistent (particularly where tidal action is restricted, and degradation limited by anoxia). PAHs derived from petroleum or oil spills and present in the environment can, in some circumstances, be used to identify specific sources (Boehm *et al.*, 1997). In general, PAHs occur in combination rather than as single substances, and despite weathering and biodegradation, the chromatograph profile of PAHs from isolated hydrocarbon mixtures can be indicative of certain sources (Law and Biscaya, 1994); for instance, the ratios of specific PAHs can be used to identify likely sources. 3-ring alkylated PAHs are particularly useful for petroleum source (NB oil spill) identification (Douglas *et al.*, 1996), and 4-6-ring hydrocarbons are generally indicative of pyrogenic origin, being generated by the combustion of fossil fuels and of recent organic material (Dahle *et al.*, 2003).

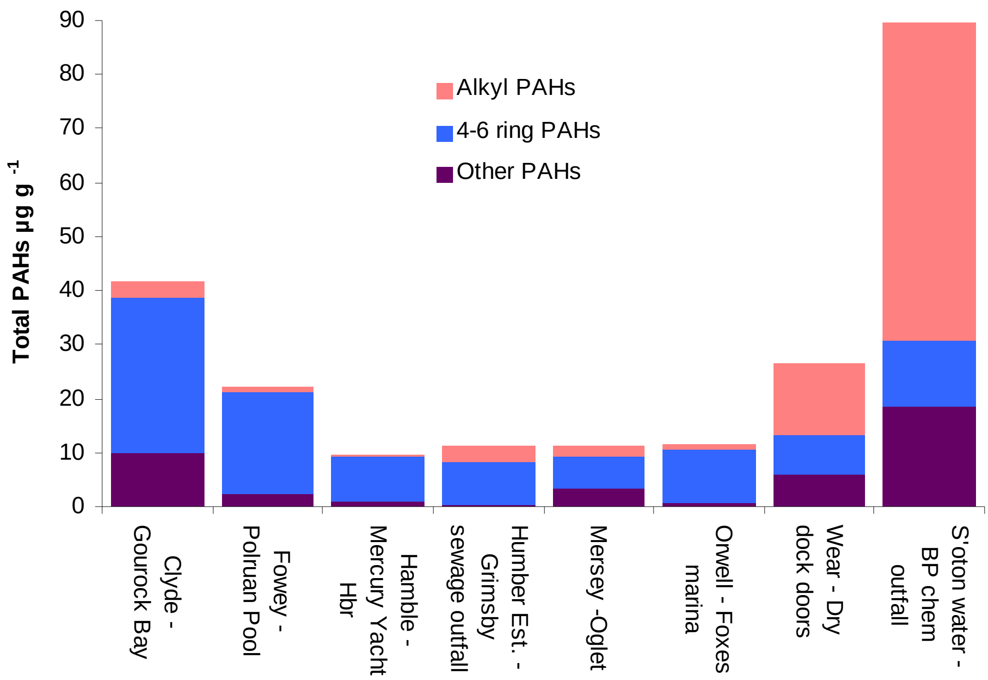



**Figure 39. ΣPAH concentrations (µg $g^{-1}$) in sediments from UK estuaries, subdivided into three categories – alkylated PAHs, 4-6 ring PAHs and others. (Drawn from data in Rogers 2002)**

However, the identification of specific PAH sources in estuarine sediments is often hindered by the complexity and diversity of inputs, together with the dynamic nature of estuarine systems. This may be the case in the Mersey; Rogers (2002), studied PAHs in ten UK estuaries and found that Mersey sediments had a mixed PAH profile throughout its tidal range. Figure 39 shows total PAHs in sediments from the different estuaries for comparison, subdivided into 2-3 ring alkylated PAHs and 4-6 ringed PAHs. Rogers (2002) considered the mixed source profile for the Mersey to be due to mixed petrogenic inputs from numerous discharges, and continuous resuspension, coupled with tidally-driven mixing of historically contaminated surficial sediments.

Data from this study shows that concentrations in UK estuaries range from 0.45 µg $g^{-1}$ at Cloch Point in the Clyde, to a very high level of 89.6 µg $g^{-1}$ dry weight near the BP chemical outfall in Southampton Water. Within this range, total PAH concentration in sediments from Mersey sites would probably classify as moderate (range 0.66 to 11.2 µg $g^{-1}$ dry weight).

ΣPAH concentration in sediments collected from sites along the Mersey is shown in figure 40. Highest levels were recorded at Oglet, across the Estuary from Stanlow and Ellesmere Port. The highest concentrations of alkyl PAHs in the estuary were also recorded here (Rogers, 2002).

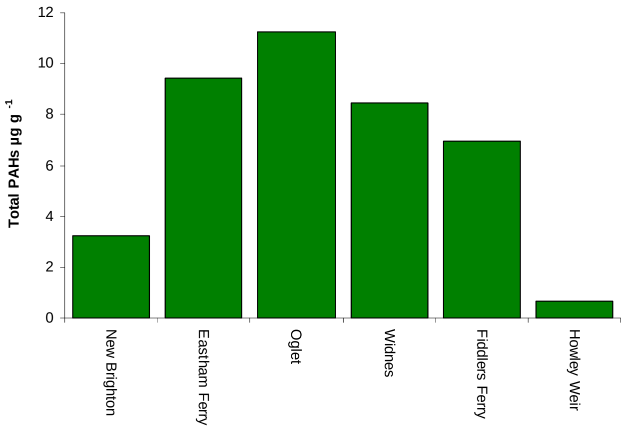



**Figure 40. ΣPAH concentrations (µg $g^{-1}$) in sediments from sites along the Mersey Estuary (drawn from data in Rogers 2002)**

Maintenance dredging to maintain harbour depths and navigation channels has been a feature of the Mersey since the late 1800's. In recent years, CEFAS have determined various pollutants in the dredged material from many UK estuaries including the Mersey, and since 1998, concentrations of PAHs have also been determined, in an attempt to establish current levels of contamination and develop guideline limit values for use in the approval process (Law, *et al.,* 2005). From the suite of PAHs analysed, PAH observed in each sample have been tentatively assigned to sources i.e. individual PAH have been assigned as predominantly oil derived or predominantly combustion-derived on the basis of earlier studies using principal components analysis for source discrimination (Law *et al.,* 1999). No raw data is given, however, representations of ΣPAH in dredged material from the Mersey appears to show concentrations of between 5 – 50 µg $g^{-1}$ PAHs. Sources are mixed, with a slightly larger percentage of PAHs in the dredged material originating from combustion inputs.

CEFAS have also performed similar analyses on samples from the dredge disposal sites. For the Mersey, the disposal site is out in Liverpool Bay, and received 1,732,091 and 1,491,540 dry tonnes of dredged material during 2002 and 2003 respectively (Law, *et al.,* 2005). Concentrations of PAHs at the site are depicted as being between 1 – 10 µg $g^{-1}$ PAHs, similar to that of the dredged material before disposal, although assignment of sources in the samples show a slightly larger percentage of PAHs originating from oil inputs. This apparent anomaly is likely to be due to small patches of bulk oil contamination (Law, *et al.,* 2005).

Away from the disposal site in Liverpool Bay, much lower concentrations (0.033µg $g^{-1}$ dw) of ΣPAHs have been reported by CEFAS (Law, *et al.*, 2005).

King *et al.*, (2004) developed a solid-phase microextraction (SPME) –gas chromatography (GC)-mass spectrometry (MS) analytical method for simultaneous separation and determination of 16 PAHs from aqueous samples. This method is potentially very useful as it allows differentiation between freely available dissolved compounds and those associated with humic material which may be biologically unavailable. The method was applied to porewater samples collected from the Mersey Estuary (site not specified). Total PAH concentrations in porewater are shown in figure 41, and varied widely (between 0.095 and 0.742 µg $l^{-1}$) with depth in the sediment core. 2-4 -ring PAHs predominated (reflecting petroleum contamination) and concentrations of 5-6 -ring PAHs were generally below the limit of detection, possibly be due to a high DOC concentration in the porewater (King *et al.*, 2004).

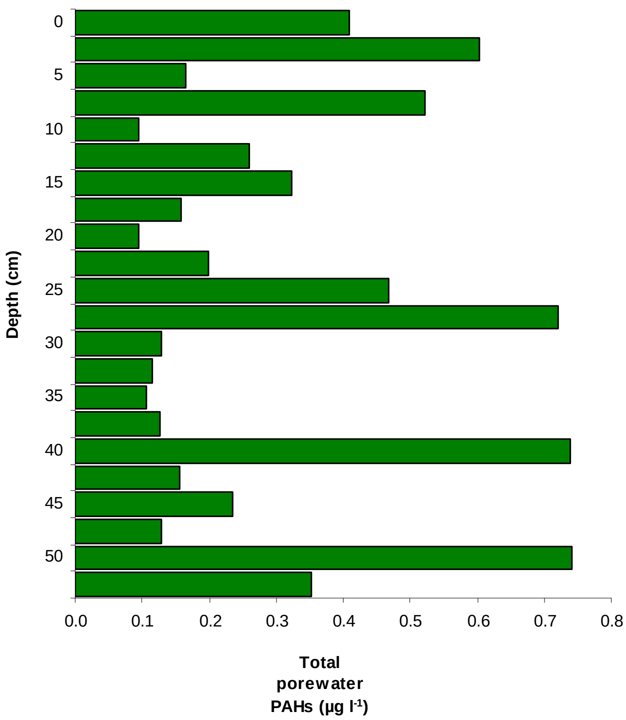



**Figure 41. Depth profile of dissolved ΣPAH concentrations (µg $l^{-1}$) in porewater samples from a sediment core from the Mersey Estuary (drawn from data in King *et al.*, 2004)**

Thus, the literature indicates that PAH enrichment in Mersey sediment is consistent with an anthropogenic origin. The source of these PAHs may include oil spills, industrial discharges, airborne particulates derived from combustion products, urban run-off, various trade and domestic inputs, and marina activity.

*Recent PAH monitoring data*

There is no available information in the EA monitoring data set for total or dissolved PAHs in tidal- or fresh-waters of the Mersey. Figure 42 depicts the NMMP monitoring data for sediments (dry weight) between 2000 and 2005 inclusive, for

Seacombe Ferry. Median concentrations of all PAHs exceed the TELs, and with the exception of naphthalene and anthracene, 75th percentiles are above PELs. Maximum concentrations for all PAHs recorded during this period exceed PELs.

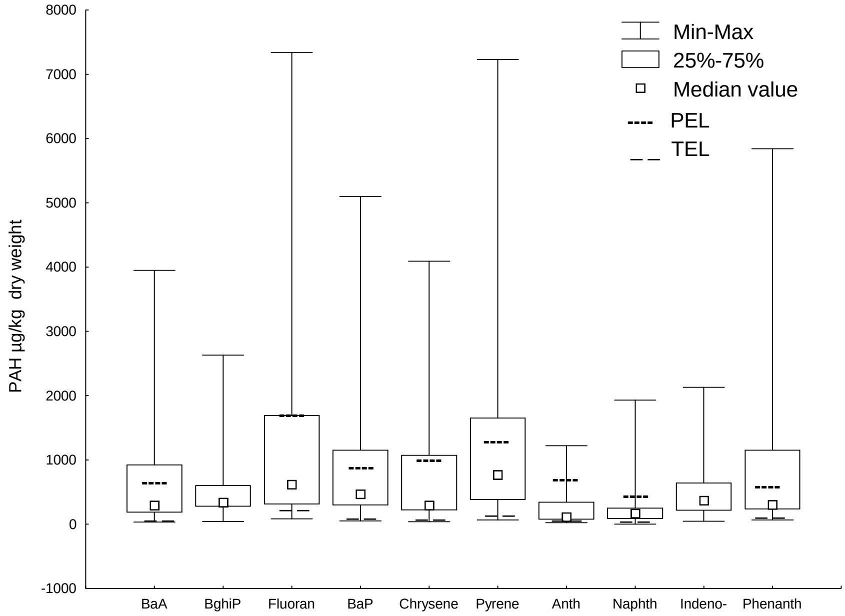



**Figure 42. PAH concentrations (µg $kg^{-1}$ dry weight) in sediments from the Mersey Estuary (Seacombe Ferry) 2000-2005 (data source EA/NMMP). PELs = Probable effect levels and TELs = Threshold effect levels are shown for individual PAHs where such levels have been set.**

Annual median concentrations of PAHs have generally declined over this sampling period, although there is considerable variation in the data. This is illustrated for naphthalene (figure 43) which shows with an *increase* in the number of values exceeding the PEL in 2004.

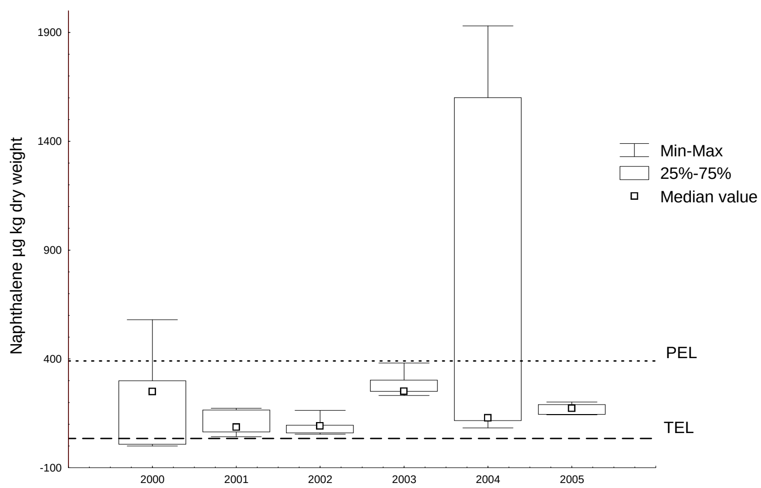



**Figure 43. Trends in naphthalene concentrations (µg $kg^{-1}$ dry weight) in sediments from the Mersey Estuary (Seacombe Ferry) 2000-2005 (data source EA/NMMP). PELs = Probable effect levels and TELs = Threshold effect levels are shown.**

PAH data are available for only one other NMMP site, Buoy C1 outside the mouth of the estuary (figure 44). Concentrations in sediments are generally much lower here, although median concentrations are above TELs for all PAHs but anthracene. PELs were not exceeded during the sampling period.

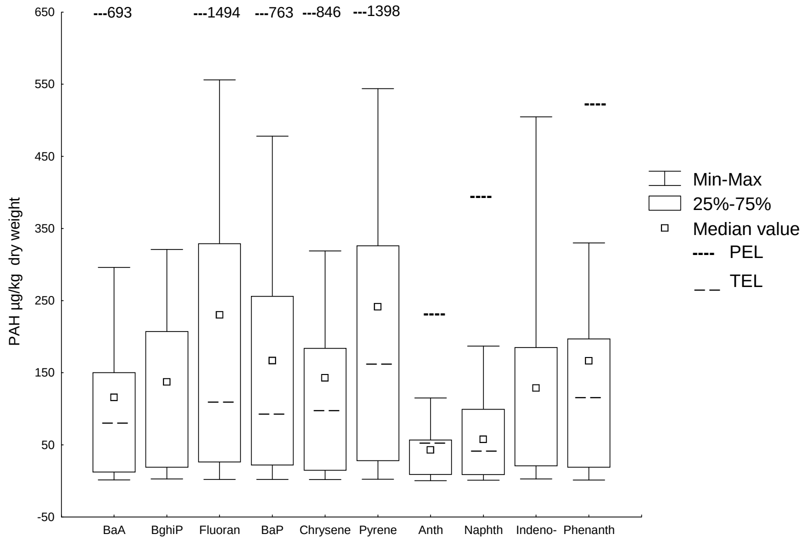



**Figure 44. PAH concentrations (µg kg$^{-1}$ dry weight) in sediments from Buoy C1 2000-2005 (data source EA/NMMP). PELs = Probable effect levels and TELs = Threshold effect levels are shown for individual PAHs where such levels have been set.**

Recent monitoring data (EA/NMMP) appears to be limited to only one site within the actual estuary (Seacombe Ferry), giving little or no indication of spatial distributions of PAHs, or values within the European Marine Site. The following figures (45 and 46) represent CEFAS monitoring data for 2001 which gives a modicum of spatial coverage, and includes sites within the Narrows, and out into the Crosby Channel (outside the EMS). The figures represent those PAHs for which sediment quality guidelines are set, and show the general distribution of PAH contamination and it's relevance in terms of TEL's and PEL's.

Maximum values, many of which exceed the guideline TELs, generally occur within the Narrows, although high values of many PAHs also occur in the Crosby Channel south of Formby Point. On this basis chronic effects in the mid-upper Mersey cannot be excluded. Further offshore in Liverpool Bay, PAH concentrations are much lower. PELs are not exceeded for any individual PAH and effects are unlikely.

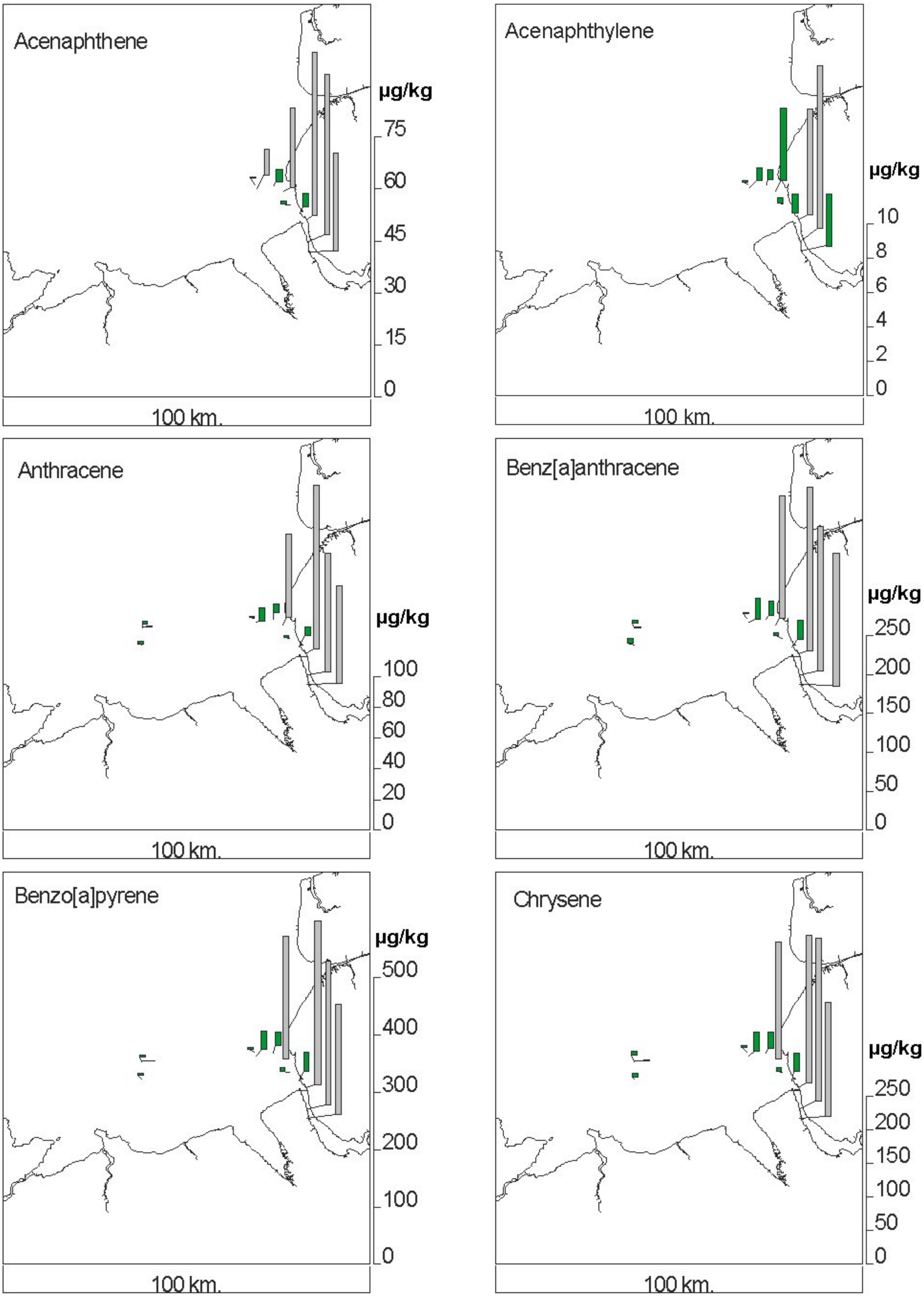



**Figure 45. Individual PAHs in sediment, 2001. Classification of Mersey Estuary and Liverpool Bay sites into zones based on interim marine sediment quality guidelines (ISQG's) and probable effect levels (PEL's) (from CCME 1999). Data source: EA/CEFAS.** Red = effects expected; Grey = possible effects cannot be excluded; Green = no harm to the environment expected.

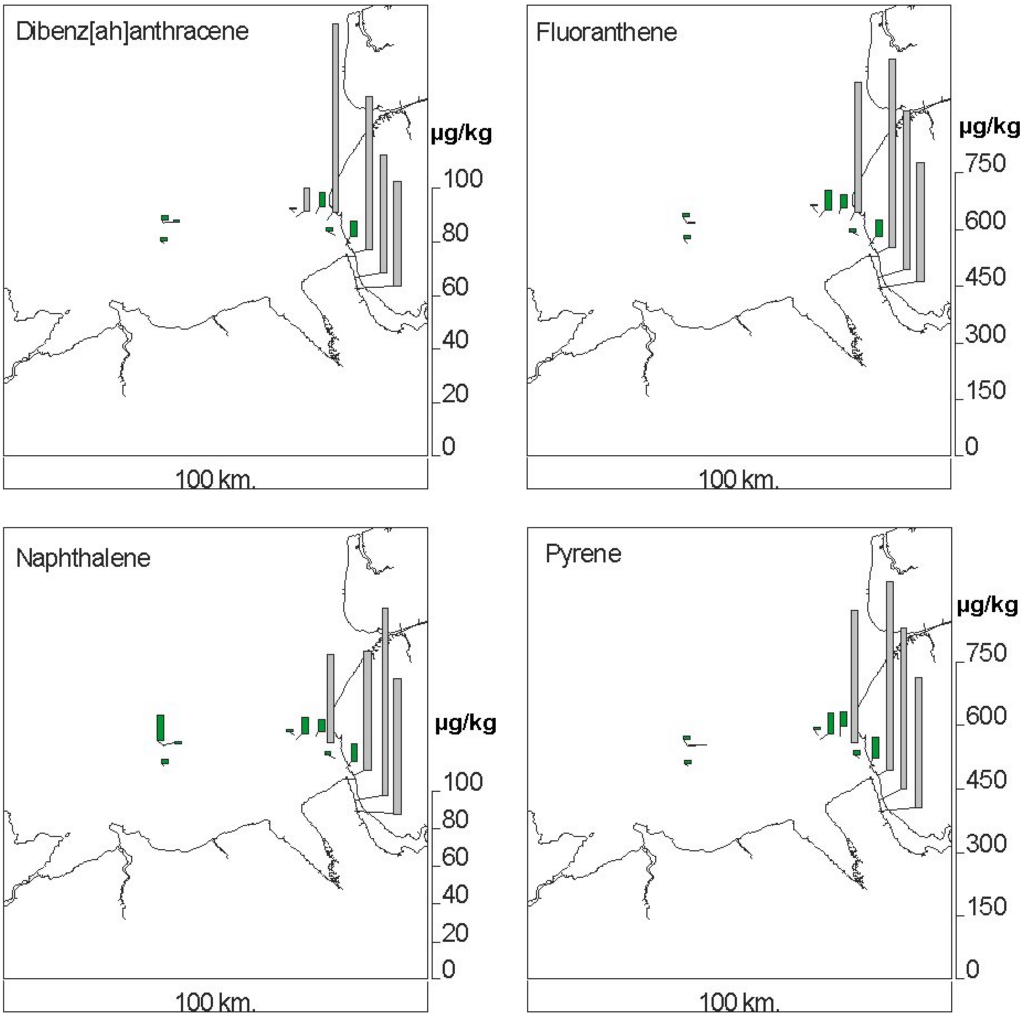



**Figure 46. Individual PAHs in sediment, 2001. Classification of Mersey Estuary and Liverpool Bay sites into zones based on interim marine sediment quality guidelines (ISQG's) and probable effect levels (PEL's) (from CCME 1999). Data source: EA/CEFAS.** Red = effects expected; Grey = possible effects cannot be excluded; Green = no harm to the environment expected.

*Volatile organics (solvents, chlorinated hydrocarbons).*

A number of volatile organic compounds (VOCs) are, potentially, endocrine disruptors, as well as being toxic directly and may be discharged into the European marine site in varying quantities (see section 4). These compounds include:

Trichloromethane (Chloroform)

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

Trichloromethane has an EQS of 12µg $l^{-1}$ (annual average) in all waters. Data for tidal waters of the Mersey Estuary are summarized in figure 47. The majority (28%) of values at the seaward sites (nb New Brighton and Seacombe) were below detection limits of 0.1 µg $l^{-1}$. Concentrations increase in an upstream direction with maximum values at Fiddlers Ferry and Monks Hall. However, even at these sites median values were below the EQS by an order of magnitude implying that trichloromethane is not a significant concern in tidal waters.

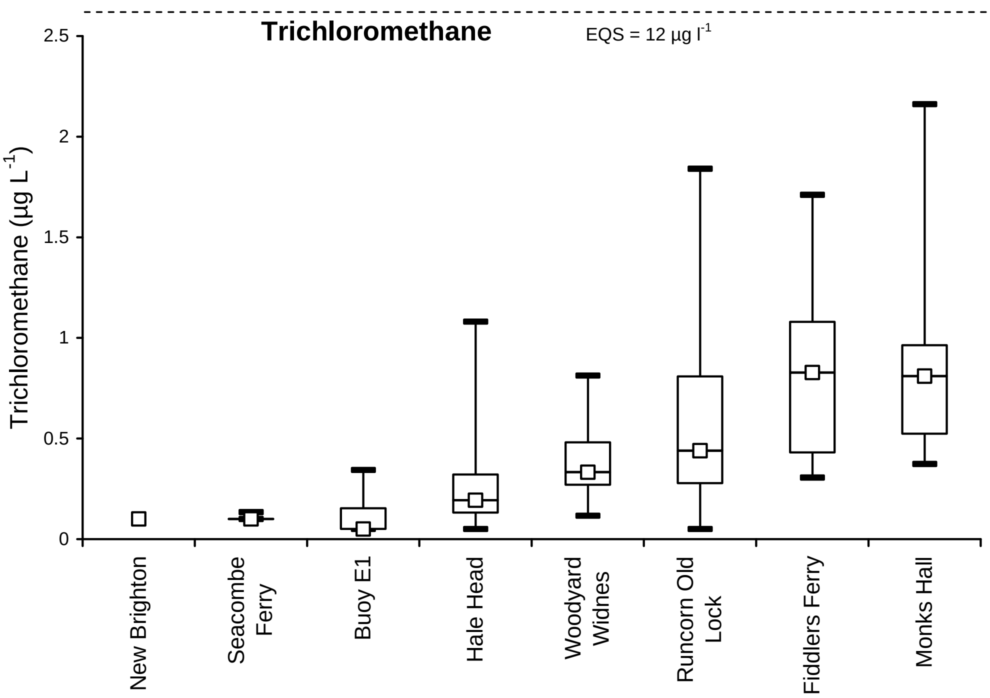



**Figure 47. Trichloromethane in tidal waters of the Mersey Estuary (2002-2004; data source EA)**

Tetrachloromethane (Carbon tetrachloride)

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

Tetrachloromethane is a List I compound, with an EQS of 12µg $l^{-1}$ (annual average) in all waters. Of the data for Mersey tidal waters the majority of values (95%) were below detection limits (0.1 µg $l^{-1}$) and were only detectable on occasions at sites between Hale and Fiddlers Ferry, where the highest concentration was 0.4 µg $l^{-1}$ (at

Runcorn Old Locks); at seaward stations (New Brighton, Seacombe and Buoy E1) concentrations were consistently <DL. Average concentrations at all sites were below the EQS by two orders of magnitude, implying that tetrachloromethane is not likely to be a significant concern in tidal waters. However it should be noted that little sampling has taken place within boundaries of the SPA.

Chlorinated Ethylenes (e.g. trichloroethylene= trichloroethene)

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

Data for trichloroethylene (trichloroethene) are examined here as being representative of this group of compounds. More than 80% of data for Mersey tidal waters were below detection limits (0.1 µg $l^{-1}$). Detectable levels were present upstream though median concentrations were, invariably, below the EQS (figure 48) implying that trichloroethene is not a significant concern in tidal waters.

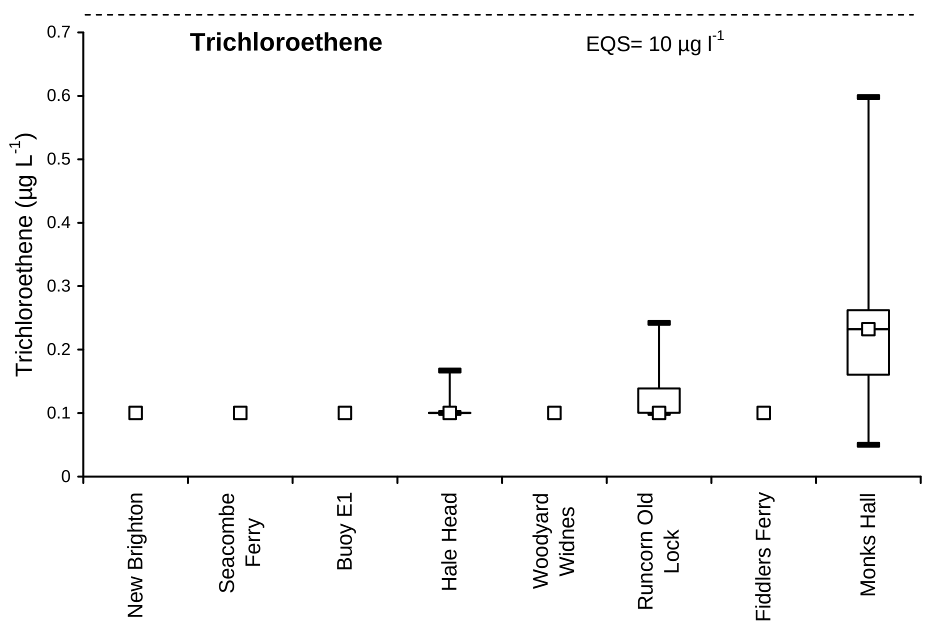



**Figure 48. Trichloroethene in tidal waters of the Mersey Estuary (2002-2004; data source EA)**

Trichloroethane

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

1,1,1 Trichloroethane has an EQS of 100µg $l^{-1}$ (annual average) in all waters. All Mersey tidal water samples were below the detection limit of 0.1 µg $l^{-1}$ and therefore are considered to be of little direct toxicological relevance.

It seems unlikely, therefore, that volatile organics represent a significant threat to the European marine site, though confirmation of sources of trichloromethane and to a lesser extent trichloroethene, would seem important to establish.

## 6.2 Non-Toxic Contaminants

This section deals with non-toxic contamination in the Mersey Estuary EMS. Concentrations of non-toxic substances are an important issue in marine sites. 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). Ammonia, a nitrogen species, is included in this section, although as discussed below, unionised ammonia can be toxic.

### 6.2.1 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 treatment works (WwTWs), discharges from some industrial processes (including detergents and fertilizers) 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 13 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 13. 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 |

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 Mersey Estuary indicates that the Mersey has a long history of severe pollution from industrial and domestic effluents, which, in the past, were discharged into the estuary with little or no treatment. Consequently, extended dissolved oxygen sags occurred throughout the tidal cycle, particularly during the summer months, over long reaches of the estuary. Aesthetic impacts included heavily fouled beaches (crude sewage, and fatty material - mainly from edible oil manufacturers) and tarry residues from bulk handling of hydrocarbons (tanker operations and general shipping - for a historical perspective see Jones, 2005). A cleanup scheme was initiated in the early 1970's, the principal aims of which were to improve water quality at the tidal-limit (particularly BOD and ammonia), to construct interceptors and effluent treatment works providing primary sewage treatment and to impose stringent control on industrial discharges (Jones, 2005). These measures, coupled with the need to comply with the European Union Urban Wastewater Treatment Directive of 1991 (91/271/EEC) (secondary treatment for all estuarine discharges) resulted in significant improvements to the water quality of the estuary.

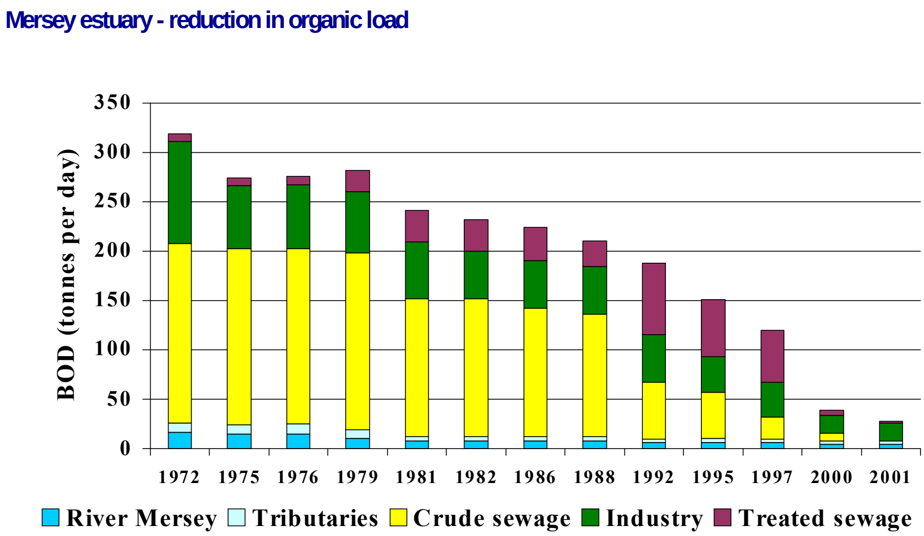



**Figure 49. Changes in the components of effluent discharges 1972 – 2001 (from Jones, 2005)**

Figure 49 exemplifies the temporal trend in organic load (BOD) to the estuary and highlights a gradual reduction in the substantial load from crude discharges (by the phased introduction of treatment), and a dramatic reduction in the increasing load from treated effluents in 2000, when secondary treatment was introduced. The contribution from the River Mersey appears to be relatively minor; however, as noted above, the potential for nutrient enrichment and localised effects is determined by characteristics of the site, and because of lack of dilution in the estuary, the impact was significantly greater than for discharges from Birkenhead and Liverpool (Jones, 2000).

Thus, despite improvements, the Mersey may still suffer from a degree of nutrient enrichment.

**Table 14. Loads of nutrients in STW (sewage treatment work) effluents input directly (below the tidal limit) to the Mersey Estuary (average of loads for 1995 and 1996). Loads are in units of Mmol (moles x $10^6$) nutrient $y^{-1}$. STW (Sewage Treatment Work) input load is shown as % of total (STW + fluvial) load. (from Nedwell *et al*., 2002).** Note; Fluvial loads will include all upstream STWs.

| TOxN* | | | $NH_4$ | | | $PO^{3-}_4$ | | |
|---|---|---|---|---|---|---|---|---|
| STWs | Fluvial | % | STWs | Fluvial | % | STWs | Fluvial | % |
| 8.8 | 2667 | 0.3 | 83.2 | 1295 | 6 | 9.8 | 146.8 | 6.3 |

* TOxN = Total Oxidised Nitrogen = nitrite + nitrate

Nedwell *et al*., (2002) estimated nutrient loads in WwTW effluents input directly (below the tidal limit), and fluvial inputs to several UK estuaries including the Mersey (table 14). This survey showed inputs of ammoniacal nitrogen to be the highest of all the 93 estuaries in the study, and $TO_xN$ and orthophosphate inputs to the Mersey Estuary to rate amongst the highest in the UK (Nedwell *et al*., 2002).

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 Mersey were above detection limits, and ammonia, nitrite, phosphate and silicate were particularly elevated in comparison to other UK sites. A second report also notes that the highest concentrations of ammonia in UK estuaries occurred in the low salinity waters of the Mersey (MPMMG, 2004). The more recent survey focuses on inshore sites, which for the Mersey is in Liverpool Bay. Here, concentrations of phosphate and TOxN exceeded the OSPAR assessment criteria. Surveys of winter nutrient levels at NMP sites also indicated that Liverpool Bay is a relative hotspot for ammonium (6.8µm compared to typical coastal water values <1µm), influenced presumably by inputs from the Mersey (CEFAS 2003). Not surprisingly, enrichment in chlorophyll *a* was also observed during this survey (though chlorophyll may, in part, represent input from estuarine microalgae rather than in situ production).

Concentrations of silicate are elevated in the Mersey; at the tidal-limit they were typically three times the values found in the Ribble (7,500 $\mu g.l^{-1}$ and 2,500$\mu g.l^{-1}$ respective means for the 20-year period 1984-2004, (P.D. Jones, EA, *pers comm*)). This is considered to be a consequence of the greater domestic/industrial activity in the Mersey Basin rather than differences in the respective geologies. This is contrary to the view expressed by a number of authors (Nedwell *et al.,* 2002; Gowen *et al.,* 2002) who suggest that silicate loads are relatively independent of anthropogenic influences. This phenomenon is also observed in other industrialised systems such as the Clyde, Thames and Belast Lough (MPMMG, 2004). Below the tidal-limit there is an additional significant input of silicate from a detergent manufacturer based in Warrington. The impact on the Mersey and the local coastal waters is uncertain but may enhance diatom production and/or alter the species composition as diatoms tend to dominate ecosystems whenever silicate is abundant (Egge & Aksnes, 1992).
A recent EA/University of Liverpool collaborative project investigating the seasonality and distribution of nutrient salts and phytoplankton in the northern Irish Sea during 2002 (Kennington, 2004) also reported that winter concentrations of DIN and P recorded from Liverpool Bay exceeded the recommendations of the CSTT (1997) and the OSPAR commission (2002). Additionally, recorded summer chlorophyll concentrations were in excess of these recommendations for at least one month during the summer of 2001.

This study concludes that under these recommendations Liverpool Bay (the Mersey and Dee Estuaries in particular) could be classed as hypernutrified[13] and possibly be prone to future eutrophication. Indeed, an EEA report investigating eutrophication in Europe's coastal waters, notes that in the Celtic Seas eutrophication is restricted to a few areas, including the Irish Sea, Liverpool Bay and Mersey Estuary (EEA, 2001). The report states that in many estuaries of the Irish Sea concentrations of both nitrate and phosphate have been anthropogenically enhanced, although the Mersey Estuary/Liverpool Bay area is one of the few areas considered to be showing signs of

[13] See Glossary

eutrophication - 'undesirable' biological changes associated with increased nutrient concentrations. A CEFAS study identified the Mersey as one of the major sources of nutrients to the coastal waters of England and Wales (CEFAS, 2003).

Also reported are decreases in oxygen concentration in the heavily urbanised Mersey Estuary and, at times of stratification (primarily during late spring and summer) in Liverpool Bay (EEA, 2001). Fluxes of TOxN, phosphate, ammonium and silicate to sea have been derived for the Mersey and Thames Estuaries as part of the Joint Nutrient Study Phase (JoNuS II) project (CEFAS, 2001). At both sites there were elevated nutrient inputs in winter months when loads from rivers were high and biologically driven removal processes minimal. The Thames delivered a greater seasonal TOxN, phosphate and silicate flux to the coast than the Mersey, although there was an elevated ammonium flux into Liverpool Bay which was higher than the Thames all year round (by 6 and 16 times, in winter and summer respectively).

There is very little specific information on sensitivity of estuarine macrofauna, or on special interest features within the EMS, to nutrient enrichment. For example there are no specific studies available of nutrient enrichment impact on faunal/algal or saltmarsh communities, or bird populations. Perhaps contra-intuitively, the British Trust for Ornithology have voiced concerns that reductions in BOD load via sewage inputs in several estuaries including the Mersey, may have serious implications for marine life and bird populations in terms of declining prey availability (Burton *et al.*,, 2003) (see section 5).

Nevertheless, it appears from the literature, that eutrophication as a result of nutrient enrichment is generally considered to be a significant threat for the Mersey Estuary and Liverpool Bay. Results from the JoNuS II project showed that during a spring bloom, the euphotic zone standing stock of phytoplankton in Liverpool Bay was ~3 times that observed at an Irish coastal station, and summer biomass was also significantly higher. Nutrient and phytoplankton data collected during the study provided *prima facia* evidence that enrichment of Liverpool Bay stimulated productivity and biomass of phytoplankton (CEFAS, 2001). Unfortunately most of the data available is for Liverpool Bay, outside of the SPA, although as noted above, the Mersey is considered to be a major source of nutrient and ammoniium inputs to the Bay.

Elsewhere, locally elevated nutrient levels (e.g. from sewage, agricultural runoff or aquaculture) have result in increased growth of epiphytic and blanketing algae, e.g. Poole Harbour (Langston *et al,* 2003). Mudflats and other intertidal habitats can be damaged through smothering and by de-oxygenation. Microalgal blooms may also be a problem; shellfish kills as a result of *Phaeocysti*s bloom crashes have occurred in the area[14], and summer blooms of bioluminescent dinoflagellate *Noctiluca scintillans*, (responsible for red-tides) such as that of 1997 have clear potential to promote anoxic conditions after bloom die-back (Shammon *et al.,* 1997; Kennington *et al*., 1998; Gowen *et al*., 2000).

[14] http://www.cheshire-biodiversity.org.uk/habitat-mudflats.htm

Nutrient Quality Criteria.

Nutrient monitoring is required by the EC Urban Waste Water Treatment Directive (UWWTD) (91/271/EEC), the Nitrates Directive (91/676/EEC) and the OSPAR Strategy to Combat Eutrophication. The aim is to determine whether waters show signs of eutrophication: defined as ‘an undesirable disturbance to the balance of organisms present and to the quality of the water concerned, which results from the accelerated growth of algae and higher plant forms caused by anthropogenic sources of nutrients’ (91/271/EEC). Both the EC and OSPAR measures require action to reduce inputs when there are reasonable grounds for concern that eutrophication already affects waters or may occur in currently unaffected waters. The UWWTD requires treatment of point source discharges so as to reduce their nutrient content, the Nitrates Directive requires reduction of diffuse inputs of nutrients and OSPAR seeks to reduce all nutrient inputs to marine waters (MPMMG, 2004).

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. The EA’s Technical Guidance for Water Quality assessment framework (WQTAG089a) is divided into the assessment of a) the risk of eutrophication impacting on sites and b) the extent of ecological impact. Parameters including modelled predictions and temporal trends in nutrient loadings, nutrient concentrations, and impacts (phytoplankton biomass and species, DO status, evidence of species decline) are recommended for considering the risks and impacts of eutrophication in SAC and SPA estuaries for the purposes of reviewing new and existing permissions as required under the Conservation (Natural Habitats &c) Regulations, 1994. This “weight of evidence” based framework attempts to facilitate evaluations in a transparent way. However, judgement of nutrient status in the Mersey Estuary EMS, as elsewhere, still consists, to a certain extent, on 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 statutory standards, Background Reference Concentrations (BRCs) and Ecotoxicological Assessment Criteria (EACs) do not 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 Mersey Estuary, and for initiating management responses:

- EU nitrates directive 91/676/EEC, on the protection of all waters against pollution caused by nitrates from agricultural sources, calls for the identification of all waters that contain **50mg $l^{-1}$ nitrate**.
- The USEPA is still in the process of arriving at their national nutrient strategy but has for many years proposed a limit of **10mg $l^{-1}$ nitrate** 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 are suggested draft common assessment criteria for areas of UK waters subject to the OSPAR Common Assessment Procedure for eutrophication (table 15). The most recent NMMP report (MPMMG, 2004) uses these tentative values to evaluate present levels of contamination against pristine conditions, with the caveat that 'the results must be treated with a great deal of caution because BRC values do not yet reflect regional differences in geochemistry and EAC values have been extrapolated from limited datasets'.

**Table 15. Draft Common Assessment Criteria for the OSPAR Comprehensive procedure** (from MPMMG, 2004)

| | Dissolved Inorganic Nitrogen (salinity related and/or region specific) background cconcentration | Elevated winter Dissolved Inorganic Nitrogen levels (roughly set at >50% above salinity related and/or region specific background concentration) | Dissolved Inorganic Phosphorus (salinity related and/or region specific) background concentration | Elevated winter Dissolved Inorganic Phosphorus levels (roughly set at >50% above salinity related and/or region specific background concentration) |
|---|---|---|---|---|
| Offshore North Sea | 10 µmol $l^{-1}$ | >15 µmol $l^{-1}$ | 0.6 µmol $l^{-1}$ | >0.8 µmol $l^{-1}$ |
| Channel | 9 µmol $l^{-1}$ | >15 µmol $l^{-1}$ | 0.4 µmol $l^{-1}$ | >0.8 µmol $l^{-1}$ |
| Irish Sea (saline waters) | 12 µmol $l^{-1}$ | >18 µmol $l^{-1}$ | 0.8 µmol $l^{-1}$ | >1.25 µmol $l^{-1}$ |

- There is a proposed EQS of **0.021mg $l^{-1}$ un-ionised ammonia ($NH_3$-N) AA (Annual Average)** 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).

- In recognition of the impact that the ammonium ion may have at higher salinities, a total ammonia limit of **1.1 mg $l^{-1}$ -N AA (annual average)** and **8.0 mg $l^{-1}$ –N MAC (maximum allowable concentration)*** is also proposed for UK waters based on USEPA, 1989, 1999 recommendations and a review carried out by Eddy (2004) for the Environment Agency

*WQTAG guidance also sets these standards as targets for the RoC (WQTAG, 2005a)

Recognising the dilemma in arriving at standards, there have been other 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 16):

**Table 16. 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 Mersey Estuary 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 the Mersey Estuary

- comparisons with other areas
- validity of guideline values and classification schemes

*GQA scheme: TIN and TRP*

Cole *et al*., (1999)[15] 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 classifications for TIN and TRP for the Mersey are graded B and C respectively (table 17).

**Table 17. 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 |

[15] An updated version of Cole *et al.,* (1999), prepared in 2003 by Power, B., Girling, A. and Fisk, B. (independent Environmental Consultants) is now available (ISBN: 1 85716 747 3), 206pp + Appendices.

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 Mersey 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. Current assessment criteria (WQTAG guidance) takes assessment through logical progression ie from nutrient load/exposure to algal growth to undesirable impacts. 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:

{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).

**Recent monitoring data**

EA data for nutrients in the EMS are for tidal waters, and generally for the period 2002-2004, therefore it is not possible to determine long-term trends. Data has not been made available for concentrations in freshwater inputs (including the Manchester Ship Canal), WwTWs or industrial discharges.

**Phosphate**

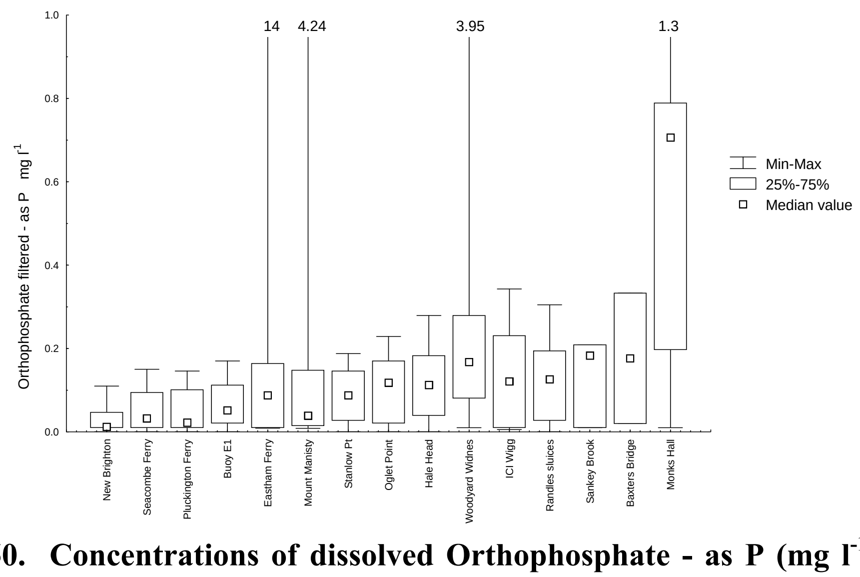



**Figure 50. Concentrations of dissolved Orthophosphate - as P (mg $l^{-1}$) in tidal waters of the Mersey Estuary. 1997. Data source: EA . Data are for 2002 - 2004.**

EA data for phosphate in tidal waters of the EMS are for the period 2002-2004. The more extreme phosphate concentrations (up to 14mg $l^{-1}$ at Eastham Ferry - 2004) have occurred downstream of freshwater and point source inputs (figure 50): notably Eastham Ferry - close to Eastham Locks, where the Manchester Ship Canal joins the Estuary, Monks Hall - close to the Mersey river at the tidal limit of the Estuary, Mount Manisty and Widnes - in the vicinity of the waste water treatment works. Unfortunately data is not available for concentrations in freshwater inputs, WwTWs or industrial discharges, therefore high levels cannot be directly attributed to sources.

Median concentrations of phosphate for the period are also generally more elevated toward the freshwater end of the Estuary - up to 0.71 mg $l^{-1}$ at Monks Hall, again suggesting that the origins of much of the phosphate load are outside the Estuary. The approximate background for the tidal waters (25$^{th}$ percentile) in the estuary is in the range 0.01 – 0.197mg $l^{-1}$, invariably above the 0.1µg $l^{-1}$ (0.0001 mg $l^{-1}$) criteria set by the EPA(US) to protect estuarine and marine organisms, but generally in the upper middle range reported by Parr *et al* (1999) for coastal waters (0.007 – 0.165mg P $l^{-1}$). Despite the dense population and large conurbations in the Mersey catchment, there are also extensive areas of farmland and uncultivated peat mossland in the Mersey catchment. Livestock farming is the major agricultural use in the uplands of the region, whilst large-scale arable farming is prevalent in the Mersey Valley. Livestock and fertilisers therefore represent a potential source of phosphates in freshwaters of the SPA and probably contribute to the phosphate load in the estuary.

**Nitrogen Species**

The available EA monitoring data for nitrogen species in tidal waters of the Mersey consists principally of TON (total oxidised nitrogen - nitrate + nitrite), nitrite and ammonia values 2002 – 2004. There is also some limited data for nitrate. All are for dissolved (filtered) as N).

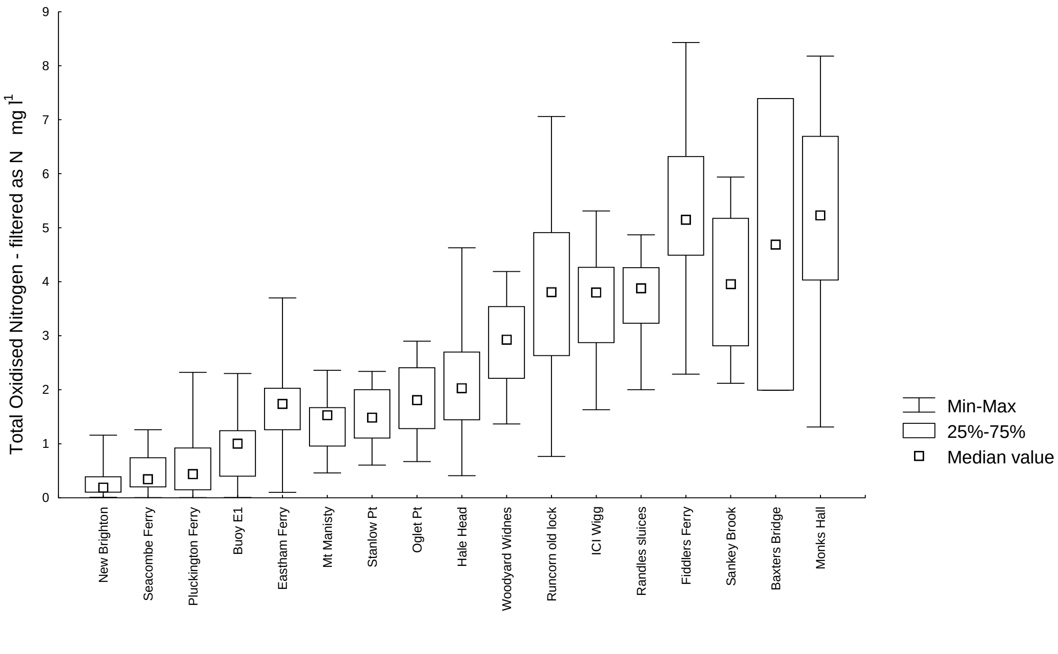
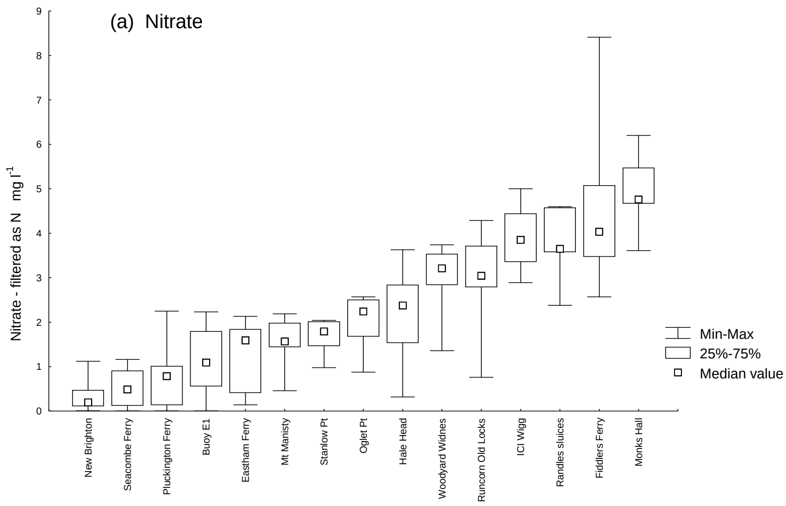



**Figure 51. Nitrogen –total oxidised filtered – as N (mg $l^{-1}$) in tidal waters of the Mersey Estuary 2002 – 2004. Data source: EA**

TON values for the period are shown in figure 51. The more elevated concentrations occurred at inner estuarine sites (up to 8.4 mg $l^{-1}$ at Fiddlers Ferry – 2004). Median concentrations for the period are also more elevated toward the freshwater end of the estuary, up to 5.23 mg $l^{-1}$ at Monks Hall, and there was a small peak at Eastham Ferry in the vicinity of the Manchester Ship Canal lock gates, and another at Fiddlers Ferry.

Figure 52 exemplifies EA monitoring data for nitrate and nitrite. Perhaps unsurprisingly, nitrate values are higher than those for nitrite (up to 8.41 mg $l^{-1}$ at Fiddlers Ferry) indicating that nitrate comprises the greater proportion of TON (nitrate typically makes up the largest proportion of nitrogen inputs to estuaries, with nitrite and ammonia usually accounting for < 10%). Recalculated as nitrate (as opposed to dissolved nitrate as N), maximum values are 27-37 mg $l^{-1}$ - still below the EC nitrate Directive's 50 mg $l^{-1}$ threshold for any waters. The 25$^{th}$ percentile values for dissolved nitrate are calculated to be between 0.1 and 4.67 mg $l^{-1}$, which arguably approximates to a background reference for the area.



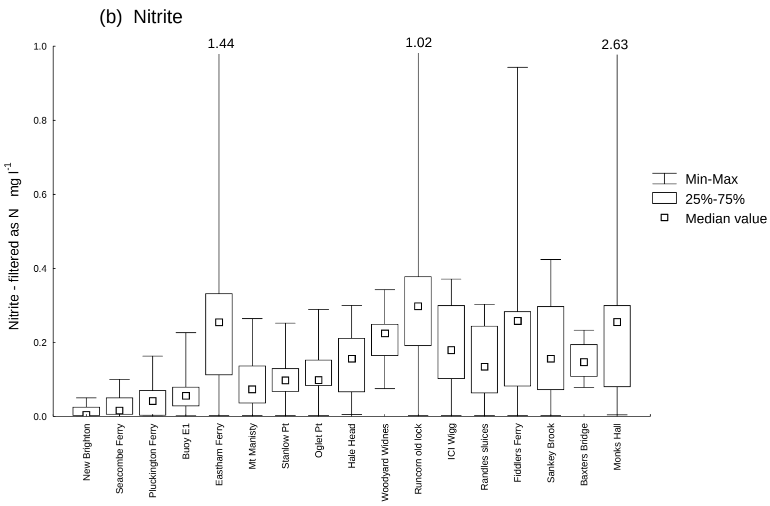




**Figure 52. Nitrate (a) and Nitrite (b) concentrations - filtered as N – (mg $l^{-1}$) in tidal waters of the Mersey Estuary. Nitrate values are for 2003 – 2004; Nitrite for 2002 – 2004. Data source: EA . NB Note the different scales**

Almost all nitrate values, (roughly 92% - n = 126) for tidal waters sites 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 68% 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).

Both nitrate and nitrite levels are generally higher toward the freshwater end of the estuary, although peaks in nitrite occur at Eastham Ferry, Runcorn Old Lock, Fiddlers Ferry and Monks Hall, suggesting that the nitrite (or ammonia) component of inputs might be responsible for similar peaks observed in TON (figure 51). Again data is not available for concentrations in freshwater inputs, WwTWs or industrial discharges; therefore the 'hotspots' cannot be directly attributed to sources.

Effects on many of the species in the EMS are largely unresearched, but in view of the conservation importance of the site, 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.

**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.

Cole *et al.,* (1999) noted that in the Mersey Estuary, at a mean unionised ammonia concentration of 0.008 mg $NH_3$ (N) $l^{-1}$, a diverse invertebrate population was present and this region was passable by flounder and salmonids.

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 in estuaries 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 as
un-ionised and ionised species ($NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$), even if only at very low concentrations. It is derived either from the breakdown of organic nitrogen (mineralisation) or by the reduction of nitrate (denitrification). Ammonia as an intermediate stage in nitrogen fixation (conversion of atmospheric $N_2$ to fixed nitrogen and subsequent incorporation into microbial proteins, etc) is a relatively unimportant source in comparison to mineralisation (Cole *et al.,* 1999). However, anthropogenic sources are generally more important in estuaries, notably sewage treatment effluent and, in some situations, run-off from agricultural land (Seager *et al* 1988). In tidal waters, the primary source of ammonia is direct discharge from Waste Water Treatment Work (WwTW) 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.

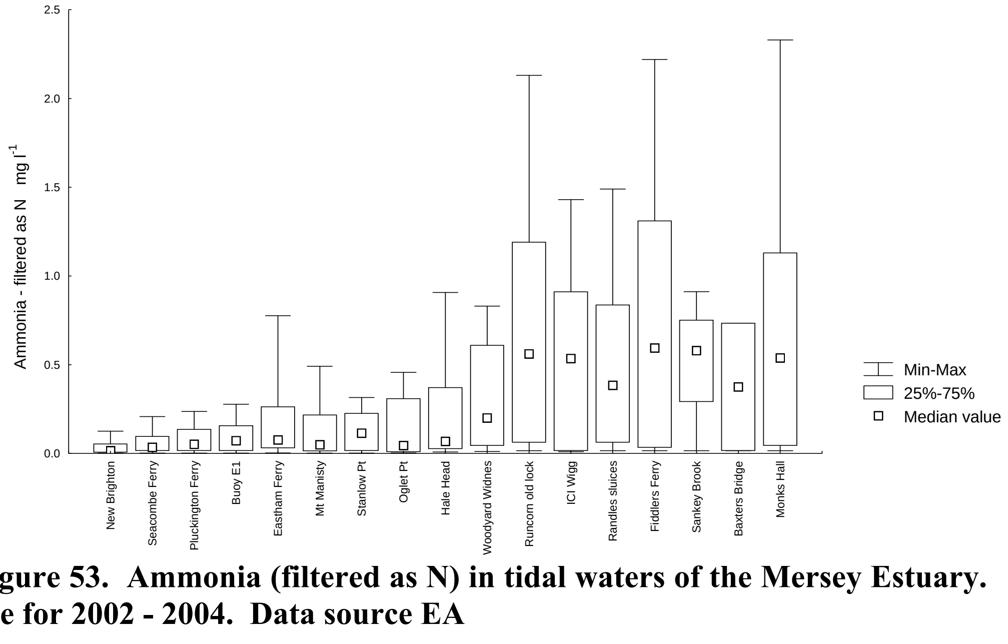



**Figure 53. Ammonia (filtered as N) in tidal waters of the Mersey Estuary. Data are for 2002 - 2004. Data source EA**

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.

The available EA monitoring data for ammonia (filtered as N) in tidal waters of the Mersey Estuary are summarised in figure 53. Highest individual concentrations were recorded towards the freshwater end of the estuary (up to 2.33mg $l^{-1}$ at Monks Hall), with a small peak again at Eastham Ferry. Median concentrations are all below 0.1mg $l^{-1}$, the most elevated (0.59 and 0.58 mg $l^{-1}$) occurring at Fiddlers Ferry and Sankey Brook in the inner Estuary.

In order to compare values with standards and guidelines for ammonia, EA data are also plotted as annual averages in figure 54. The guideline value of 1.1 mg $l^{-1}$ -N (AA) was exceeded in 2003 at Monks Hall. Maximum allowable concentration was not exceeded. Over the three-year period, mean ammonia levels have varied, and were highest throughout the estuary generally in 2004, notably at Randles Sluices, ICI Wigg and Fiddlers Ferry where annual averages also approached the guideline value. Temporal trends in annual averages for this period are shown in figure 54.

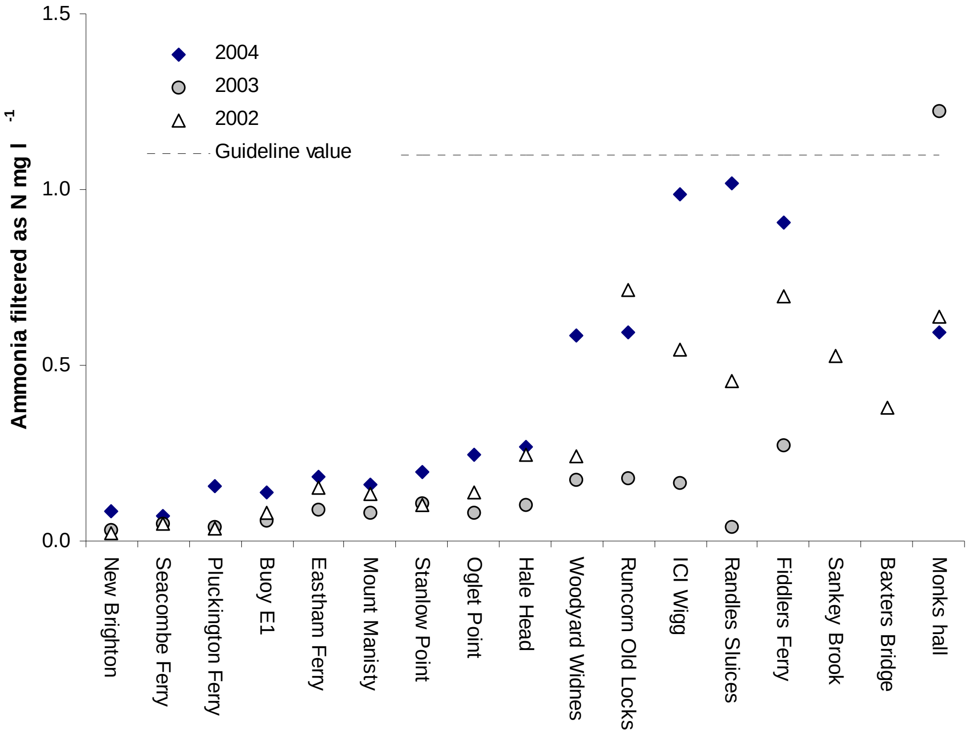



**Figure 54. Mean annual levels of ammonia (filtered as N) in tidal waters of the Mersey Estuary. Data are for 2002 - 2004. Data source EA**.

Note that the ammonia data in figures 53 and 54 are for ammonia as N, and values for the more toxic unionised ammonia, $NH_3$ (N), have to be calculated, 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.

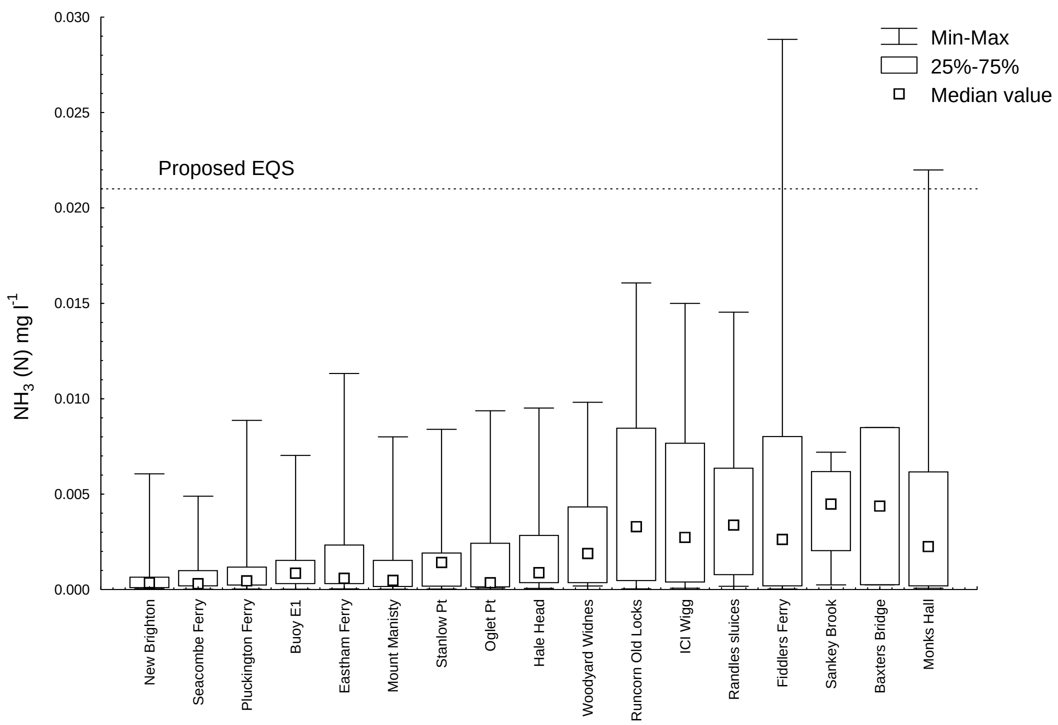



**Figure 55. Unionised ammonia, $NH_3$ (N), in tidal waters of the Mersey Estuary. Data are for 2002 - 2004. Data source EA**. NB **The proposed EQS of 0.021mg $l^{-1}$ $NH_3$ (N) is shown for information only as it relates to an annual average.**

Using monitoring data, EA have calculated the equivalent unionised ammonia, $NH_3$ (N) from some of this data and the results are shown in figure 55. Again, highest individual concentrations occurred at the freshwater end of the estuary (up to 0.029 mg $l^{-1}$).

Expressed as annual averages for the three years, values range from 0.0003 to 0.011 mg $l^{-1}$ and therefore do not exceed the unionised standard of 0.021mg $l^{-1}$ $NH_3$ (N) AA at any of the sites. However this threshold level has been exceeded on occasions at two of the sites; Fiddlers Ferry and Monks Hall, and over the period, unionised ammonia levels have varied, but were highest throughout the estuary generally, in 2004. Temporal trends in annual averages for this period are shown in figure 56.

Again data is not available for concentrations in freshwater inputs, WwTWs or industrial discharges; therefore the ‘hotspots’ cannot be directly attributed to sources.

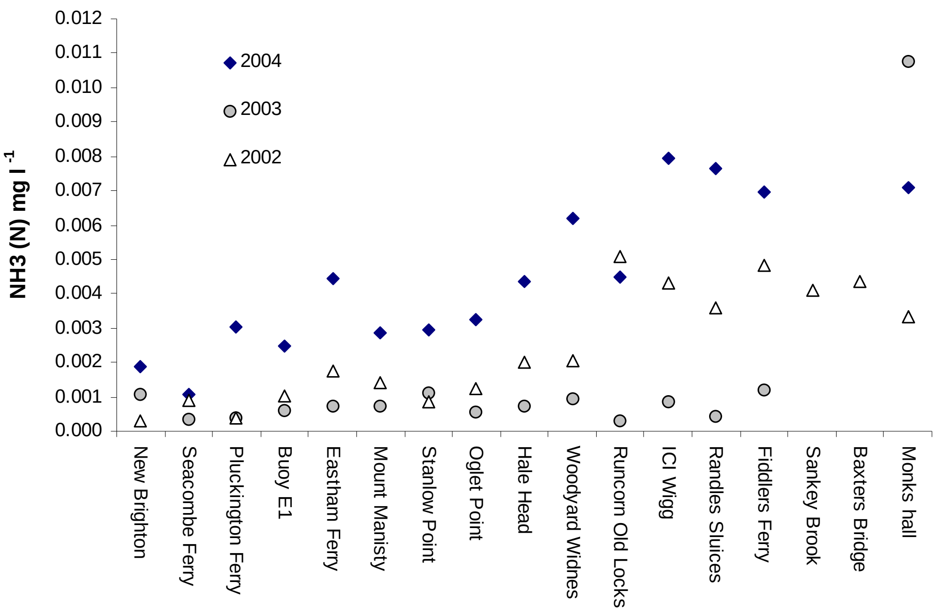



**Figure 56. Mean annual levels of unionised ammonia, $NH_3$ (N), in tidal waters of the Mersey Estuary. Data are for 2002 - 2004. Data source EA**.

Thus, although the 0.021mg $l^{-1}$ EQS for $NH_3$ (N) as an annual average has not been exceeded in estuary between 2002 and 2004, further increases in ammonia concentrations from discharges should be avoided, as a precautionary requirement.

Surveys of winter nutrient levels conducted at NMP sites in 2001 indicated that Liverpool Bay is a relative hotspot for ammonium (6.8µm compared to typical coastal water values <1µm), influenced presumably by inputs from the Mersey (CEFAS 2003). Not surprising enrichment in total oxidised nitrate, phosphate and chlorophyll a were also observed during this survey (though as previously noted, chlorophyll may, in part, represent input from estuarine microalgae rather than in situ production).

### 6.2.2 Microalgae -Chlorophyll

It is important to distinguish between natural blooms and those induced by "artificial" causes. Blooms occur more often in the spring/summer when sunlight penetration is at a maximum and the water column is starting to stratify. This reduces mixing between the layers and the nutrients remain in the photic zone. When nutrients are in abundance, the phytoplankton rapidly grow and reproduce, zooplankton predation cannot keep up with the growth, resulting in an algal bloom. This is a totally natural phenomenon, and levels of chlorophyll would be expected to increase in spring due to the bloom. Nutrient inputs e.g. from sewage, can artificially enhance and extend the life of a bloom and it is these 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). Criteria used to inform UWWTD and WFD risk assessment suggests a concern when chlorophyll-a concentrations reach >100 µg $l^{-1}$ (max) and 25µg $l^{-1}$ (annual average) in fresh water or 10 µg $l^{-1}$ in fully saline waters. In addition, for its OSPAR assessments of marine waters, the UK has adopted an annual average value of 15µg $l^{-1}$ to indicate a "problem area". This is based on waters having 50% higher chlorophyll levels than regional background (WQTAG, 2005b).

EA monitoring data for chlorophyll concentrations in the Mersey Estuary are summarised in figure 63. The available data for 2002 – 2004 are very patchy, and is for chlorophyll a+b combined. For most sites, values represent samples taken 5 to 12 times per year, mostly between March and October, although measurements taken in November and December are included at some sites. Nevertheless figure 63 gives a general indication of levels in the estuary. The thresholds 10 and 15 µg $l^{-1}$ are for fully saline waters and are included for reference. Few of the sites are within the EMS.

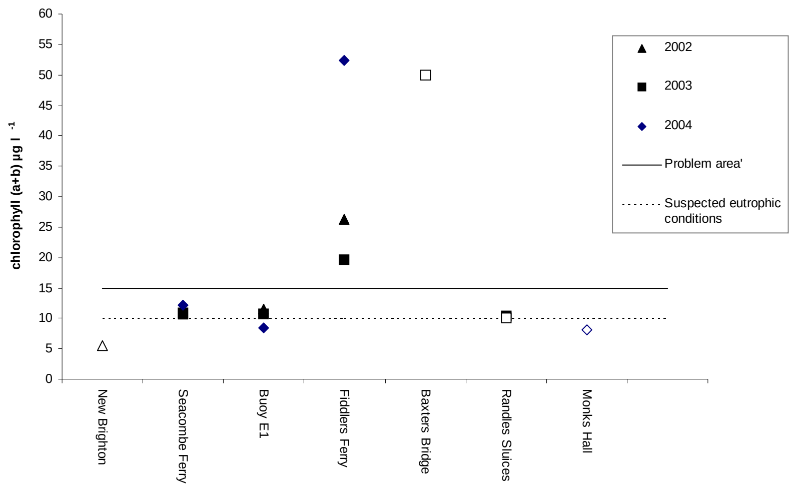



**Figure 63. Annual chlorophyll (a+b) (µg $l^{-1}$) for tidal waters of the Mersey Estuary. Closed symbols represent annual means, open symbols represent individual values. Data are for 2002 - 2004. Data source:EA.**

Individual values for chlorophyll range from 2.3 to 80.3 µg $l^{-1}$; generally within the normal range during spring and autumn blooms (up to 80µg $l^{-1}$) and not indicative of widespread significant plankton blooms. Highest values were recorded between May and October. Mean annual concentrations appear to be most elevated in 2004 at Fiddlers Ferry, where levels exceed the criteria indicating a 'problem area', although with such patchy data, it is not possible to assess the situation with any confidence.

For waters of the lower estuary (New Brighton, Seacombe Ferry, Buoy E1) mean annual concentrations of chlorophyll for the three-year period scarcely exceeded 10µg $l^{-1}$ saline waters threshold for suspected eutrophic conditions.

More information is needed to assess potential risks to the SPA.

### 6.2.3 Dissolved Oxygen

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.

DO is measured in estuaries and coastal waters in terms of either a concentration (mg $l^{-1}$) or as a percent saturation (%). Table 18 shows recommended EQS values for saline waters derived from the review of Nixon *et al.,* (1995).

**Table 18. 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 19) 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 19. 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 Water Quality Technical Advisory Group (WQTAG) (joint EA/EN/CCW) have recommended that a salinity related standard is the most practical approach as the solubility of oxygen declines as salinity increases; e.g. the solubility at 10°C declines from 11.3 mg $l^{-1}$ in fresh water to 9.1 mg $l^{-1}$ in sea water (Wither, 2004). The threshold determined for triggering likely significant effects for dissolved oxygen levels in estuaries is based on a saline level of 5 mg $l^{-1}$ (annual 5%ile) and is consistent with the EQS recommended in Nixon *et al.,* (1995) to protect sensitive saltwater life (table 18). In freshwater the salinity adjusted level is 6 mg $l^{-1}$ This is consistent with the Freshwater Fish Directive which sets an annual 5%ile of 6 mg $l^{-1}$ as the trigger level in salmonid waters. The salinity related threshold is represented by the line in figure 57.

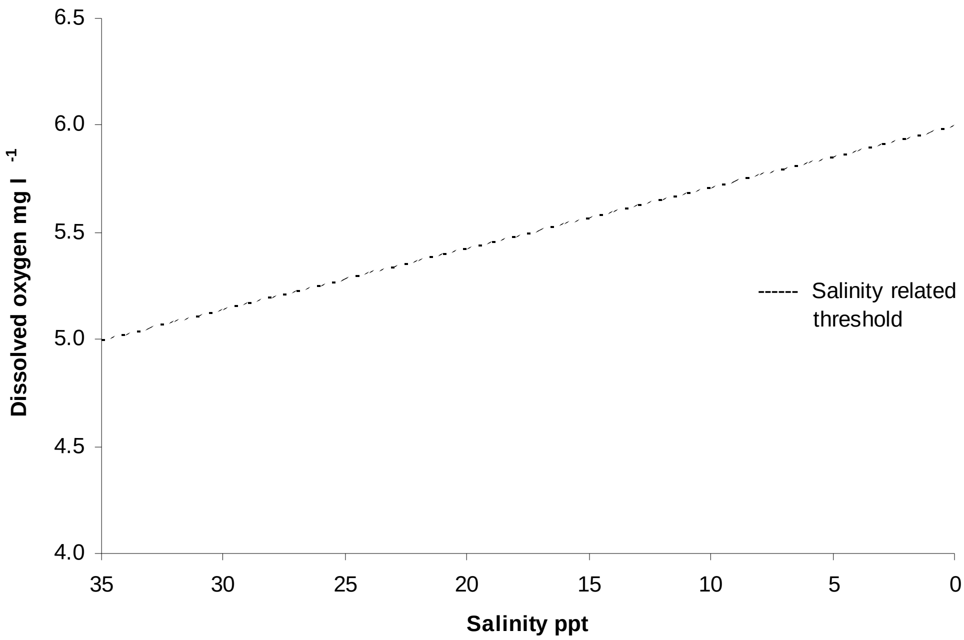



**Figure 57. Dissolved oxygen threshold vs salinity.**

As the appropriate threshold value changes with salinity, calculating the 5%ile from field data can be difficult. Suggested approaches to calculation of the 5%ile include:

- Plotting field data against salinity and check whether 5% or more of the points lie below the threshold line

- Converting all data to the 'zero salinity equivalent value' using the following simplified equation: DO (adjusted to salinity zero) = DO (at salinity x) + x/35 then calculate the 5%-ile and compare with a value of 6mg/l.[16]

Parts of the Mersey Estuary may be particularly vulnerable DO problems, as 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). In the Manchester Ship canal during the summer, the dissolved oxygen regime in the 6 miles between Woolston Weir and the Mersey confluence (Irlam Weir) is very poor (~ 20%). This clearly restricts the passage of migratory fish. In the autumn, the conditions improve somewhat and fish are apparently able to reach the confluence with the River Bollin. In the Mersey Estuary DO concentrations have undoubtedly improved since the anoxic conditions of the 1970s (Jones, 2005) although reduced DO levels might still be anticipated in some areas of the SPA, such as the inner estuary.

The available EA monitoring data for dissolved oxygen in waters of the Mersey are for the period 2002 to 2004 and are for tidal waters. The data are recorded as % saturation and mg $l^{-1}$ enabling comparison with EQSs. Some tidal cycle monitoring data are also available.

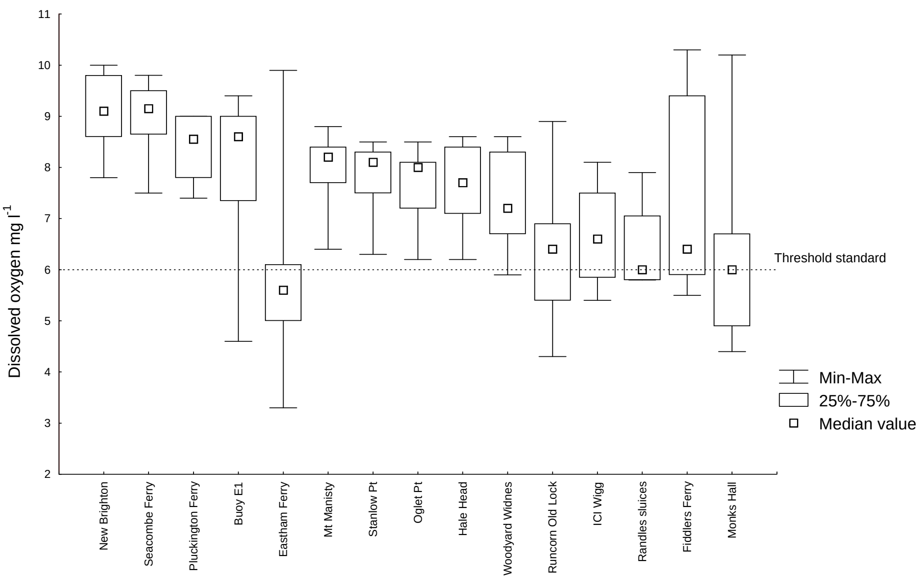



**Figure 58. Dissolved oxygen (mg $l^{-1}$) in tidal waters of the Mersey Estuary 2002 - 2004. Data source:EA**

Median values for DO in waters of the Mersey range from 3.9 to 9.1 mg $l^{-1}$, generally in the low- to mid-range reported by MMPMG (1998) (4 - 11mg $l^{-1}$). DO levels generally decreased toward the inner estuary, although lowest values occurred at Eastham Ferry and Runcorn Old Locks (3.3 and 4.3 mg $l^{-1}$). Unsurprisingly, summer values reflect the greatest oxygen depletion. Median DO for the period fell below the

[16] NB. It is noted in the guidance notes that estimations of the 5%ile are not necessarily required for each individual sample point, and that it might be inappropriate to represent all the data for one estuary on one plot. The estuary may therefore be divided into a number of 'representative' areas and the 5%ile estimated for each of those areas. Subjective judgement will be needed to define these areas (Withers, 2004).

threshold 6 mg $l^{-1}$ recommended EQS for sensitive saltwater life at several sites during the period therefore the data has been plotted against salinity as recommended by Wither (2004) (figure 59).

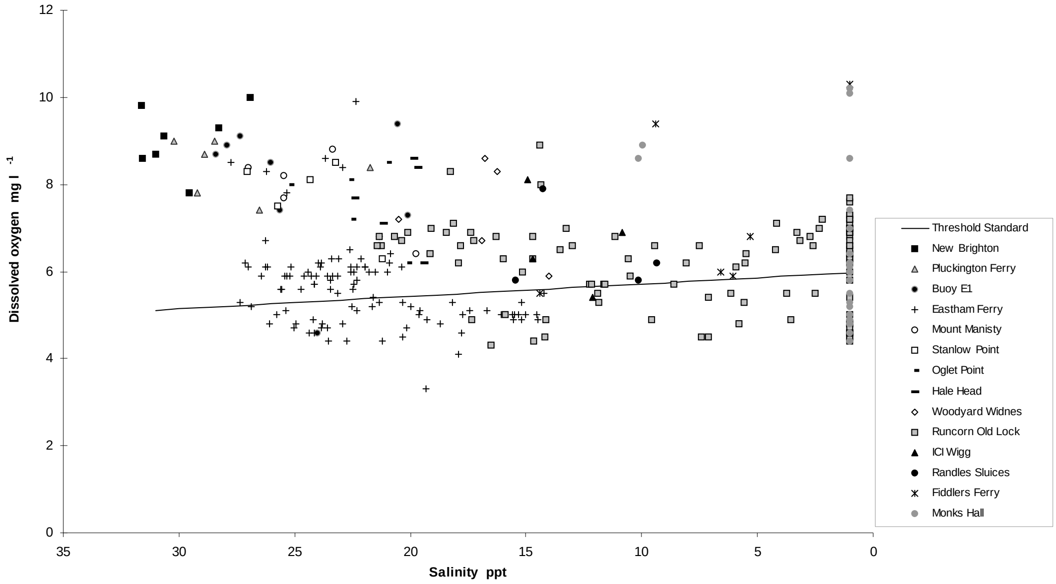



**Figure 59. Dissolved oxygen (mg $l^{-1}$) vs salinity in tidal waters of the Mersey Estuary. NB; Data for Seacombe Ferry, are not included. Source:EA**

A plot of raw data vs salinity for the period (figure 59) suggests that 5% of the values fall below the salinity-related threshold (43% <6 mg $l^{-1}$ ; 19% <5 mg $l^{-1}$). The 5%ile values of the EAs DO data for 2002-2004 (adjusted to salinity zero as described above) fall below 6 mg $l^{-1}$ at several sites along the estuary, notably the mid-estuarine site of Eastham Ferry, and several sites in the upper estuary (figure 60).

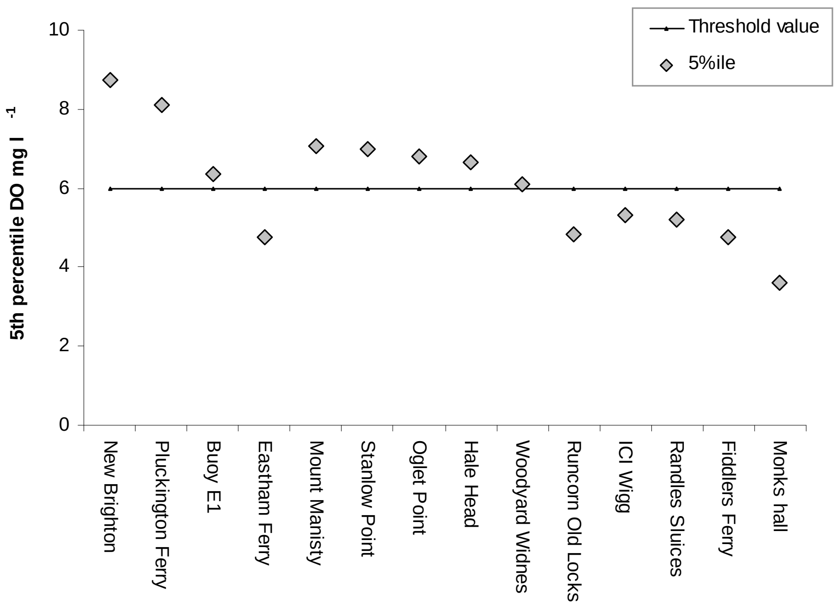



**Figure 60. 5%ile values for dissolved oxygen (mg $l^{-1}$ - adjusted to salinity zero) in tidal waters of the Mersey Estuary 2002 - 2004. NB; Seacombe Ferrry, data are not included. Source:EA**

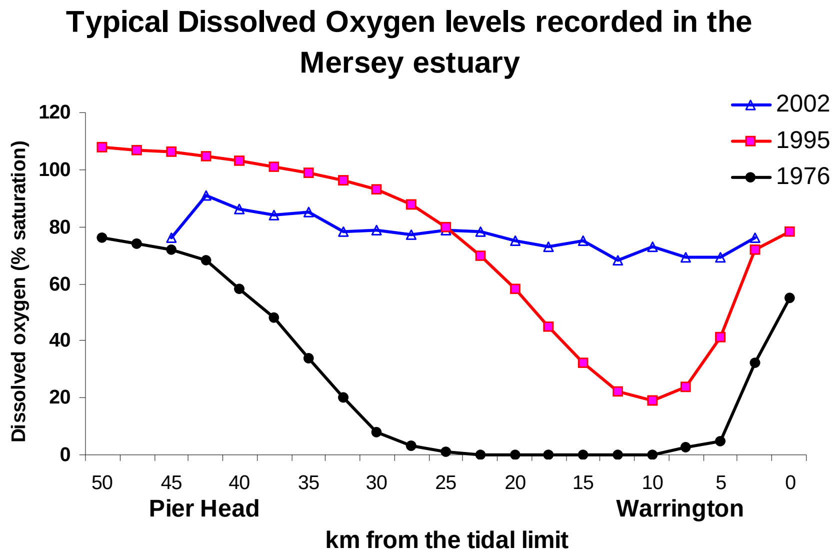



**Figure 61. Temporal trends for 'typical' dissolved oxygen levels (% saturation) in tidal waters of the Mersey Estuary. Source EA.**

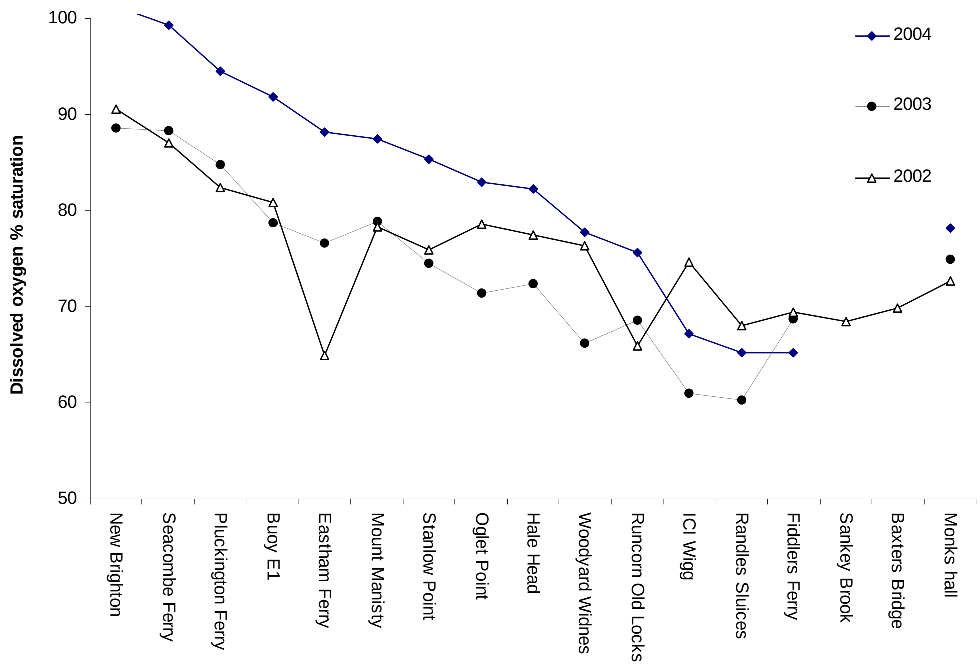



**Figure 62. Mean annual levels of dissolved oxygen (% saturation) in tidal waters of the Mersey Estuary. Data are for 2002 - 2004. Data source EA.**

On a temporal scale, dissolved oxygen levels are considered to be recovering along the Mersey. Figure 61 supplied by the EA shows dramatic improvements along the estuary between mid 1970's and 2002 (expressed as % saturation). Since then, mean annual values derived from available EA data have remained above 60% throughout the estuary (figure 62).

However, it is worth noting that some individual values have exceeded 100% saturation indicating possible $O_2$ supersaturation. This applies to 13% of the values for 2004, mostly toward the outer estuary (New Brighton, Buoy E1, Eastham Ferry, Pluckington Ferry and Seacombe Ferry). This situation can occur when elevated levels of nutrients in estuarine waters stimulate growth of macroalgae and/or phytoplankton (algal bloom) and result 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. In severe cases, 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.

### 6.2.4 Turbidity and Suspended Solids

The Mersey is considered to be a naturally turbid estuary and this is undoubtedly an important factor influencing its ecology (by affecting food supply, habitat, transport and bioavailability of contaminants.

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) and 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.

Measurements of suspended solids @105°C are used by the EA for quantifying turbidity in waters of the Mersey Estuary EMS. Data for March 2002 – December 2004 are summarised in figure 64. During this the period, mean values ranged from 100 - 508mg $l^{-1}$, with highest values generally toward the freshwater end of the estuary. The more elevated mean values for the period are for Baxters Bridge and Runcorn Old Locks. It is important to note that these data are collected near to “local” high water moving upstream in a fast launch. They do NOT represent maximum values during the flood/ebb tide (P.D. Jones, EA, *pers comm.*).

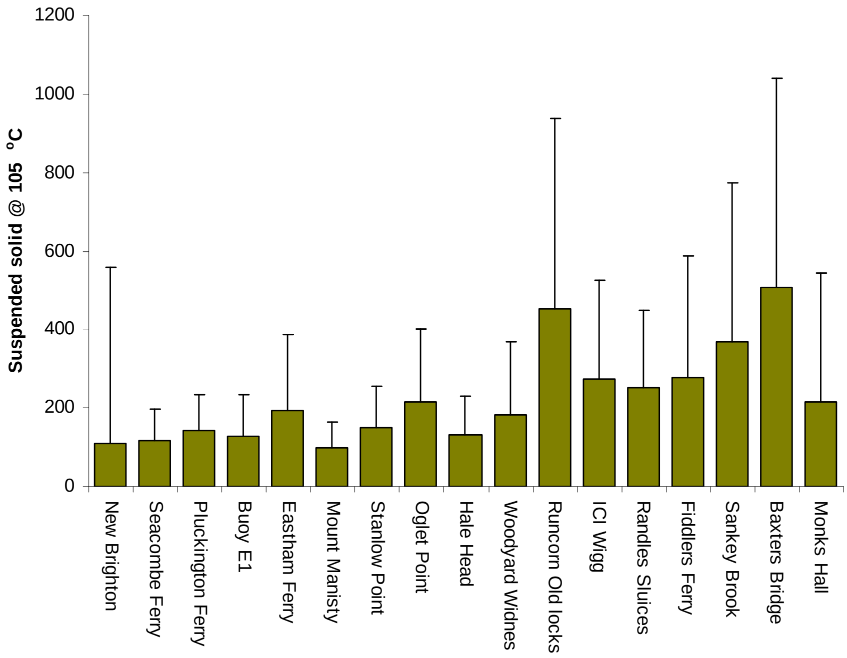



**Figure 64. Mean values for suspended solids (mg $l^{-1}$ @105°C) in waters of the EMS (2002 – 2004) (error bars represent standard deviation of the mean). Data source; EA**

To put these turbidity levels into some perspective, Cole *et al* (1999) 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. Using this criterion, the EMS therefore experiences relatively high turbidity.

Increased or sustained turbidity in the water column can 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. However, 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 (Cole *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). Turbidity measurements will be significantly influenced by these natural characteristics as opposed to anthropogenic impacts.

To reiterate - the Mersey is a naturally turbid estuary and concentrations of suspended solids generallt appear to increase in an upstream direction. Withoput further information on discharges and freshwater inputs it is not possible to comment on principal sources.

## 7. BIOLOGICAL IMPACTS

These are reviewed here under two sections. The first deals with bioaccumulation (an indication of exposure to contaminants) whilst the second lists evidence for biological effects at various levels (biochemical and molecular to community structure and function).

### 7.1 Bioaccumulation

#### 7.1.1 Metals in biota

Sediment geochemistry and metal distributions in Mersey Estuary and offshore samples have been characterised and compared in several ways to assess techniques which best signals contamination and resultant bioavailable fractions. Most of the schemes tested suggest there is a superficial resemblance between potential for bioaccumulation and the patterns in anthropogenic metals in sediments as established by partial extractions and from geological fingerprinting techniques (see section 6.1.1; Ridgway *et al*. 2003). However, sometimes metal concentrations in biota can be altered dramatically due to changing environmental conditions (which modify chemical speciation), as opposed to any obvious change in inputs (described below for clams from Egremont). Direct measurement of body burdens in appropriate bioindicators is clearly a more rigorous means of assessing bioaccumulation. However, this complex issue is further complicated by the fact that there is no single universal bioindicator. Different organisms react differently to pollutants; usually it is preferable to examine a variety of different ecological/feeding types to appreciate the range of responses (Bryan *et al*., 1985).

For this reason we have examined a range of available information to provide a broad impression of bioaccumulation, and to assess whether or not body burdens are influenced by anthropogenic activities. EA and CEFAS biomonitoring data focus on fish and shellfish from the NMMP sites, though these are outside the EMS boundary. Between 1980 and 1997 MBA, in collaboration with the EA and it's predecessors, conducted studies specifically designed to evaluate the issue of bioavailability in inter-tidal flats of the Mersey, using appropriate bioindicators (e.g. *Nereis diversicolor*, *Macoma balthica*, *Scrobicularia plana*, *Mytilus edulis*, *Cerastoderma edule*, *Littorina* spp. *Fucus* spp). Though much of the data are comparatively old (and in need of updating), they nevertheless provide a useful background to assess characteristics of the site and some of the issues surrounding metal bioavailability to the bird populations for which the site is designated. They also act as a valuable baseline for assessing temporal changes in relation to the abundance and distribution of these important invertebrate prey species. The main findings of these surveys are discussed in detail in the latest of these reports (Pope *et al*., 1998), from which the following highlights are extracted.

Although metal concentrations in Mersey biota rarely approached levels comparable to those found in estuaries in SW England which receive metal-mining waste, the Mersey was considered unusual, in the early 1980s, in being moderately contaminated by a wide range of metals (Langston, 1986). Particular concern at the time centred around levels of mercury, which were consistently high in the Mersey for reasons already described. Lead levels were also a cause for concern, following extensive mortality amongst over-wintering estuarine birds during 1979 – 1982. This was attributed to the food-chain magnification and toxicity of tri-alkyl lead compounds, released into the estuary via the Manchester Ship Canal (Wilson *et al.*, 1986).

In general terms, there were substantial early reductions following efforts to reduce inputs of Hg and Pb. During the 1990s reductions slowed down, with the approach of 'steady state' conditions for concentrations in many biota (Langston, 1988, Pope *et al* 1998). Comparative data for metals in the omnivorous ragworm *Nereis diversicolor* and clams *Scrobicularia plana*, from the Mersey and other UK sites, have been selected for discussion here to give an indication of the relative scale of concentrations, together with spatial and temporal patterns (tables 20 & 21 and figures 65 & 66).

Polychaetes are among the most widespread inhabitants of contaminated and uncontaminated sediments. Nereids such as *Nereis diversicolor* accumulate a number of metals in amounts which reflect bioavailability in their sedimentary environment (Bryan *et al.,* 1980; 1985; Langston, 1980, 1982). Tolerance to a wide range of salinity also makes *Nereis* extremely useful for monitoring in estuaries and *N. diversicolor* is relatively abundant throughout most of the Mersey SPA.

**Table 20. *Nereis diversicolor.* Average metal concentrations (µg $g^{-1}$ dry weight) in the Mersey (1997) and other UK estuaries. UK min represents a background value for the species** (lowest measured value for species in MBAs UK database- data source MBA).

| | Ag | Cd | Cr | Cu | Fe | Mn | Ni | Pb | Zn | Hg | As | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Mersey** | **1.37** | **0.38** | **0.52** | **29.1** | **477** | **27.7** | **3.08** | **6.0** | **175** | **0.37** | **14.7** | **0.31** |
| **Poole** | 0.49 | 0.64 | 0.6 | 12 | 337 | 11.5 | 8.9 | 3.6 | 165 | 0.24 | 7 | 1.1 |
| **Severn** | 8.01 | 3.79 | 0.52 | 54.4 | 396 | 14.3 | 4.94 | 3.56 | 264 | 1.42 | 12.8 | 0.31 |
| **UK min** | 0.06 | 0.02 | 0.03 | 7.69 | 210 | 4.03 | 0.63 | 0.16 | 87.8 | 0.02 | 3.22 | 0.05 |
| **Mersey ÷ UK min** | 23 | 19 | 17 | 4 | 2 | 7 | 5 | 38 | 2 | 19 | 5 | 6 |

Table 20 shows metal concentrations in *Nereis diversicolor* from the Mersey (1997). For comparison, equivalent data from the Severn Estuary SAC, SPA and Poole Harbour SPA are shown, together with the average of the lowest ten sites (UK min) in our UK data set.

The average degree of enrichment for Mersey *Nereis*, relative to baselines, is included in table 20 highlighting the significance of pollutant-type metals. Enrichment decreases in the order Pb>Ag>Hg=Cd>Cr>Mn>Sn>As=Ni>Cu>Fe=Zn. The relatively low enrichment of the latter two metals is almost certainly a result of the

capacity of *Nereis* to regulate these essential elements (*Nereis* body burdens therefore may underestimate contamination with Fe and Zn).
The deposit-feeding clam *Scrobicularia plana* has also proved to be a valuable indicator species, particular in terms of understanding trends in sediment metal bioavailability. Though less widespread in distribution in the Mersey than *Nereis,* and in places much less abundant, *Scrobicularia* tends to be the better accumulator and indicator of metals (with the exception of Cu), and has the advantage of not regulating Zn. Ranges of these infaunal clams in the Mersey extend upstream as far as Mount Manisty/Hale, approximately (see section 7.2).

Table 21 shows mean summary statistics for metals in *Scrobicularia plana* from the Mersey (1997), in comparison to Poole Harbour, the Severn, and UK min. These indicate that degree of enrichment is generally of similar order to that displayed by *Nereis,* with some variation on ranking:
Ag>Cr>Mn>Hg>Pb>Sn>Cd=Fe>Ni=Zn>Cu=As.
Again it is the anthropogenic metals which display greatest enrichment. As none of these metals is naturally enriched in upstream sediments of the catchment, the biological enrichment is presumed to be largely of industrial and urban origin (see also Ridgway *et al*., 2003).

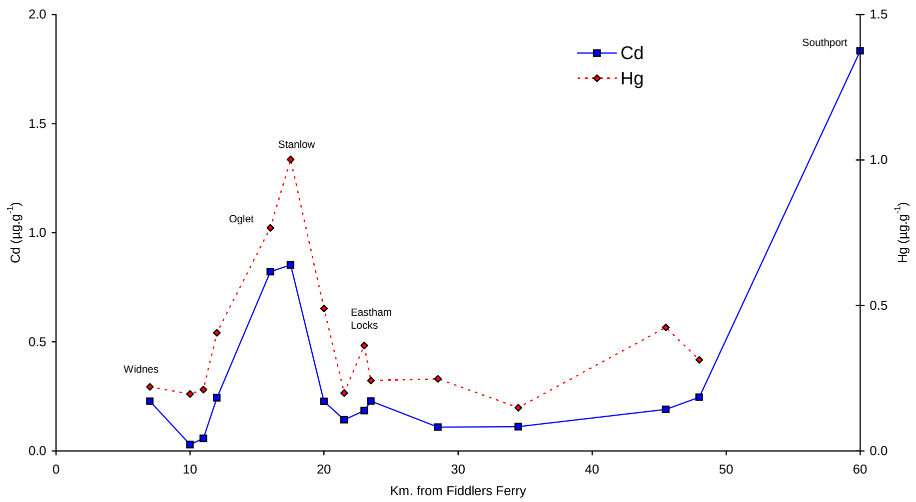
**Table 21. *Scrobicularia plana*. Metals concentrations (µg $g^{-1}$ dry weight) in the Mersey (1997) and other UK estuaries. UK min represents a background value for the species** (lowest measured value for species in MBAs UK database- data source MBA).

| | Ag | Cd | Cr | Cu | Fe | Mn | Ni | Pb | Zn | Hg | As | Sn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Mersey** | 3.19 | 0.63 | 6.5 | 30.1 | 1139 | 104 | 3.62 | 39.4 | 780 | 0.59 | 17.2 | 0.56 |
| **Poole** | 22.5 | 12 | 5.8 | 46 | 1490 | 6 | 10.7 | 18 | 878 | 1.08 | 13 | 1.44 |
| **Severn** | 8.37 | 7.18 | 3.68 | 47.4 | 1271 | 69 | 6.44 | 43.5 | 775 | 0.64 | 20 | 0.39 |
| **UK min** | 0.05 | 0.13 | 0.26 | 9.5 | 226 | 4.8 | 0.89 | 3.79 | 193 | 0.04 | 5.7 | 0.08 |
| **Mersey ÷ UK min** | 64 | 5 | 25 | 3 | 5 | 22 | 4 | 10 | 4 | 15 | 3 | 7 |

Spatial trends in metal bioaccumulation along the estuary are highly variable (depending on metal and species) and only a few examples are illustrated here to highlight certain features (figures 65-68). Detailed descriptions can be found in the original reports (e.g. Pope *et al*., 1998).

The ragworm, *Nereis diversicolor* extends as far upstream as Widnes, and represents the most useful species to occur in numbers in the inner part of the estuary. Cadmium and mercury concentrations in worms increase downstream from Widnes to reach high levels at Oglet and Stanlow (figure 65). However, high levels for Cd were also seen at Southport. Similar patterns were repeated for Ag, Cu, Pb and Zn (not shown).

Clearly there appear to be sources both within and outside the estuary responsible for increased bioavailability.



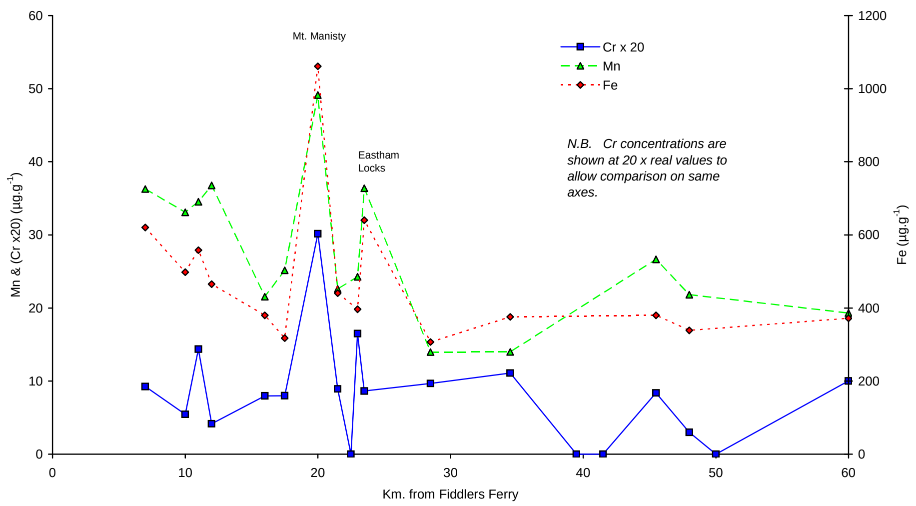
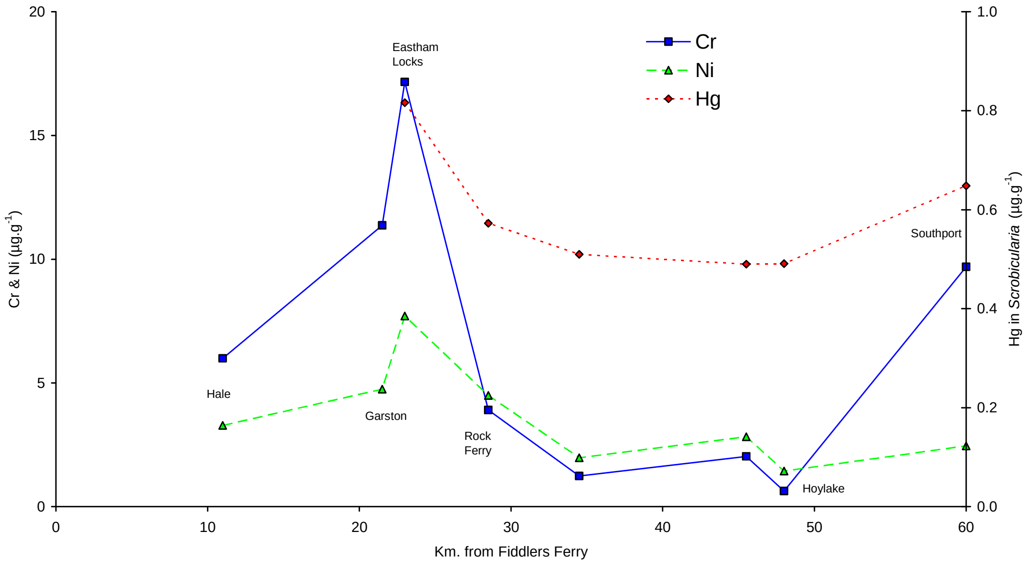




**Figure 65. *Nereis diversicolor*. Spatial trends in Cd and Hg bioavailability (top), and Cr, Mn and Fe bioavailability (bottom) in the Mersey Estuary, 1997 ( from Pope *et al*., 1998)**

Fe, Mn and Cr burdens were all highest in worms from Mt. Manisty on the south bank, with a secondary peak at Eastham or Eastham Locks (Figure 65) indicating a different pattern of bioavailability for these elements. Since Fe, Mn and Cr are all redox sensitive elements; there is the possibility that this could be a contributory factor to the observed profiles. Alternatively there may be sources of metals in the vicinity of Mount Manisty/MSC.

Cr, Ni, Hg, (Cd and Sn) burdens in clams *Scrobicularia plana* were also dominated by high levels at Eastham Locks suggesting that there may have been some input of these elements via the Manchester Ship Canal (figure 66, top). In contrast silver and copper profiles in clams were dominated by anomalously high concentrations from Egremont (Figure 66, bottom) as observed in earlier studies (Langston, *et al*., 1994). Sediments at this site had become notably anoxic, which may have affected metal bioavailability (and survival) of sensitive burrowing species (see later in this section).



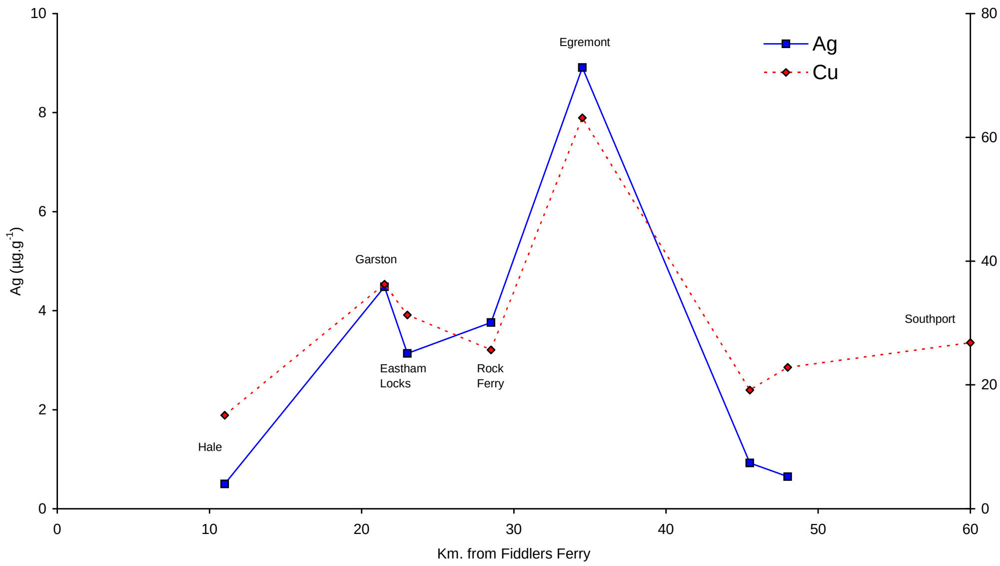
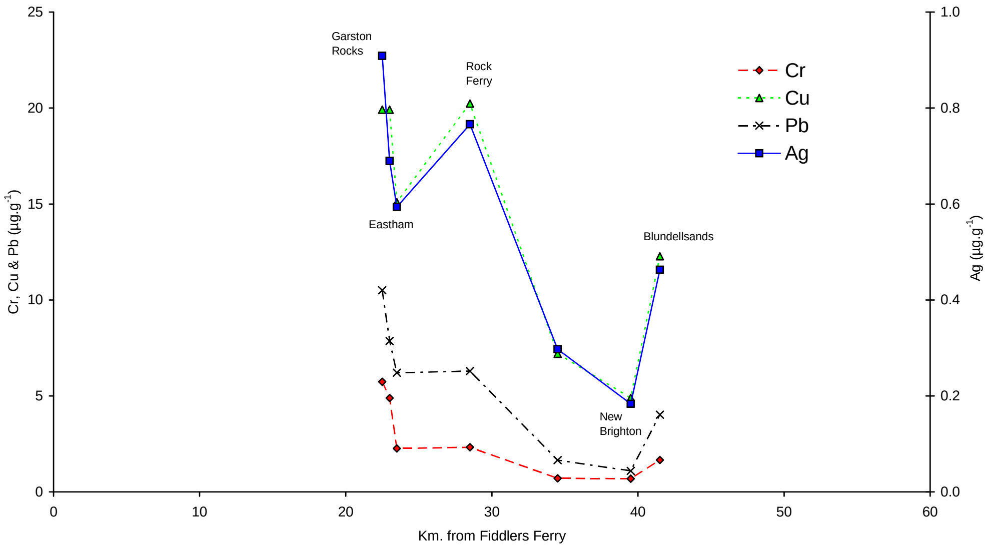




**Figure 66. *Scrobicularia plana*. Spatial trends in Cr, Ni and Hg bioavailability (top), and Ag and Cu bioavailability (bottom), in the Mersey Estuary, 1997 (from Pope *et al*., 1998).**

The seaweed *Fucus vesiculosus* accumulates its metal burdens mainly from solution, and therefore acts primarily as an indicator of dissolved metals. Ag, Cu, Cr, Pb (figure 67); Mn, Fe and Zn (not shown) show a significant decrease seawards through the estuary from Garston Rocks to New Brighton and Blundellsands, reflecting a decrease in dissolved concentrations of these elements in that direction, but with an upturn in availability at Blundellsands[17]. Sn and Hg concentrations were highest in seaweeds from Eastham Locks (figure 67). This suggests that there may inputs of dissolved Hg, and bioavailable Sn (most likely as TBT) from the water of the Manchester Ship Canal, released as lockage and leakage at that site.



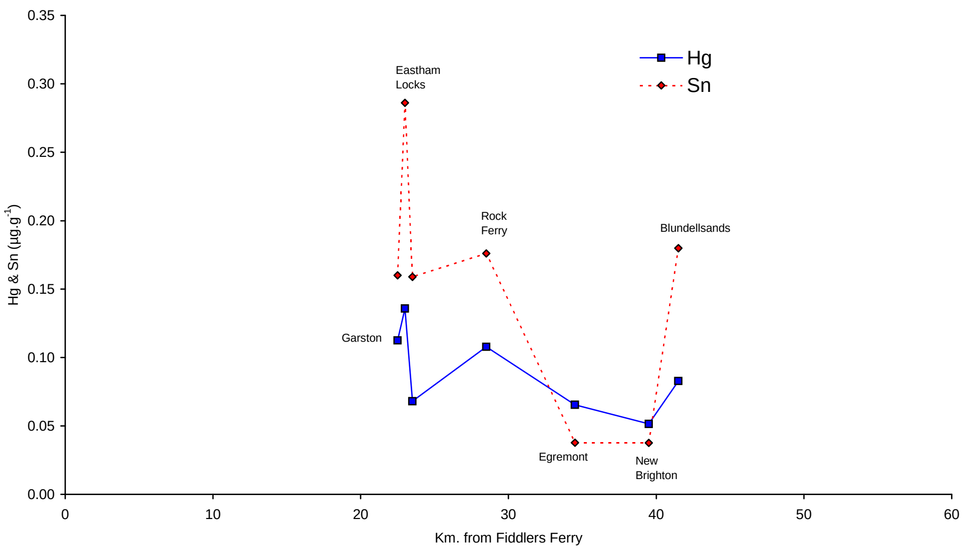




**Figure 67. *Fucus vesiculosus*. Metals in seaweed from the Mersey Estuary, May 1997 (Pope *et al*., 1998).**

Mussels *Mytilus edulis* are filter feeders, primarily responsive to dissolved and suspended particulate metal concentrations in seawater. Se, Cr, Ni, Zn; Pb, As, Cd burdens in mussels show a broadly similar pattern, with concentrations decreasing

[17] Increases at Blundellsands might be due to the influence of the River Alt (P.D. Jones, EA, *Pers comm.*)

downstream from Garston Rocks to New Brighton. Again there is evidence of higher concentrations at Blundellsands (see footnote [17]) and an increase in concentrations at Southport implying impact from sources outside the estuary. This is also demonstrated for Hg and Fe in figure 68.

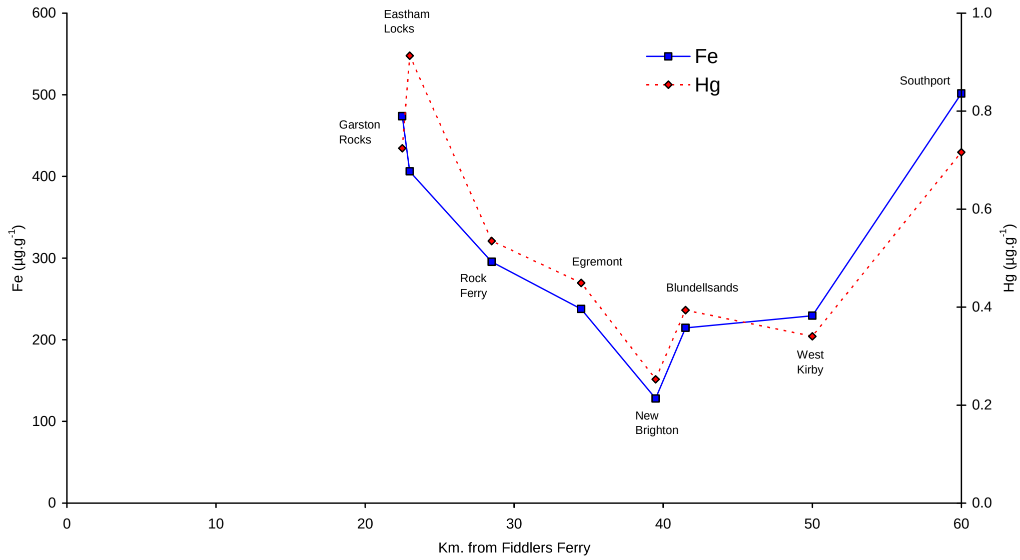



**Figure 68.** ***Mytilus edulis*****. Hg and Fe in mussels from the Mersey Estuary, May 1997.**

Summing up spatial trends in bioavailability, it would seem that one area of concern regarding metal bioaccumulation can be sourced to mid-upper estuary. For infaunal species (*Macoma, Scrobicularia* and *Nereis*), the patterns in bioavailability mirror to a large extent distributions in the surrounding sediments (with exception of Ag and Cu at Egremont). The metals most likely to be of significance toxicologically are Hg, Ag, Pb, Cd and Cr. Sn levels also tend to be high, locally possibly due to the presence of organotin species which are much more biologically available than inorganic Sn (Langston *et al.*, 1990, 1994; see also following section). Patterns of metal bioavailability in other species are not dissimilar to those of infauna, but point to some interesting if transient anomalies such as elevated levels in the outer estuary (eg Southport and Blundell Sands), perhaps due to lower levels of complexing ligands coupled with localized sources. Patterns in *Fucus* generally show increasing metal levels upstream but marked differences between banks have sometimes been observed on occasions, usually with high levels towards the mouth of the MSC, suggesting this may be an important, if transient source, of bioavailable dissolved metal.

Most bioindicators mirror temporal trends in levels of environmental metals (eg sediment concentrations in figures 23 and 24, section 6.1.1) showing that there have been reductions in bioavailable metals as a result of water quality improvements in the post-industrial era. The most successful and consistent of these were major reductions in tissue concentrations of Hg (and Pb) in most indicator species during the early 1980's, together with a pattern of declining Zn and As concentrations (see examples figure 69). These reductions were probably the result of improved industrial processes and stricter controls.

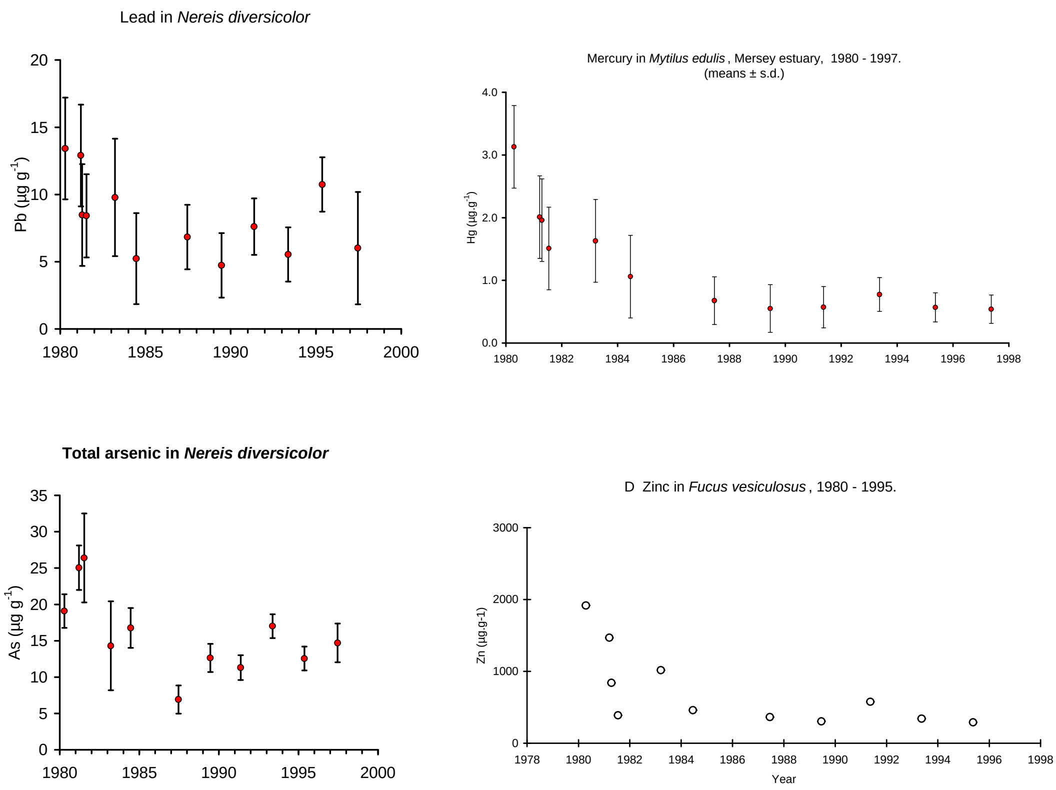



**Figure 69 Examples of reductions in metal bioaccumulation in the Mersey Estuary: Pb in worms *Nereis diversicolor* , Hg in mussels, *Mytilus edulis*, As in *Nereis diversicolor*, Zn in seaweed *Fucus vesiculosus* (MBA data: see for example Langston *et al* 1993; Pope *et al.*, 1998)**

The most recent MBA survey of metal burdens in Mersey biota (comparison 1995 v. 1997), indicated that improvements may still be ongoing even if they are slowing down (Pope *et al*., 1998): only for Fe and Zn (which may be regulated by many organisms) and Hg, were there no significant changes. All other metals showed a significant change in at least one species of indicator, and in most cases the change was a decrease in accumulated levels. There were only three instances where mean metal burdens in biota have increased since 1995 (As in *Nereis diversicolor*, Mn in *Cerastoderma edule*, and Se in *Fucus vesiculosus*).

Temporal variation at individual sites is sometimes not representative of estuary-wide trends. This is best demonstrated in profiles for sediment Cu (figure 70, from Pope *et al*., 1998). Despite differences between sites, however, *overall* temporal and spatial trends tend to be consistent. Some of the site variation could be due to changing inputs but also the mobile nature of the fine sediments in the inner estuary, which may be eroded and re-deposited in response to tidal, seasonal and episodic events. Thus, while there may have been no significant changes in the *mean* sediment concentrations of many metals in recent years, the distribution and character of these sediments may have undergone considerable local changes which can affect biota in those areas. Therefore some changes in metal burdens of biota may be related to the redistribution of sediments, besides overall changes in contamination, the two factors being, to a certain extent, inseparable.

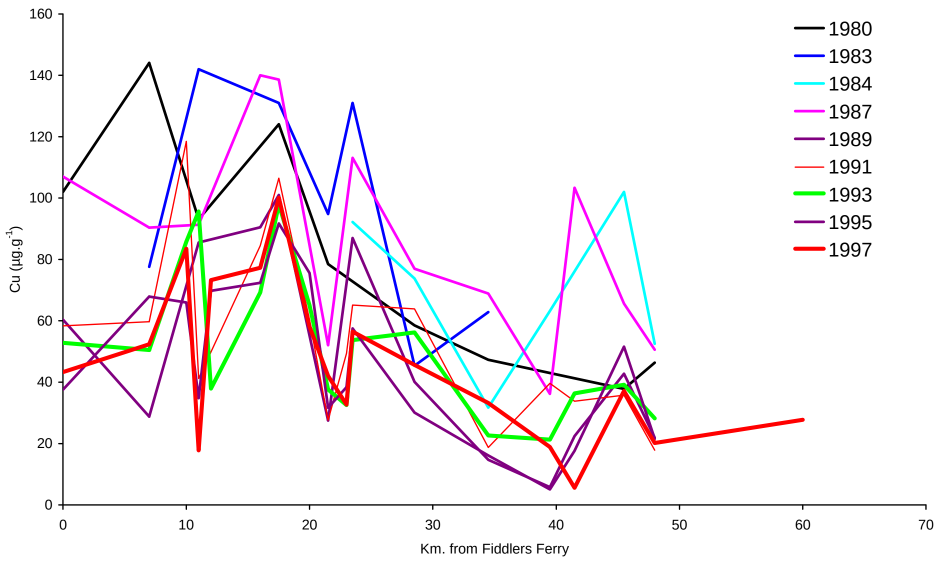



**Figure 70. Trends in Cu in Mersey Estuary surface sediments from Fiddlers Ferry (left) to Liverpool Bay (right) showing how temporal variability can differ between sites; nevertheless overall, patterns are comparable (<100μm fraction, nitric acid digest) (from Pope *et al*., 1998).**

Thus, there are some notable site-specific exceptions to the overall downward trend in metals. At Egremont, Ag concentrations in clams increased dramatically between 1987 and 1991, despite the absence of any change in environmental (sediment) Ag concentration. (figure 71) . The same is true of Hg and Cu (figure 71). These changes were accompanied by a decline in clam numbers at this site (no individuals found in 1993). It seems that changing conditions in the sediment (redox) may have been responsible for a dramatic increase in bioavailability of these metals, with the combined effects causing a crash in the population. By 1995 clams had returned to the site, accompanied by a return to 'normal' levels of bioavailable Ag, Cu and Hg.

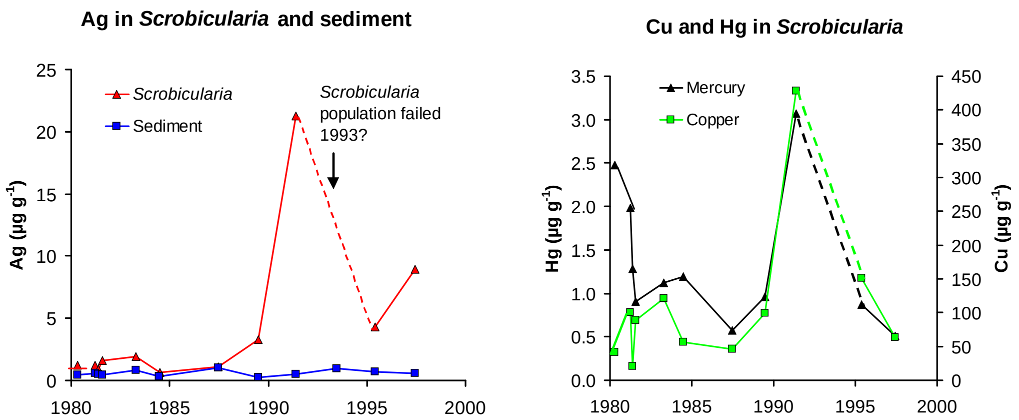



**Figure 71. *Scrobicularia plana*. Anomalous increases in bioavailable Ag, Cu and Hg at Egremont during the early 1990s. (Langston *et al* 1994; Pope *et al,* 1996)**

Precise causes of these temporary adverse conditions at Egremont are unknown, but the example illustrates that site-specific changes in environmental characteristics can drastically affect the bioavailability of contaminants, even though overall environmental loadings may not change. This may be an important issue to consider when assessing the condition of Mersey Estuary SPA, given its legacy of sediment-bound contaminants.

Another important factor is the issue of metal speciation and particularly the presence of organometal species. Just as alkyl lead and organotin compounds are highly bioavailable and toxic (see below), it is the methylated form of Hg which is most toxicologically significant in terms of potential transfer to birds and other higher organisms within the Mersey Estuary SPA.

Methylmercury was measured in 1995 in a number of ecosystem components, including sediments and benthic organisms, along the length of the Mersey estuary (Langston *et al* 1996). The methylmercury concentration in sediments was 6.8 ± 2.1 ng $g^{-1}$ dry weight, representing only a small proportion (>1%) of the total Hg. Concentrations of MeHg in sediments decreased in a seaward direction, along with total Hg, but unlike the inorganic form, concentrations were similar to those taken a decade earlier. Average MeHg concentrations in biota were between 10 (*Fucus*) and 100 (*Mytilus*) times higher than sediments, indicating biomagnification from the environment (figure 72). The major concentration step for MeHg in the food chain appears to be at this low trophic level (i.e. onto particulate surfaces and thence to primary consumers and detritivores) rather than between higher predators, including fish and man. For invertebrates, the proportion of MeHg/total Hg ranged from 16% in *Nereis* to 71% in *Mytilus*. Methylmercury concentrations in benthic fauna generally decreased in a downstream direction in the Mersey, reflecting sediment contamination. This was not evident for the alga *Fucus* which probably derives most of its MeHg from solution. Temporal trends in mean MeHg burdens in biota, between 1987 and 1995, were the subject of marked inter-site variability, but indicated some reductions. MeHg concentrations in shellfish, particularly mussels (0.415 µg $g^{-1}$), were sometimes close to, but did not exceed, statutory guidelines for Hg in food. Nevertheless they are likely to represent a significant source for transfer of this toxic contaminant through estuarine food chains and may merit further investigation regarding risks to the avian interest features of the SPA and other consumers such as eels.

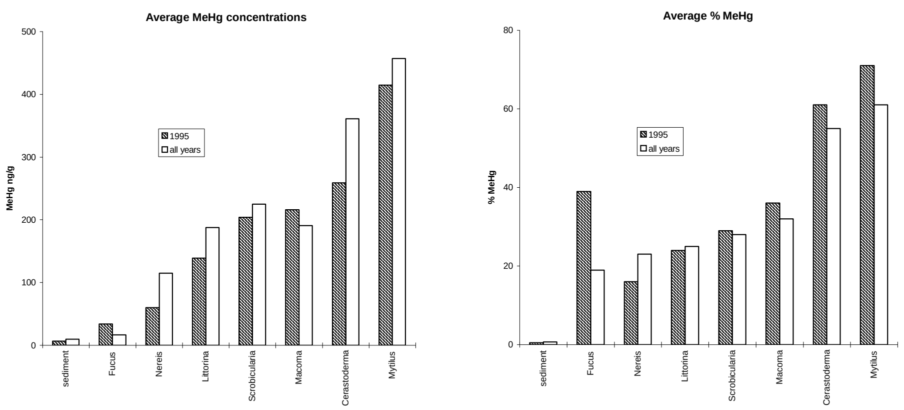



**Figure 72. Summary data (means, all sites) for MeHg in Mersey sediments and biota (from Langston *et al.*, 1995)**

Thus, these long-term surveys of benthic invertebrates and macroalgae illustrate that the use of a validated suite of indicator species is a useful way of estimating metal and organometal bioavailability around the system, and sometimes highlight unexpected events which may be of significance for the interest features of the EMS. The current status of the SPA needs to be more extensively defined in similar fashion, and at intervals in the future, to ensure bioavailability does not increase either through changing inputs or more general site characteristics.

OSPAR have set background/reference concentrations for Hg (0.005-0.01 mg $kg^{-1}$ wet weight), Cd ( 0.07-0.11 mg $kg^{-1}$), Pb (0.01-0.19 mg $kg^{-1}$), Cu (0.76-1.1 mg $kg^{-1}$) and Zn (11.6-30 mg $kg^{-1}$) in mussels. These reference values may be converted to dry weights by multiplication by 0.15 (assuming a water content of 85%). Applying these criteria to the 1997 MBA data for mussel sampled between the mouth of the estuary and Eastham Locks, average values exceed the upper reference by almost an order of magnitude for Hg and Pb, but by a small margin for Cu and Zn (figure 73). However, partial regulation of Cu and Zn may mean that mussels underestimate contamination of these essential metals.

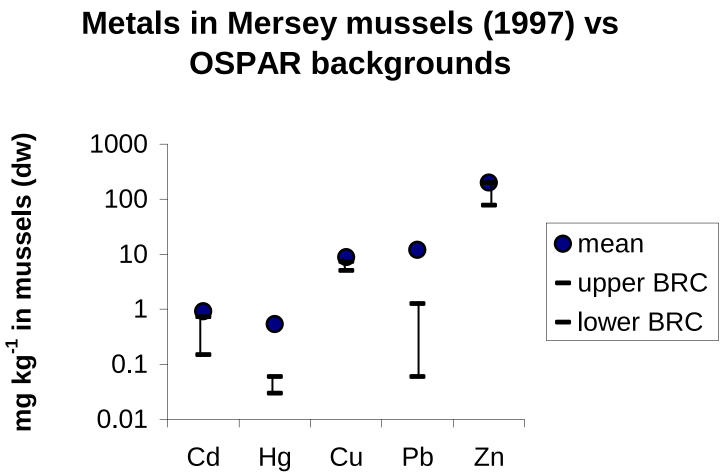



**Figure 73. Average metal concentrations in Mersey mussels (1997) compared with upper and lower background/reference concentrations (BCR) set by OSPAR, converted to dry weights (data source MBA).**

Long-term observations of Hg in muscle of fish caught in Liverpool Bay as part of the NMMP display similar trends to those in invertebrates, above, and reflect historic inputs with major losses occurring in the early 1980s and more or less constant values in recent years (figure 74, CEFAS, 2005). The average value in 2002 for a mixture of cod, whiting, dab, plaice and sole[18] was 0.17 μg $g^{-1}$ wet weight – within the OSPAR JMP 'medium' category for contamination (0.1- 0.3 μg $g^{-1}$ wet weight) and below the directive maximum limit of 0.5 μg $g^{-1}$ wet weight in individual fish species (93/351/EEC –mercury in fish products). It is also less than the mercury EQS, required in areas receiving significant mercury inputs, 'that the concentration in a representative sample of fish flesh chosen as an indicator should not exceed 0.3μg $g^{-1}$ wet weight, set by the Paris Commission in 1980.

[18] Flounder were originally part of the fish sampling protocol but have not been included in recent years due to an apparent decline in numbers (CEFAS, 2005)

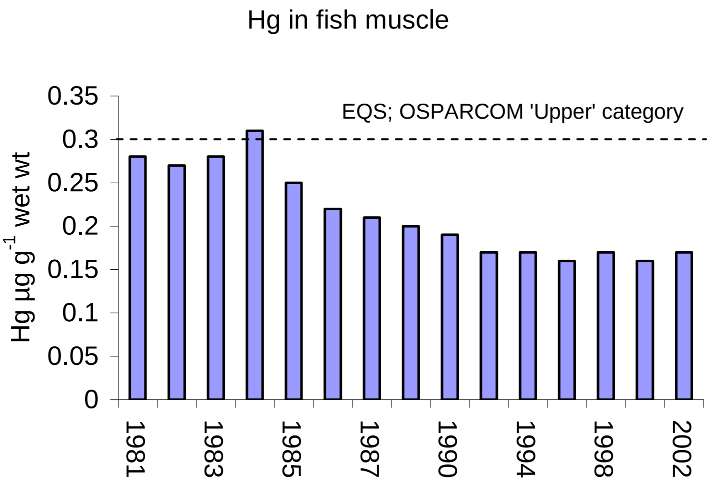



**Figure 74. Trends in Hg in muscle of fish from Liverpool Bay (Plotted from data in CEFAS, 2005)**

In comparisons of Hg in flatfish (dab, flounder and plaice) from around the UK, in 1999-2001, the highest concentrations occurred in the Mersey Estuary ( up to 0.374 $\mu g\ g^{-1}$ wet weight) and Liverpool Bay (up to 0.221 $\mu g\ g^{-1}$) – both significantly above the relevant OSPAR background concentration range of 0.030-0.07 $\mu g\ g^{-1}$ (NMMP, 2004). Pb concentrations were also elevated in dab and flounder from the Mersey (medians in the range 0.2-0.7 $\mu g\ g^{-1}$, and a maximum of 2.7 $\mu g\ g^{-1}$, one of the highest recorded in the UK survey).

Data for eels from Albert Dock were reported to be relatively high (0.61-1.3 $\mu g\ g^{-1}$ wet weight) more than a decade ago (Johnston *et al.*, 1990) and an NRA report published in 1995 indicates that body burdens may sometimes exceed recommended limits (NRA, 1995). It would be interesting to use this species in a bio-monitoring capacity to help with contemporary chemical and biological assessments of the estuary (see section 7.2).

Thus, whilst the majority of data show that there has been a trend towards a reduction in metal bioavailability in Mersey biota over time, continued monitoring of metals is essential to determine which of these changes are part of longer-term trends brought about by improved management, and which represent short-term variations. It is also important to identify localised events within the SPA which may not comply with trends in recovery for the estuary as a whole.

### 7.1.2 Organic contaminants in biota

Compared with metals, information on the bioavailability of organotins, pesticides, PCBs and other bioaccumulating organics is relatively sparse.

*TBT and other organotins*

The MBA long-term investigations into bioaccumulation in Mersey biota measured total tin in common intertidal organisms including macroalgae (*Fucus vesiculosus*), polychaetes (*Nereis diversicolor*) and several molluscs (*Littorina littorea*, *Scrobicularia plana*, *Macoma balthica*, *Mya arenaria*, *Cerastoderma edule*, *Mytilus edulis*), as part of a larger suite of metals (see 7.1.1 above; Pope *et al*., 1998). Because TBT is much more bioavailable than inorganic Sn (Langston *et al*., 1990) it is likely that total tin body burdens are a surrogate for TBT. Most species showed the expected seaward decrease in concentrations, though superimposed on this trend were peaks at Garston and Blundellsands for a number of bioindicators (see examples figure 75).

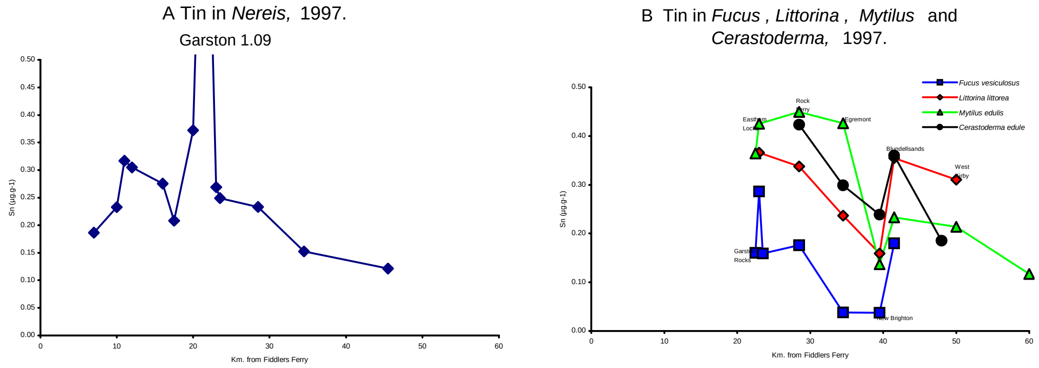



**Figure 75. Total Sn concentrations in intertidal organisms from the Mersey Estuary, 1997 (from Pope *et al.,* 1998)**

Butyltin (BT) concentrations and composition were compared in greater detail in the same (1997) samples from the Narrows section of the Mersey Estuary (Harino *et al*., 2005). Total concentrations of BTs were generally highest in sediment-dwelling fauna, particularly bivalves, and indicated the occurrence of bioaccumulation relative to sediments - notably, TBT in *M. arenaria* (bioaccumulation factor = 22). In contrast, bioconcentration factors in epibenthic species were generally not significantly above unity. Uptake from particulates (mode of feeding) and differences in relative rates of TBT metabolism probably explain much of this variation. The composition of organotins in *Mya* was dominated by the parent compound, TBT, indicating a slow rate of metabolism. However, compared to values found in the 1980s at impacted sites elsewhere (e.g. 5.55 - 11.47 mg $kg^{-1}$ dry wt. in from Poole Harbour (Langston *et al*. (1990)) results for TBT in *M. arenaria* from the Mersey were not exceptional (0.278-0.701 mg $kg^{-1}$ dry wt.).

In contrast to sediments (4% total tin as organotin), 85 % of the total tin in mussels surveyed in 1995 was made up of highly bioavailable BTs, the most predominant of which was TBT (Harino *et al*., 2003). Concentrations of TBT in mussels increased from 0.058 µg $g^{-1}$ dry wt at the mouth of the estuary to 0.214 µg $g^{-1}$ dry wt at their upstream limit, close to the entrance to the MSC at Eastham (figure 76) and were broadly consistent with trends seen in the sediment data. The proportions of various BT species in mussel are of reasonably constant composition, irrespective of location and total body burden: for MBT, DBT and TBT these proportions were 19-32%, 23-32% and 45-55%, respectively (Harino *et al*., 2003).

The TBT concentrations in mussels *M. edulis* from the Mersey Estuary are not exceptional by global standards. Values in mussels from polluted harbours and marinas may occasionally be an order of magnitude higher (Morcillo *et al*.,1997).

They are, however, consistently higher than OSPAR ecotoxicological assessment criteria for mussels (0.001-0.01 µg $g^{-1}$ dry wt). As indicated in the EA report on TBT (2001) the tin situation in the Mersey estuary warrants a small ad hoc study on biological impacts to re-asses the situation described in these MBA studies.

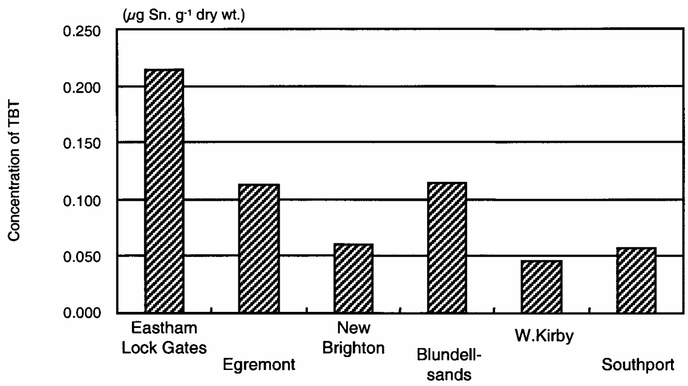



**Figure 76. *Mytilus edulis*. Concentrations of TBT in mussels from the Mersey Estuary, 1995 (from Harino *et al.*, 2003).**

Triphenyltin (TPT) compounds were not found in mussels. However TPT residues were determined in eels *Anguilla anguilla* from the Weston canal -part of the brackish section of the MSC complex, near Runcorn (Harino *et al* 2002). Although TBT was generally the most predominant of butyltin (BT) compounds present in eel tissues (and DBT the least) TPT was present up to 0.367 µg $g^{-1}$ (as Sn) in livers of these samples. To our knowledge, this is the first published report on the contamination of fish by TPT in UK waterways. Apart from its occasional use in antifouling preparations (less common than TBT) TPT is used principally in agricultural chemicals and, in particular, TPT hydroxide has been used as a crop-protectant for over thirty years. The presence of TPT in eels from the Weston Canal may therefore be associated with use as a fungicide, or even manufacturing, since a myriad of chemical industries are located in the catchment area of this site. Sources of TPT from antifouling seem unlikely.

Industry and shipping associated with the MSC appear therefore appear to be important sources of biologically available organotin in the Mersey Estuary. The fact that body burdens increase upstream in the estuary may be of significance for biota of the EMS. In view of the recognised toxicity of these triorganotins further research into their distributions and origins seems warranted.

*Pesticides and PCBs*

DDT compounds have been determined in flatfish (8-39 µg $kg^{-1}$ wet weight) and roundfish (6-17µg $kg^{-1}$) from the Mersey estuary and are somewhat lower than residues found in benthic crabs and whelks (30-50 µg $kg^{-1}$). A greater range of PCB concentrations have also been reported in invertebrates (8-105 µg $kg^{-1}$) than in fish muscle (8-43µg $kg^{-1}$ ) (Leah *et al*, 1997a, b). These PCB concentrations appear to often exceed both lower and upper Ecotoxicological Assessment Criteria (EAC) of 0.75-7.5 µg $kg^{-1}$ wet weight (for ICES7 CBs) set by OSPAR for mussels.

NMP surveys of PCBs in flatfish (dab, flounder and plaice) confirm that the Mersey and Liverpool Bay are still one of the most contaminated areas monitored in the UK (along with the Thames). Between 1999 and 2001 the median concentration for Liverpool Bay was 74 µg $kg^{-1}$ wet weight (CB 153 only). In 1993-1995, upper values for this site (170 µg $kg^{-1}$ wet weight) were the highest of 78 UK sites sampled (NMMP, 2004). PCBs in the muscle of flatfish from the Mersey estuary were up to four times higher than in Liverpool Bay fish and 20-200 times higher than in fish from the NW Atlantic and Solway Firth (Leah *et al*., 1997b).

Likewise, DDT levels in flatfish from the Mersey estuary are higher than in other UK populations (Leah *et al*., 1998). Dieldrin, lindane (γ-HCH) and hexachlorobenzene (HCB) have also been found concentrated in the tissues of fish and shellfish from the Mersey estuary and Liverpool Bay (Leah *et al*., 1998; McNeish *et al*., 1997a; McNeish *et al*., 1997b). Results for lindane were consistent with the finding that γ-HCH concentrations were high in the waters of the Mersey estuary at the time (MAFF, 1992; MAFF, 1995).

PCB data for eels from Albert Dock were reported by Johnston *et al*. (1990) as being very high more than a decade ago (7380 µg $kg^{-1}$ wet weight expressed as Arochlor 1254) and updated sampling would help to establish trends and risks in the estuary. By comparison values for lindane (90µg $kg^{-1}$), DDE (20µg $kg^{-1}$) and dieldrin (90µg $kg^{-1}$) were less notable.

Mussel surveys conducted in 1994 and 1998 describe spatial and temporal trends in organochlorines - including DDT, dieldrin, HCB, the methyl derivative of HCH (α-MHCH) and PCB (ICES 7) (Connor *et al* 2001). All organochlorines decreased markedly from Rock Ferry (the most upstream site sampled) towards the mouth of the Mersey, and continued to decrease upstream in the adjacent Dee Estuary (see examples in figure 77), largely as a function of distance from sources (presumed to be in the mid-upper Mersey).

There was a marked temporal reduction in α-MHCH residues (four- to ten-fold, at upstream sites in the Mersey) during the 1990s, as a result of controls on a chemical plant manufacturing pharmaceutical intermediates[19] in the inner estuary (Connor *et al,* 2001, see figure 77). This reduction was much more marked than most other OCs measured, which generally have a longer history of inputs and a more persistent

[19] MHCHs are generated as a by-product of continuous chlorination of toluene and are presumed to have physicochemical properties akin to lindane (γHCH). Manufacturing started in the 1960s but MHCH contamination was first reported in the 1990s (Connor *et al*, 2001). Since then there have been improvements to the treatment and disposal of wastes, presumably responsible for reductions in body burdens.

sediment repository. Nevertheless downward trends were observed for all OCs, attributed to improvements to sewage and trade effluents. For DDT (Σ*pp*DDE+*pp*DDD+*pp*DDT) reductions in mussel burdens between 1994 and 1998 were in the range 25-60%, similar to dieldrin and HCB (hexachlorobenzene, a bi-product of the chlor-alkali industry, now substantially regulated). For PCBs (the most persistent OCs) reductions were smaller (10-25% across most sites, no change at New Brighton) and were more detectable for the volatile congeners (e.g. CB 28 and 101)[20] than the more highly chlorinated, particle-seeking, components (e.g. CB 138 and 153). For the latter congeners it may be decades before the legacy of PCB contamination disappears. It is estimated that at the most contaminated site monitored in 1998 (Crosby), values were just in the JMP upper category (>100 μg $kg^{-1}$ wet weight, as Aroclor 1254), whilst other mussel samples were 'medium' 20-100 μg $kg^{-1}$ (Connor, *et al*., 2001).

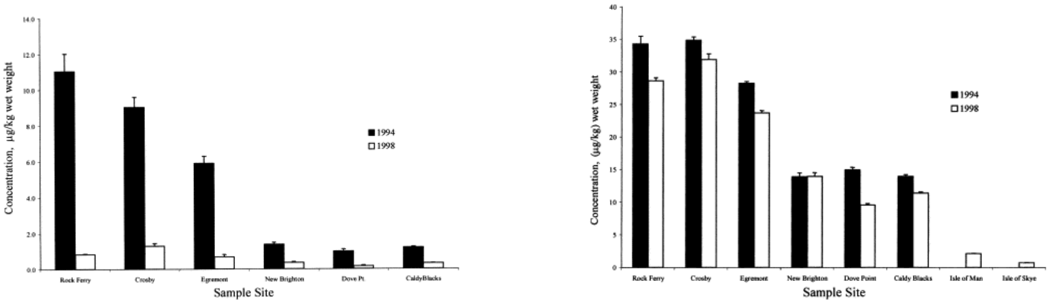



**Figure. 77. Trends in α-MHCH (left) and PCBs (right) in mussels from the Mersey Estuary (1994 vs. 1998).(Reproduced from Connor *et al.*, 2001, with permission from Elsevier Science Limited)**

CEFAS monitors commercial species in Liverpool Bay (cockles and mussels) as part of the UKs responsibilities under the shellfish directive. In line with most commercial beds around the UK these species do not appear to pose a human health risk. Even for high level shellfish consumers, estimated dietary intake of pesticide residues, based on 1998 data, appears to represent a small (<2%) proportion of the Acceptable Daily Intakes (ADI) / Provisional Tolerable Daily Intakes (PTDI) (CEFAS, 2001). Polychlorinated biphenyls were elevated in Liverpool Bay mussels though these were more than an order of magnitude below guidelines set by Norway/Sweden (at 2 mg $kg^{-1}$ wet weight). They are, however, above the lower Ecotoxicological Assessment Criteria (EAC) of 5 μg $kg^{-1}$ dw (~0.75 wet weight, for ICES7 CBs) set by OSPAR (NMMP 2004).

Bioaccumulation surveys therefore indicate substantive reductions in body burdens of metals and persistent organochlorines in recent years. These coincide with a range of regulatory pressures and directives, coupled with major investment in sewage treatment. In terms of the Mersey SPA, monitoring of detritivores and other infaunal types should be incorporated as a priority in long-term surveillance programmes, as suggested above. This is essential to address the issue of bioavailability of sediment contaminants. Soft-substrate habitats occupy most of the SPA and are becoming

[20] One point source of PCBs, notably contaminated with lower congeners such as CB28, was the landfill site at Alvanley close to Frodsham Marshes. This was remediated by EA in 1996 (Connor *et al*, 2001).

increasingly important, relatively, as diffuse sources (where rocky shore indicators are often atypical or absent). Many infaunal species are also important prey items for predators including the birds for which the SPA is designated.

The issue of food chain transfer of key contaminants such as Hg and PCBs, to higher predators, is difficult to assess because of the extremely small number of samples and uncertainty of movements and condition. Johnston *et al* (1991) found exceptionally high levels of both contaminants in livers of (dead) grey seal found in Liverpool Bay, tentatively linking these with abnormalities in the reproductive tracts of females (Baker, 1989). Previously this condition had been described for Baltic seal populations contain high levels of organochlorine contaminants (Reijnders, 1980). Hg and Pb burdens in livers of stranded marine mammals, sampled opportunistically throughout the Irish Sea, were found to be highest in Liverpool Bay - presumably as a result of transfer along the food chain (Law *et al.*, 1992). Work on the assessment of bioaccumulation of contaminants in bird species of the SPA would seem an important requirement for the future.

## 7.2 Biological Effects

The increasing emphasis on biological assessment and monitoring of estuarine ecosystems has highlighted the need to deploy appropriate effects indices for these locations. The options for biological effects monitoring involve deployment of biomarkers, bioassays and ecological indices or combinations thereof. To date there have been a number of attempts at using these techniques, in fish and shellfish, which show promise in informing on the status of biota in the Mersey Estuary and Liverpool Bay. Some of these would be useful for future assessments of the biological condition of the EMS, but may require trials with alternative species.

### 7.2.1 Biomarkers

Biomarkers in Fish

*Acetylcholinesterase activity:*

Acetylcholinesterase is an enzyme that was been widely used as a biomarker for neurotoxicity. It may be a particularly sensitive marker for organophosphate and carbamate pesticides, which inhibit the enzyme, resulting in a build-up of acetylcholine and excessive activity of the neuromuscular system.

Inhibition of muscular cholinesterase (ChE) was a feature of flounder *Platichtys flesus* from the Mersey, during comparisons with a range of other estuarine sites sampled in 1997, including the Alde, Tyne,Tees, Wear, Humber and Tamar (Kirby *et al.,* 2000). At Speke, values were reduced by almost a third, relative to 'control' fish from the Alde, whilst those from Bromborough, just downstream, were reduced by two-thirds (the lowest encountered in the survey). In attempting to identify causes, analysis of organophosphate (32) and carbamate (20) pesticides was conducted on water samples, though only eight OP and six C compounds were detectable across the entire survey.

None were detected in the Alde, whilst Mersey samples contained 36 ng $l^{-1}$ Diazinon, 13-29 ng $l^{-1}$ Fenthion and 18-31 chlorfenvinphos ng $l^{-1}$ (all OPs) and 8 ng $l^{-1}$ of the carbamate Ethiofencarb. Whilst these are unlikely to be responsible for major acute toxicity, they could, in view of their potency and additivity, be responsible for anti-cholinesterase effects. Since these studies were conducted pesticide concentrations may have decreased: most of the above OPs were below detection limits in the Agency 2002-2004 data-base. Diazinon occurred in only two of 24 samples from Seacombe Ferry, up to 71 ng $l^{-1}$ (MAC 150 ng $l^{-1}$). It is possible however, that acetylcholinesterase may also respond to metals, hydrocarbons, detergents and some algal toxins (and combinations thereof), or that OPs and carbamate pesticides accumulate via sediment and dietary routes rather than water (Kirby *et al.,* 2000). These possibilities require further investigation.

Assays of muscle from plaice collected from Liverpool Bay in 1997 indicated that levels of acetylcholinesterase were somewhat lower than many other UK sites (42% lower than fish from Dundrum Bay); a similar, if less pronounced, trend could be seen in dab (CEFAS, 2001). It is possible that biota from the system may therefore be responding to chronic exposure to neurotoxins, emanating from the Mersey, though as with EROD induction described below, there is as yet no certainty as to the cause.

*Metallothionein*

The physiological significance of metal burdens, can be examined specifically by determination of metallothionein (MT) induction and intra-cellular metal-binding patterns. The MT assay may act as an 'early-warning' indicator of metal exposure. There is also scope to deploy the assay to show temporal trends; i.e. to demonstrate improvements arising from planned schemes to reduce metals, standstill provisions of the Dangerous Substances Directive, or as may be required under the Habitats Directive to achieve Favourable Condition.

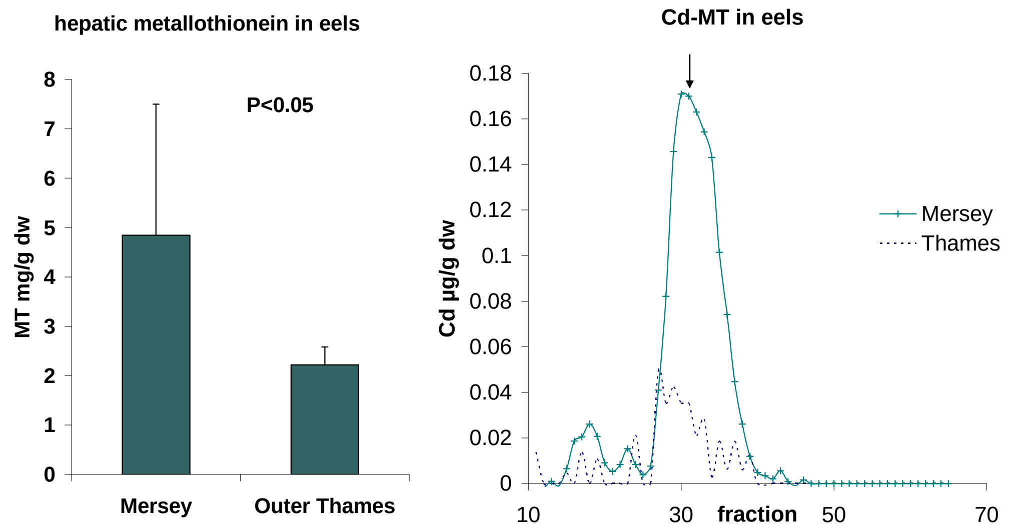



**Figure 78. Metallothionein in eels *Anguilla anguilla* from the Merseyside (Weston Canal) and outer Thames (own unpublished data).**

Preliminary studies to demonstrate the value of the technique were undertaken in 1999 using eels *Anguilla anguilla* from the Weston canal. Measurement of the MT protein in livers show significantly higher levels of induction in the Merseyside eels compared with eels from the outer Thames Estuary (figure 78). Metal binding profiles in livers confirm the presence of high levels of Cd-MT compared to the less-impacted Thames site. Further work on metallothionein within the EMS would be useful to indicate whether organisms are attempting to respond, or are adapted, to metal stress. Studies (in 2001) have measured the protein in dab livers at 16 sites around the UK. Metallothionein levels in Liverpool Bay fish do not appear to be exceptionally elevated and variability at each site was relatively high. Concentrations were most consistently correlated with Cu in both sexes and to a lesser extent with Pb (males) and Zn, Hg and Cd (females) (NMMP 2005). Further MT studies within the estuary, and the SPA, would be useful to indicate whether organisms are attempting to respond or are adapted to metal stress.

*EROD*

PAHs, PCBs (planar), dibenzo-b-dioxins and dibenzofurans can, when absorbed by benthic flatfish, induce the synthesis of the cytochrome p450 group of enzymes, typified by CYP1A1-dependent EROD (ethoxyresorufin-O-deethylase) activity. The close association of these fish with sediments (which tend to scavenge hydrophobic contaminants) may make them a particularly useful biomarker of this type of contamination.

EROD activity is one of the key biomarkers deployed in recent years as part of the UK National Marine Monitoring Programme (NMMP) to monitor biological effects. Surveys of EROD levels in dab *Limanda limanda* conducted at NMMP sites in 2001 indicated that, as in previous years, fish from Liverpool Bay have elevated levels compared with less contaminated coastal regions (CEFAS 2003). This was also observed in a survey conducted in 2002, with dab from the Burbo Bight and Liverpool Bay (figure 79) displaying mean activities of 604 and 654 pM/min/mg protein – more than ten times higher than fish caught in the Humber – suggesting long-term exposure to organic contaminants (though condition of fish and pollutant interactions can be confounding factors). Highest values in the survey (1208 pM/min/mg protein) were at Amble, off the NE coast (CEFAS, 2005).

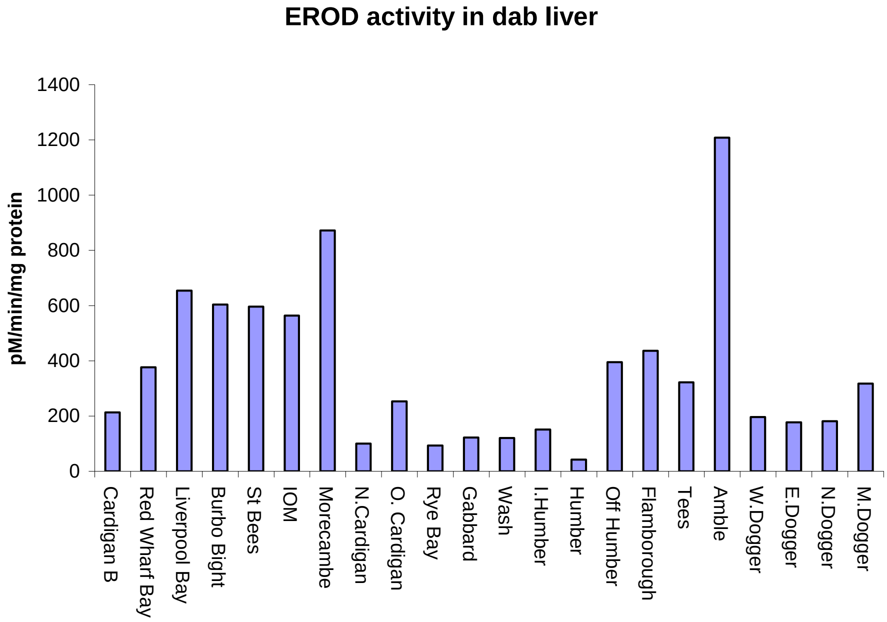



**Figure 79. EROD activity in liver of dab *Limanda limanda*, 2002 (from CEFAS 2005).**

Within the Mersey Estuary itself, flounder *Platichthys flesus* exhibit significantly elevated levels of EROD; Kirby *et al*., (2004a) reported a mean EROD activity of 164.8 pM/min/mg protein for male flounder collected from Eastham Sands, and an overall mean (males and females) of 134.9 pM/min/mg/protein. This was the second highest EROD activity recorded in flounder from five UK estuaries sampled, and significantly elevated in comparison to a reference site on the Alde Estuary.

Flatfish within the EMS are not the only fish reported to display high levels of EROD activity; EROD activity in eels *Anguilla anguilla* from the Weston Canal, adjacent to the estuary, was found to be higher than in eels from seven UK water bodies, and 13-fold higher than the Tamar reference site (Doyette *et al.*, 2001) (figure 80).

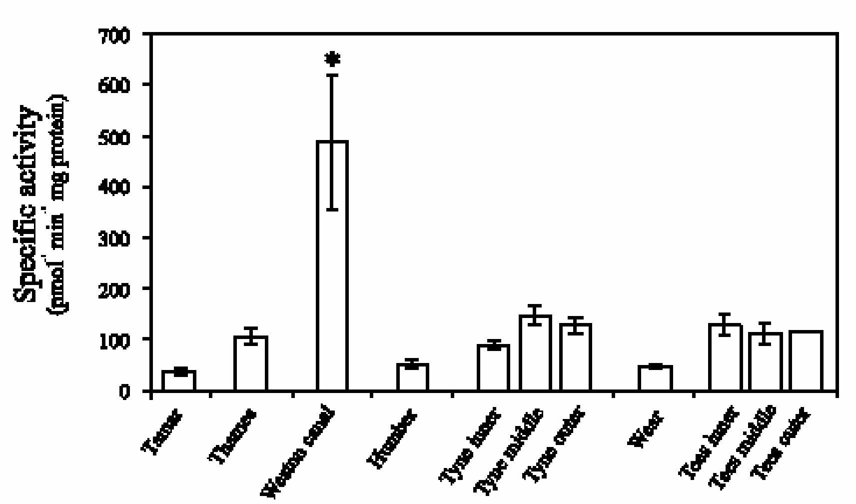



**Figure 80. EROD activity in liver of eels *Anguilla anguilla* from UK estuaries Values are means ±SE (n=5-9, outer Tees, n=1). * Significant difference (<0.05) to Tamar reference site (Doyette *et al.*, 2001, reproduced with permission from Elsevier)**

Causative agents of such EROD induction in the field are not easily established or interpreted, although numerous field studies have linked elevated hepatic EROD activity in fish with chemical contaminant levels such as PCBs and PAHs (e.g. Kirby *et al*., 1999; Sleiderink & Boon,1995; Bucheli and Fent, 1995; Goksøyr, 1995; Stagg *et al*., 1995; Collier *et al*., 1998).

*Major bile metabolites*

PAHs are rapidly metabolised in the liver. Analysis of major bile metabolites (e.g. 1-OH Pyrene) may be a useful surrogate measure of exposure, as indicated by CEFAS screening of dab: samples from Liverpool Bay were among the most elevated with values at the NMP 705 site (306 µg $l^{-1}$) two-fold higher than lowest levels (figure 81 ; compiled using data in CEFAS, 2005). Since dietary status can also affect bile components this too must be considered in the interpretation of results. Given this constraint, bile metabolites may be a useful indicator of PAH exposure, though as indicated in comparisons between patterns in figures 79 and 81, there are no unambiguous links between PAH exposure and EROD induction, and in some cases EROD distributions can be difficult to explain.

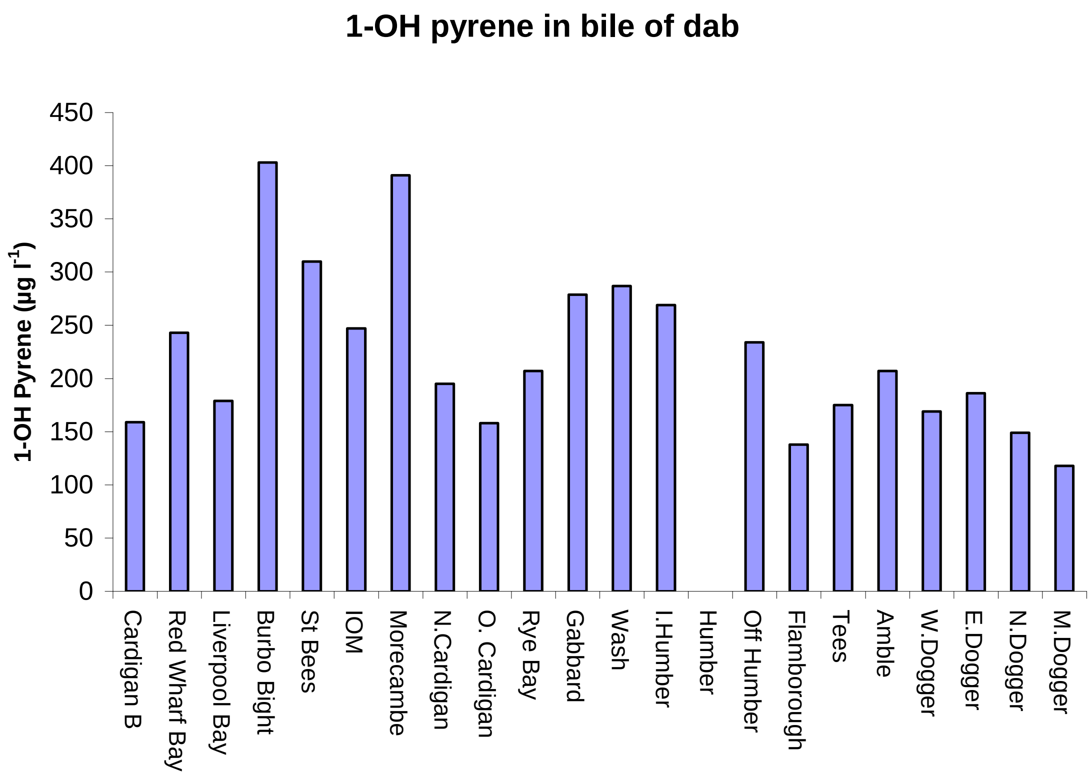



**Figure 81. 1-OH Pyrene, a biomarker of PAH exposure, in bile of dab *Limanda limanda*, 2002 (from CEFAS 2005).**

*DNA adducts (electrophilic molecules or free radicals bound to DNA)*

These are highly reactive metabolites, notably of some PAHs (e.g benzo[a]pyrene and benzo[a]anthracene), which are capable of binding to DNA and are potentially early warning indicators of carcinogenesis and other pathologies in fish. Numerous studies have established correlations between the formation of DNA adducts and incidence of hepatic neoplasia in fish populations and the presence of genotoxins, including polycyclic aromatic hydrocarbons (PAHs) in the sediment (reviewed by Stein *et al.* 1994).

Analysis of these adducts in the livers of dab from Liverpool Bay (2001) showed the number of adducts per $10^8$ undamaged nucleotides to be 7.5 compared to a maximum of 16.2 in dab from Burbo Bight, and a minimum of 0 (e.g outer Cardigan Bay) and indicates exposure to PAHs and other genotoxins. DNA adducts found in flounder from the Mersey (7.4 adducts per $10^8$ undamaged nucleotides) also indicated elevated exposure compared to a reference site in the Alde (1.7-3) (NMMP, 2004). This ties in to an extent with evidence from PAH exposure patterns, based on bile metabolites, described above.

In a (2002) survey of flounder from eight UK estuaries, Lyons *et al.,* (2004) found highest levels of hepatic DNA adducts in fish from Southampton and lowest in Belfast (means = 93.9 and 4.2 adducts per $10^8$ undamaged nucleotides, respectively) (see figure 82). The Mersey Estuary ranked fifth in terms of affected fish (17.4 adducts per $10^8$ undamaged nucleotides), which was nonetheless considered to be high, and characteristic of exposure to complex mixtures of aromatic/hydrophobic genotoxins (Lyons *et al.,* (2004).

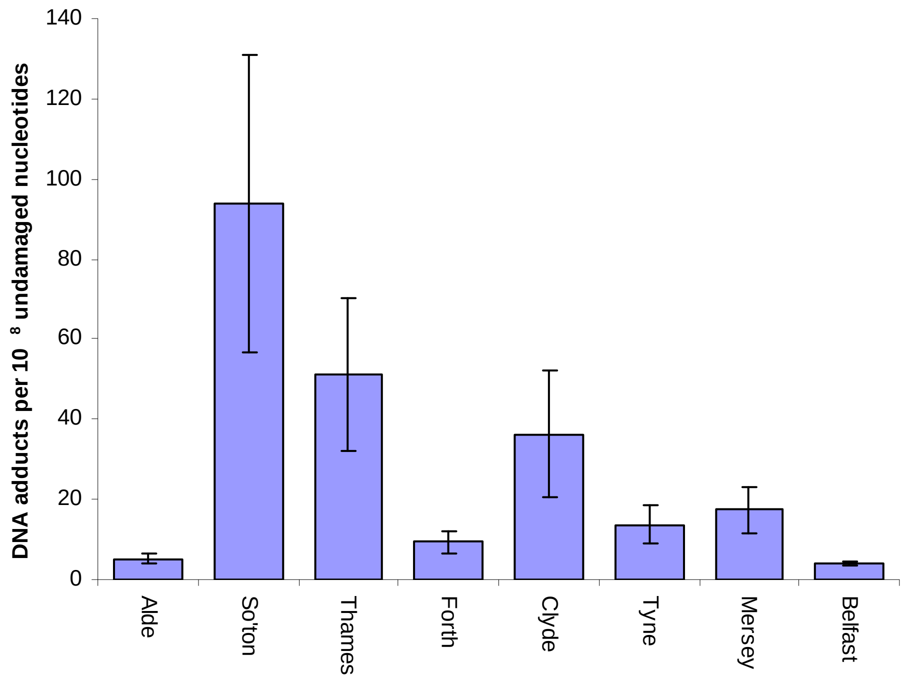



**Figure 82. Mean number of hepatic DNA adducts (per $10^8$ undamaged nucleotides) in flounder *Platichthys flesus* from UK estuaries. Error bars represent SE of the mean (Drawn from data in Lyons *et al.,* (2004).**

*Fish Pathology and disease biomarkers.*

Fish diseases and histopathology, with a broad range of causes, are increasingly being used as indicators of environmental stress since they provide a definite biological end-point of historical exposure (Stentiford *et al.,* 2002). CEFAS have established prevalence of external disease and pathological changes in dab from Liverpool Bay in recent years, as part of the NMMP programme (CEFAS, 2005). Disease symptoms observed included lymphosystis, epidermal ulceration, epidermal papilloma, hyperpigmentation, macroscopic liver lesions and number of parasites. The incidence and severity of disease and histopathological lesions appears to fall within the range observed at a number of other sites sampled around the Irish Sea (and North Sea) but are higher than a proposed reference site in Rye Bay. Highest levels of disease prevelance have for a number of years been associated with fish from the Dogger Bank. A summary of histologically characterized liver lesions in dab populations (CEFAS, 2001) is shown in figure 83.

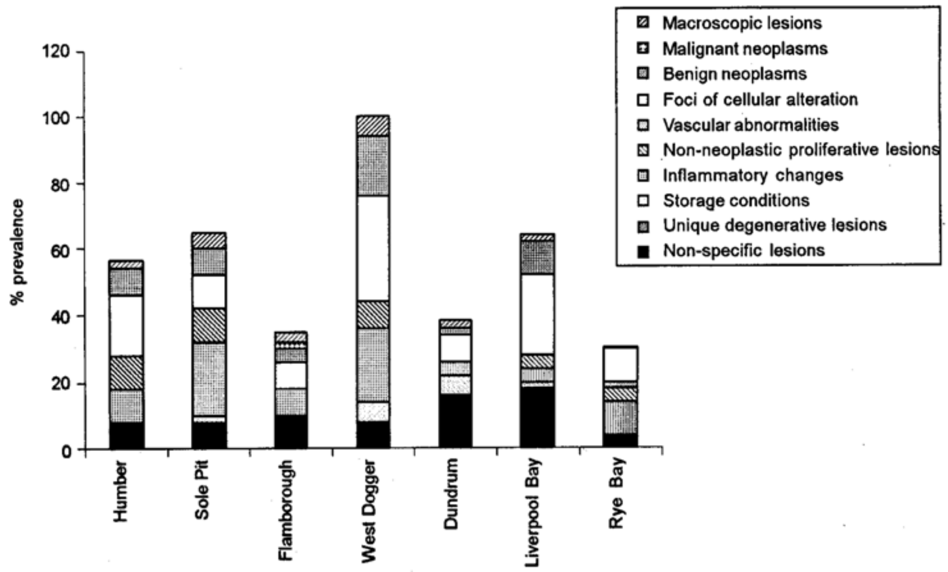



**Figure 83. Frequency of histologically characterized hepatic lesions in dab, sampled at sites in the North Sea and Irish Sea (from CEFAS, 2001; with permission).**

Trend analysis for Liverpool Bay fish suggests a slight increase in the frequency of liver nodules and also epidermal hyperplasia since 1998, though factors responsible for this change are unknown. Nevertherless, since several categories of disease observed in these fish can be caused by exposure to organic contaminants, and in view of evidence of exposure based on other biomarkers (EROD, bile metabolites, DNA adducts) further attempts to establish links between cause and effects seem to be justified (CEFAS, 2005).

Histopathological biomarkers have also been reported in fish from within the Mersey Estuary. Examining selected organs and tissues from estuarine fish (flounder *P. flesus,* sand goby *Pomatoschistus minutus* and viviparous blenny *Zoarces viviparus*) from four estuaries (Tyne, Tees, Mersey and Alde), Stentiford *et al.,*(2002) reported that the presence of pre-neoplastic and neoplastic toxicopathic lesions was highest in *P. flesus* from the first three sites, in comparison with fish from the Alde reference site. In particular, the prevalence of hepatic foci of cellular alteration (FCA's) and hepatocellular adenoma were highest in *P. flesus* from the Mersey Estuary (up to 43.3% and 10% respectively). Hepatocellular FCAs are regarded as early stage pathologies in the stepwise formation of hepatic neoplasia in fish, and consequently provide a histopathological biomarker of carcinogen exposure. Similarly, hepatocellular adenoma is a lesion type important in the development of carcinogenesis, and was only recorded in flounders from the Mersey estuary. The latter is considered to be an important category for inclusion in histopathological surveys of this type (Stentiford *et al.,* 2002). The prevalence of hepatocellular fibrillar inclusions (an unusual proliferation of the rough endoplasmic reticulum and/or an extensive formation of microtubules (Köhler, 1990)), was also highest in flounders from the Mersey estuary, as was prevalence of lamellar fusion of hyperplasia of the gill (Stentiford *et al.,* 2002).

With the exception of hepatic nuclear and cellular pleomorphism, gobies and blennies did not present the same array of pathologies found in flounder from the same sites. Notably, the incidence of this in gobies and blennies from the Alde was considerably lower than in the Mersey Tyne, and Tees.

A later study re-examined flounder liver, and found a similar range of lesions (Lyons *et al.,* 2004). Of eight UK estuaries, the Mersey was the only estuary that contained flounder with all four categories of FCA (basophilic, eosinophilic, vacuolated and clear cell). Significantly, this study detected elevated levels of FCAs at those sites deemed to be the most contaminated by PAH (Tyne, Mersey and Thames). Other histopathological biomarkers in Mersey fish included hepatocellular fibrillar inclusions, nuclear pleomorphisms along with non-toxicopathic changes/alterations, such as those associated with cell turnover (apoptosis, necrosis, regeneration) and immune-related functions (melanomacrophage aggregates, inflammation). Generally, the lowest prevalence of these lesion types was again seen in flounder from the Alde estuary, with higher prevalence (particularly of melanomacrophage aggregates, inflammation and necrotic foci) seen in fish from the Mersey and other contaminated sites (Lyons *et al.,* 2004).

Longshaw *et al.,*(2004) found a number of different parasites and prokaryotic infections have been found in greater pipefish *Syngnathus acus* from the Mersey Estuary, which indicates poor condition. Pipefish have no commercial value and their role as prey items is unknown, however they could have an important role in disease transmission to commercial stocks. Longshaw *et al. (*2004) suggest *S. acus* should be considered as a target species in biological assessments of contaminants in estuaries where their numbers are sufficient.

*Endocrine disruption*

The initial observations of endocrine disruption in freshwater fish populations suggested that oestrogenic effects decreased rapidly within relatively short distances from sources (usually WwTWs). It was therefore anticipated that dilution in estuaries and the open sea would render the threat harmless in these environments. Since then, the discovery that some benthic estuarine fish, notably flounder (which have close contact with sediment and feed on benthic infauna), also exhibit symptoms of impact from oestrogens, has led to the recognition that adsorption to particulates may be responsible for impeding dispersal and dilution and that sediments could be acting as a secondary source (Allen *et al.,* 1999a, b).

Habitat and feeding preferences make species such as flounder vulnerable to the type of sediment-associated pollution which occurs in estuaries. Thus, bioaccumulation and biomagnification of ED compounds, via infaunal organisms, could contribute to the oestrogenic responses (raised vitellogenin - VTG - and ovotestis) seen in male flatfish (Lye *et al.*, 1999; Matthiessen *et al.,* 2002). However, as there are likely to be complex mixtures of other endocrine disrupting chemicals in sediments, including oestradiol, oestrone, oestriol, ethynyloestradiol, alkylphenols, PCBs and OC pesticides, phthalates and other xenoestrogens, the causative agent(s) may well be acting in combination and the relative contributions of each remains uncertain (Matthiessen *et al.,* 1998; Lye *et al*., 1999).

An indication of the scope and scale of effects in fish is beginning to emerge. Allen *et al*. (1999b), for example, found that male flounder from the Mersey Estuary in the mid 1990s contained the highest recorded plasma VTG concentrations of all UK marine sites sampled (40,000 µg $ml^{-1}$). Many fish also displayed advanced ovotestis (though ecological significance is difficult to assess on these observations alone). Ovotestis (intersex) was also recorded in 8.3% of male *P. flesus* captured from the Mersey Estuary (Stentiford *et al.,* 2002). Flounder trawled from Liverpool and Red Wharf Bays contained the highest recorded VTG concentrations of all offshore sites but did not show ovotestis (Matthiessen *et al*., 1998). Between 1996 and 1997 plasma VTG in male flounder caught at Eastham Sands in the estuary was reported to have dropped by an order of magnitude from 10,000 µg $ml^{-1}$ to a reported 100µg $ml^{-1}$ in 2001 (NMMP, 2005) with only 30% of Mersey fish affected (NMMP, 2005). Kirby *et al*., (2004b) reported VTG concentrations of 600µg $ml^{-1}$ in Mersey flounder during 2001. There appears to be some discrepancy in actual levels of VTG reported, nevertheless, these concentrations still represent high levels compared to most other estuaries (NMMP, 2005). Examining evidence and potential for endocrine disruption in European Marine Sites in England, Allen *et al,* (2000) identified the Mersey Estuary as a high priority site for further research in this field.

Between autumn 1997 and summer 2000, a series of detailed studies, completed mainly within the EDMAR framework, focused on effects of endocrine disrupting compounds on flounder in the Mersey, in comparison with the Dee Estuary (a 'control' site). Kleinkauf *et al.,* (2004a) found a marked seasonal cycle in plasma VTG concentrations: levels in male flounder from the Mersey varied from <0.01µg $ml^{-1}$ in September to a maximum of 11500µg $ml^{-1}$ in February, whilst in flounder from the Dee, minimum and maximum values were <0.01 and 17.2µg $ml^{-1}$ and VTG showed no evidence of a seasonal cycle. This study indicates that plasma VTG in male flounder from the Mersey was still very high in 2000. The seasonal pattern observed by Kleinkauf *et al.,* (2004a) in the Mersey fish may help to explain the discrepancies in VTG levels previously reported.

Kirby *et al.,* (2003) investigated morphological changes in the urogenital papilla of male gobies (*Pomatoschistus* spp.) from the Mersey and several other UK estuaries. The sand goby is one of the key species in the U.K. 'Endocrine Disruption in the Marine Environment' (EDMAR) Program (Matthiessen *et al*., 2002). Evidence of feminization of male papillae was found, a condition denoted as 'morphologically intermediate papilla syndrome' (MIPS). Laboratory exposures showed that this condition is inducible by estrogenic exposure, indicating that is a form of endocrine disruption. MIPS was most prevalent (>50%) in fish from the Mersey, Tees, and Clyde.

To date, most investigations into endocrine disruption in the Mersey have focused on fish, and field studies into endocrine disruption in invertebrates are relatively few. However a recent study investigated variations in the reproductive morphology of the shore crab *Carcinus maenas* from the Mersey Estuary, and seven other UK sites (comprising a putative gradient of exposure to endocrine disrupting chemicals) for evidence of endocrine disruption (Brian, 2004). A reduction in dominant claw size in male crabs (a female trait) correlated with the exposure gradient of endocrine disrupting chemicals, as did heterochely (difference between right and left claw size). Significant differences between the degree of heterochely in crabs from the Mersey and Tees, and to a lesser extent the Clyde and Dee, were found compared with two reference sites (Arisaig and Appin). However, no consistent pattern was found for other traits (notably carapace and abdominal area measurements) among populations from reference and contaminated sites. These findings suggested that shore crabs may not be susceptible to the same type of endocrine disrupting effects that have been detected in vertebrates (most commonly mediated via the oestrogen receptor). Several other explanations for differences in the chelal morphology of crabs from the Mersey and other contaminated sites were considered, including direct and indirect effects of pollution on crustacean health, although the possibility of endocrine disruption was not ruled out. It is possible that crustaceans may be affected by a different type of chemical to those capable of interfering with the reproductive development of vertebrates (Brian, 2004).

*General condition Biomarkers*

The fact that male fish exhibit an apparently enormous capacity to synthesise VTG in response to endocrine-disrupting compounds led researchers to consider that there may be correlations between VTG plasma concentrations and some general biological condition markers. Irish Sea male flounder with elevated VTG have been found to have high hepatosomatic indices (HSI - ratios liver:body weight) indicating that oestrogenic exposure had caused abnormal liver growth (hypertrophy) in order to synthesise VTG, thus placing strain on the metabolism of these fish. (Matthiessen *et al.*,1998). Gonadosomatic index (GSI) and HSI were also found to covary with plasma VTG concentrations in flounder from within the Mersey (Eastham Channel and Eastham Sands) (Kleinkauf *et al.,*2004b).

Several other physiological parameters have been assessed in flounder to determine their potential for serving as biomarkers in the prediction of elevated VTG production in male and immature flounder (Kleinkauf *et al.,* 2004b). Despite the abnormally elevated VTG plasma concentrations in the Mersey flounder compared to those from the Dee, no significant differences were found in oestrogen receptor binding capacity or binding affinity, between the two groups. Hepatocyte proliferation was also ruled out as a VTG-related specific "biomarker of effect", and sperm motility, although higher in Mersey flounder, was not linked to an elevated VTG plasma concentration. However, immunohistochemical staining for proliferating cell nuclear antigen showed significantly higher proliferative activity in the livers of Mersey flounder than that of Dee flounder.

Although the biomarkers studied by Kleinkauf *et al., (*2004b) were not found to indicate significant differences between Mersey and Dee fish, Kleinkauf *et al., (*2004c) reported differences in flounder from the two estuaries for some other condition biomarkers. A slightly lower growth rate after age 2 was found for the Mersey flounder; lower GSI in both mature male and female animals; less precise seasonal patterns of condition factor (CF), HSI and GSI, and lower CF in immature Mersey fish. These effects were considered to be diagnostic signs of a contaminant-affected Mersey population (Kleinkauf *et al.,* 2004c). In the same study, correlations were found between burdens of various contaminants in flounder livers (PCB congeners, DDTs, HCBD, HCB, HCHs) and CF, HSI, GSI, and liver lipid concentrations.

Biomarkers in bivalve molluscs

Shaw *et al.,* (2004) examined the relationship between various biomarkers and parameters (cytochrome P450 1A- and 2E-immunopositive proteins, lipid peroxidation, DNA strand breaks and scope for growth) in *Mytilus edulis* at different seasons and at different sites around the UK coast (New Brighton in the Mersey Estuary, Blackpool, Whitstable, River Swale and Port Quin). Findings regarding relationships between these biomarkers and parameters are as follows: Cytochrome P4501A (CYP1A)-immunopositive protein and DNA strand breaks were generally lowest in December. No correlation was found between PAH exposure (chemical measurement and CYP1A-immunopositive protein expression) and DNA strand breaks (highest at the relatively non-polluted site of Port Quin). CYP-like proteins were also maximal at most sites in May. Lipid peroxidation, in contrast, did not alter markedly throughout the year. Shaw *et al.,* (2004) conclude that DNA strand breakage was not correlated with any of the above parameters although it did correlate with "scope for growth" as did the inverse of PAH levels. The need to establish the relative contribution of DNA damage and repair processes to the production of DNA strand breaks was highlighted, and the need to consider seasonal variation in interpretation of biomarkers was also emphasised.

Findings of individual biomarker assays and parameters measured in this study, in relation to the Mersey Estuary, are discussed below.

*DNA strand breaks (Comet Assay)*

DNA strand breaks (SBs) can be used as a non-specific biomarker of genotoxicity, and elevated levels in aquatic species have been linked to mutagenic environmental contaminants such as DDT and PAHs (Mitchelmore *et al.,*1998, Cotelle & Ferard, 1999). A single-cell gel electrophoresis/ fluorescent microscopic technique known as the Comet assay is a sensitive technique to detect strand breaks, and examine DNA damage and repair at the individual cell level.

Elevated levels of SBs were found in mussels *Mytilus edulis* caged at New Brighton, at the mouth of the Mersey, compared to SBs in mussels caged at a non-industrial control site (Port Quin, Cornwall). Moreover DNA damage in mussels transplanted to New Brighton exceeded that of indigenous mussels at the site. (Shaw *et al.,* 2002). However, a subsequent study of SBs in natural populations of *M. edulis*, reported a lower incidence of SBs in Mersey mussels compared to mussels from the Port Quin reference site (Shaw *et al.,* 2004).

*Scope for growth*

This physiological stress response technique was developed for use with bivalves, particularly mussels, to give a general measure of the overall physiological health of the animal based on its energy budget. The scope for growth (SFG) is the difference between the energy assimilated from food, and the energy used in respiration, excretion and other maintenance activities. Any surplus energy is available for growth and reproduction. A reduced or negative scope for growth results when energy intake from food is reduced, as it may be in winter, or if the energy expenditure on maintenance activities is increased by environmental stress. Thus, scope for growth is useful in that it integrates both natural and pollutant impacts. Scope for growth indicates an animal's physiological condition, and has been shown to decrease in mussels *Mytilus edulis* with exposure to PAHs, as well as tributyltin and organochlorine compounds (Widdows *et al.,* 1995).

Widdows *et al*., (2002) quantified the degree of pollution along the coastlines of the Irish Sea by measuring the SFG and contaminant concentrations in the tissues of mussels collected in 1996 and 1997. On the UK mainland coast, the general trend in SFG showed a significant decline with water quality in the Mersey/Liverpool Bay region, which was associated with a general increase in contaminant levels in the mussel tissues. Contaminants that showed elevated concentrations (i.e. >10-fold higher than background or detection limits) included PAHs, TBT, ΣDDT, Dieldrin, γ-HCH, PCBs, and a few of the metals (Cd, Se, Ag, Hg, Pb). Many of these contaminants were particularly elevated in the coastal margins of Liverpool Bay. SFG in the mussel population from New Brighton fell from 8.71 to 3.17 J $g^{-1}$ $h^{-1}$ over the two year study. SFG measurement of <5 J $g^{-1}$ $h^{-1}$ is classified as 'low growth potential/high stress' (Widdows *et al*., 2002).

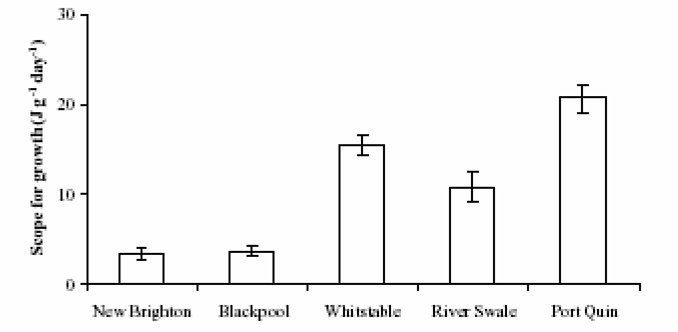



**Figure. 84. Scope for growth (J $g^{-1}$ $day^{-1}$) in *Mytilus edulis* from 5 UK sites (08/1998) presented as mean ± SE. (Shaw *et al.,* 2004)**

Exploring relationships between a number of biomarkers in *M. edulis,* Shaw *et al.,* (2004) also found reduced SFG in mussels from New Brighton. Lowest levels out of five UK sites were measured in New Brighton mussels and the highest SFG, by approximately six-fold, was found in mussels from Port Quin, the reference site (figure 84).

*CYP isoform immunopositive protein determination*

A cytochrome P450 (CYP)-like protein, similar to that found in benthic flatfish (see above), identified in mussels *Mytilus* spp. has been used to assess the biological effects of organic pollutants in mussels from the Mersey (Shaw *et al*., 2002; 2004). Levels of CYP1A-immunopositive protein were 1.5 fold higher in natural populations of mussels *Mytilus edulis* collected from New Brighton in comparison to those from Port Quin (Cornwall). Correspondingly high levels of PCBs (Σ7 CB congeners) were found in the digestive glands of New Brighton mussels (21-fold higher). In transplant experiments, levels of CYP1A-immunopositive protein in mussels transplanted from Port Quin to New Brighton increased by 1.4 fold compared to the caged controls at Port Quin (Shaw *et al*., 2002).

In a subsequent study CYP-like proteins (CYP1A and CYP2E) in mussels from five UK sites showed marked seasonality, peaking in May, with lowest levels in December. However, in contrast to the earlier study levels of CYP-like proteins were generally higher in mussels from the Port Quin reference site than the other UK sites casting some doubt as to the value of this preparation (Shaw *et al*., 2004).

*Lipid peroxidation assessment via malonaldehyde (MDA) determination*

Lipid peroxidation can result from free radicals reacting with, and damaging, DNA, RNA and biological membranes which are rich in polyunsaturated fatty acids, and are especially susceptible to this type of damage. They can react to form lipid peroxides, which are themselves unstable, and undergo additional decomposition to form a complex series of compounds. Polyunsaturated fatty acid peroxides further react to form malonaldehyde (MDA), which has become one of the most widely used biomarkers for estimating oxidative stress effects on lipids. PCBs, PAHs, some nitroaromatic compounds and various metals can increase lipid peroxidation. Shaw *et al.,* (2004) found generally higher levels of MDA in mussels from the Mersey compared to four other UK sites. This was most notable for mussels sampled in May.

### 7.2.2 Bioassays

Oyster larval development has been used in the assessment of water quality around the UK coastline by NMMP and, in 2001, incorporated sites at Seacombe Ferry (on four occasions) and Channel C1 Buoy (three times). These short-term tests indicated no significant acute toxicity compared with controls (artificial sea water).

Using whole animal bioassays with infaunal species such as *Arenicola marina* and *Corophium volutator,* toxicity in sediment samples from Liverpool Bay is implied. Significant reduction in cast production in *Arenicola*, a sign of reduced feeding activity, was observed in sediments from NMMP station 715 collected in 1998

(CEFAS, 2001). Mortalities of *Arenicola* (and *Corophium*) in the 10 day assays were 7 and 20% respectively – not significantly different to controls held in sand from Shoebury (13 and 7%, respectively). Results are interpreted as indicating diminished sediment quality, though this induces sub-lethal, rather than acute, responses. A later study, using the same bioassay found significantly reduced feeding activity in *Arenicola* held in sediments from the Mersey Estuary (No 7 Buoy) and inner Liverpool Bay (Thain & Bifield, 2001).

Mersey sediments have been used to test responses of nematode assemblages to simulated sediment deposition events (CEFAS, 2001). Microcosm experiments indicate that recolonisation of deposited sediments by some nematode species can be affected the nature of the sediment (and frequency/depth of application). Migration and survival rates tended to be lowered by Mersey sediments, presumably in response to contaminant levels and relatively anoxic status. The study demonstrated that this technique could provide useful comparisons of sediment impact on meiofauna within the estuary and also in sediments destined for dredging and disposal (CEFAS, 2001).

An in vitro bio-analytical assay, DR-CALUX (a coupled reporter-reporter gene system responsive to compounds which interact with the aryl hydrocarbon receptor), has been used to assess the presence of dioxins and dioxin-like compounds, including furans, in sediments from the lower Mersey Estuary (CEFAS, 2005). Expressed as toxic equivalents (TEQ) to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), the most active dioxin, responses in Mersey samples varied from 8.7 ng TEQ $kg^{-1}$ to 40 ng TEQ $kg^{-1}$ dry weight. These are lower than the highest value found (106 ng TEQ $kg^{-1}$ in the Forth) but higher than guideline thresholds recommended in Canada, the USA and Holland (0.85, 2.5 and 13 ng $kg^{-1}$, respectively). Adverse effects in sensitive organisms cannot, therefore, be ruled out, though it is possible that dioxins themselves are not solely responsible for the bioassay response: other compounds with dioxin-like activity could be involved.

Similarly, Thomas *et al*. (2002) used the mutagenic screening assay Mutatox to assess the genotoxic activity associated with sediment samples collected from five UK estuaries, including the Mersey. Mutatox is a mutagenicity assay which uses a dark variant marine bioluminescent bacterium (*Photobacterium phosphoreum*) which, when exposed to mutagenic compounds revert to the normal genotype and emit light. The Mutatox assay is particularly suited to toxicity identification evaluation (TIE) studies because it is easy to use, rapid, cost effective, requires low sample volumes, and allows a high through-put of samples. Importantly, the *Photobacterium* strain shows low cytotoxicity when exposed to complex environmental mixtures. In this study at least one sediment sample from each estuary that contained potential genotoxins was identified. In the Mersey, a sample from opposite Canada Dock showed mutagenic activity, and genotoxins including, PAHs, alkyl-substituted PAH, nitro-polycyclic aromatic compounds (PACs), polycyclic aromatic ketones and oxygenated PACs were identified using a bioassay-directed fractionation procedure. A remaining proportion of potentially genotoxic contaminants could not be identified (Thomas *et al*., 2002).

A combination of esterase activity and ventilation rate assays has been applied to evaluate toxicity in relation to WwTWs discharges into tributaries of the Mersey Estuary (O'Neill *et al.,* 2004). Cholinesterase and carboxylesterase activities were significantly inhibited ($p<0.05$) and ventilation rates increased ($p<0.001$) in the freshwater crustacean *Asellus aquaticus* at WwTWs sites compared to those from reference sites, indicating a decrease in neurological and physiological function. Although it is not yet possible to attribute these effects solely to sewage effluent, ventilation rate in crustaceans is known to be a sensitive biomarker of the impact of WwTWs effluent due to the effect of organic pollution on ammonia and dissolved oxygen levels (Maltby, 1995), and esterase activity is inhibited by exposure to organophosphorous pesticides, crude oil, metals and complex mixtures (Galloway *et al.,* 2002).

The combined measurement of these two biomarkers in *A. aquaticus* provided a rapid, integrated assessment of the effect of sewage effluent exposure to the isopod, and may have potential in wider assessment of WwTWs discharges, which often contain a complex mixture of natural and synthetic xenobiotics, and ultimately enter estuaries such as the Mersey via tributary rivers and brooks.

Lindley *et al.,* (1998) assessed the viability of copepod eggs from sediments as a potential technique for *in situ* bioassay of fine sediments. Calanoid copepod nauplii samples were taken from the Mersey, Humber and the Exe in 1995. The concentrations of polycyclic aromatic hydrocarbons (PAH) in the sediments were measured as an index of pollution and found to be lowest in the Exe and highest in the Mersey. Many more nauplii hatched from incubated sediments from the Exe than from the more polluted estuaries. Eggs were extracted from the samples and incubated; 92% of those from the Exe, 48% of those from the Humber and 14% of those from the Mersey hatched. This is consistent with reduction in viability of eggs with increased pollution.

### 7.2.3 Ecological indices and general site condition

As well as the qualifying bird populations, the extensive intertidal habitats (mudflats and sandflats), together with their infauna, are important ecological components of the European Marine Site, providing extensive areas for feeding. Extensive saltmarshes along the south bank are also important roosting and feeding areas for waterfowl.

The EA undertook a survey of benthic invertebrate fanua across a grid of 53 sites throughout the estuary in 2001 in order to provide updated information on spatial patterns in intertidal (36 sites) and subtidal (17 sites) communities. Data are summarised in a report to the Agency by Young Associates (EA, 2002). Results were broadly comparable to earlier surveys conducted between 1990 and 1992 (Environmental Resources Ltd) as part of the Mersey Barrage Proposal and indicated relatively large areas of low species diversity and abundance (23% of samples were devoid of macrofauna) – mainly associated with well-scoured sand flats and tide-swept channels (Hale Head, Eastham Sands, Garston Channel), contrasting with richer and more abundant communities in stable mudflats.

The extensive inter-tidal areas are characterised by species that support the important bird populations including *Macoma balthica* and to a lesser extent *Hydrobia ulvae* and polychaetes such as *Nereis (=Neanthes) diversicolor* and *Nephtys hombergii.*

Organically-enriched muds along the northern shoreline of the inner estuary are characterized by capitellids and oligochaetes (*Limnodrillus* spp).

MDS analysis of the samples collected in 2001 distinguishes five community groups (in addition to sites without fauna), four of which were relatively impoverished and differed only slightly in terms of species composition. These consisted mainly of species which are typical of clean, well swept sands in lower shore or sub-littoral areas (20sites).

The remaining group of 20 sites had a richer community with several key prey species including *Macoma, Tubificoides, Nereis, Corophium* and sometimes small aggregations of *Mytilus*. A subset of six of these sites in muddier high shore locations were considered to have a well balanced community of high abundance (along the shore by the airport, mudflats near Mt Manisty and Rock Ferry).

Quantitative temporal comparison of species abundance is made difficult because sampling sites and regimes have, in the past, tended to vary. Physical characteristics probably dominate distributions and therefore valid comparisons can only be made between surveys encompassing similar site properties. Nevertheless these surveys provide useful baselines on which future assessments may be conducted.

Benthic community analysis at Seacombe, Buoy C1 and a coastal site in Liverpool Bay has been undertaken as part of the NMMP programme and attempts to link indices such as diversity, abundance, feeding groups (infaunal trophic index – ITI) and AZTI marine biotic index (AMBI score- classification according to pollution sensitivity) with environmental parameters such as sediment contamination, type and water depth (NMMP, 2004).

At the coastal site in Liverpool Bay, the ITI index was just above the borderline between normal (> 60%) and 'changed' (30-60%). AMBI scores suggested a low degree of pollution stress (0 = unstressed; 7 = highly polluted) (table 22). Near the estuary mouth at C1, the ITI index implies a degree of alteration to the expected, though the AMBI index indicates low pollution stress. Physical characteristics of sediment (% silt/clay) and water depth, rather than contamination, appear to be the major determinand of macrofaunal community patterns at coastal sites.

Data for the estuarine site at Seacombe are broadly in agreement with the classification of low pollution stress. It is perhaps worth recording, however, that abundance of specimens was the lowest of UK estuarine sites. Multivariate analyses of the estuarine biotic data set therefore indicate that this site is a well-balanced but impoverished community (NMMP, 2004). Causative factors are not known with certainty, though correlation analysis indicates this may be due primarily to granulometry rather than contaminant levels. It may be informative in future to perform comparable classifications for sites within the Mersey EMS.

**Table 22. Benthic community scores at coastal and estuarine NMMP sites (data source, NMMP, 2004)**

| Diversity and other biotic indices | | | | | |
|---|---|---|---|---|---|
| | species | abundance | Diversity(H') | ITI* | AMBI** |
| | | | | | |
| *Coastal sites* | | | | | |
| Liverpool Bay | 37 | 196 | 2.43 | 60.41 | 1.53 |
| | | | | | |
| Buoy C1 | 11 | 89 | 1.76 | 48.84 | 0.77 |
| | | | | | |
| UK median (n=31) | 20 | 102 | 2.02 | 61.1 | 1.67 |
| *Estuarine sites* | | | | | |
| Seacombe | 9 | 68 | 0.78 | 62.75 | 1.79 |
| | | | | | |
| UK median (n=28) | 17 | 5671 | 1.44 | 40.81 | 3.29 |

*ITI- Infaunal trophic index (Codling and Ashley, 1992)
**AMBI – AZTI marine biotic index (Borja *et al*, 2000)

The Site Z disposal ground in inner Liverpool Bay (north of the estuary mouth) receives more than 1million tonnes of dredgings from the Mersey Estuary each year. Earlier surveys have indicated that, not surprisingly, near the centre of the site, macrofaunal densities are reduced, but may be enhanced at adjacent sites. This enhancement at the periphery of the site has been suggested to be the result of enhanced stabilizing and nutritional properties of the disposed fine sediments compared with surrounding sandier substrates (Rees *et al.,* 1992). Species which successfully colonise this finer material are the polychaetes *Pectinaria* and *Lanice* and the bivalve *Abra* – characteristic fauna of the muddier sediments within the Bay. No evidence of inhibition caused by associated chemicals could be found. This may well be because of the continuum of fine-sediment contamination across the area. Similarly there was no evidence of widespread surface anoxia in sediments in the disposal site, which resemble naturally deposited mud-patches in the Burbo Bight to the south.

A general N-S enrichment gradient in epibenthos across Liverpool Bay (increasing towards the mouth of the estuary) has been linked with efflux of nutrients and organic matter from the estuary, though dispersing dredge spoils could have a contributory role (Rees *et al*., 1992).

Meiofauna play an important role in ecosystem function, and nematode and harpacticoid copepod assemblages have been assessed in relation to environmental and sedimentary variables at a number of NMMP sites around the UK, including the Burbo Bight (NMMP, 2005). Of all inshore sites tested, diversity of nematodes and copepods was lowest here, coinciding with highest metal concentrations (though not necessarily proof of cause and effect).

# 8. MODELS

## Equilibrium partitioning–toxic unit (EqP-TU) model

This model, developed by Swartz *et al.,* (1995), was applied to assess PAH contamination in sediments from the Mersey and other UK estuaries (Rogers, 2002). The approach uses a combination of equilibrium partitioning, QSAR prediction of toxicity and additivity. Toxic units (TU) for individual PAHs were calculated using PAH/10-day LC50 relationships. The 10 day LC50 for 19 PAHs, including six alkylated PAHs, were calculated using a QSAR regression of 10-day LC50/octanol-water partition coefficient.

The model estimates the overall toxicity of sediments arising from PAHs only, by assuming additivity of toxic effects of the 19 PAHs. Partition coefficient values for the alkylated PAHs were not available from the literature, so were predicted using a structure activity relationship developed by Meylan and Howard (1995).

The main limitation of this model relates to the assumption that total sediment PAH loads are available for equilibrium partitioning. Furthermore, a poor correlation found between organic carbon concentrations and PAH concentrations in sediment suggested that PAH residues were associated with a variable/minor proportion of the sediment organic matter. This will have a significant effect on the overall toxicity as assessed using the Eq-TU approach. Despite these limitations, EqP-TU is considered to be a useful means of comparing the likely relative toxicity caused by PAHs in sediments from different locations (Rogers, 2002).

Toxicity in Mersey sediments showed a clear decline towards the mouth of the Estuary, with maximum toxicity (0.43TU) evident at Widnes West Bank in the inner estuary (figure 85), in the immediate vicinity of chemical industry discharges to the estuary.

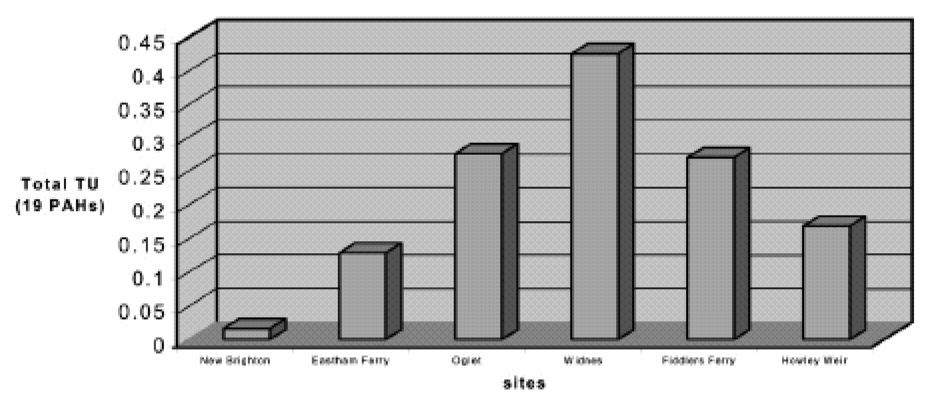



**Figure 85. Total Toxic Unit values for Mersey estuary sediments (Rogers, 2002)**

Sediments from the Clyde (King George V Dock) and Southampton Water (BP Chemical outfall) were estimated as having highest TU's (max 1.14 and 0.74, respectively) of other UK estuaries and harbours assessed and sediments from the Mersey ranked third in terms of toxic units (both mean and maximum TU). This is roughly consistent with PAH levels found in sediments in the estuaries (see section

6.1 6). However, Rogers *et al,* (2002) concluded that before the EqP-TU, and similar models are more widely applied, further investigation into biological effects threshold levels, and also the way in which physicochemical factors might modify the extent and timescale of toxicity to benthic organisms, are needed.

**MARGIS**

As part of the Stage 3 review of consents the EA planned to undertake near-field/mixing zone modelling, in early 2005, to predict impact of the discharges and consider effects in combination. Models employed were a CORMIX near-field modelling approach, and the Mersey Estuary MARGIS model (to calculate the detailed, localised hydrodynamic data that the near-field system requires).

CORMIX is a commercial software package that can analyse, display and forecast discharges in watercourses. It is a US EPA model and is the most commonly used near field mixing zone modelling tool, applied across the world in over 2,000 applications.

MARGIS is a two dimensional, depth integrated hydrodynamic model which works on a 100m x 100m grid. The model can be used for in-combination assessments in the mid and far-field. This model was developed through a joint EA and EN project in 2002/003 and is now commonly used by the EA

In the Mersey, MARGIS modelling was specifically designed to look at levels of ammonia and dissolved oxygen in the estuary. Comparisons were made with modelling results and standards for DO and ammonia and other standards produced by WQTAG. MARGIS was used to assess in-combination effects of discharges containing metals and a limited number of organic substances in the mid and far field.

Because of model run-times, and a previous (stage 2) assessment that no discharges were likely to have a significant effect alone, initial MARGIS model runs included current average and maximum consented discharge loads, and future (post AMP3/AMP4) average and maximum consented discharge loads. WQ/EQS failures were identified and pinpointed.

Modelling was for several outfalls on the Mersey, namely Sandon Dock (Liverpool) WwTW, Birkenhead WwTW, Bromborough WwTW, Warrington North WwTW , (probably MARGIS alone), Widnes WwTW, Shell UK Ltd., Cammel Laird Group PLC, AEP Energy, Granox, and Croda Colloids. These outfalls represented all continuous discharges into the Mersey Estuary downstream of the Runcorn-Widnes Bridge, and AEP Energy (a very large discharge entering the Estuary a short distance upstream of the SPA) (see figure 3 and annex 7). The assessments included near-field temperature effects.

**SIMCAT**

The SIMCAT model is a statistical water quality model used by the EA mainly to assess the impact of point source discharges into rivers. SIMCAT models have been developed for the upstream freshwater riverine catchments to provide freshwater boundary conditions for the MARGIS and CORMIX models, in combination runs in order to identify both updated current average conditions for rivers entering the Mersey Estuary and worse case conditions assuming consented discharges are discharging their full consented loads.

**Nutrients in Estuaries – CEFAS Spreadsheet Screening Model**

The EA also planned to use this modelling tool to assess the potential for eutrophication in the Mersey estuary, which was considered to be low. Nutrient loading inputs will be taken from the SIMCAT/MARGIS models described above.

**A sediment transport model of the Mersey Estuary**

Hartnett *et al.,* (2005) recently developed a sediment transport model of the Mersey to simulate the behaviour of various materials in the estuary, including nutrients, sediments, heavy metals and persistent organic chemicals. Sources of suspended sediments in the Mersey are discharges from outfalls etc. and resuspension of bed sediments. The bed sediments are of particular interest as they are contaminated with heavy metals. Results from detailed water quality modelling project indicated that during mid-flood and mid-ebb tides, strong tide-induced currents create high bed shear stress resuspending relatively large volumes of sediments. These sediments are transported about the estuary and, mostly, settle to the bed during periods of quiescent hydrodynamic activity. The authors considered the Mersey to be a complex system to model, and to perform the subsequent heavy metal simulation analyses. The authors outline how the sediment modelling was executed.

**Modelling the effects a new Mersey crossing**

ABPmer describe an additional numerical modelling study for the proposed new bridge crossing over the Mersey[21] (ABPmer had previously reported on the study investigating several route options). The proposed scheme was located between Runcorn and Fiddler's Ferry in the upper part of the estuary. The modelling study investigated different scenarios in the construction and operational phases. Boundary conditions at the seaward end of the model were driven by tidal data obtained at Gladstone Dock. The upstream boundary at Howley Weir was driven using an annual mean discharge.

Findings indicated that whilst the absolute values of bed shear stress would be altered, particularly adjacent to the proposed scheme, the overall pattern of the bed shear stress remained almost unchanged between the baseline case and the various options tested. The estuary dynamics were particularly sensitive to high spring flows and the additional effect of storm surge, coupled with high fluvial flow events, could lead to a greater impact on these dynamics. Results from modelling indicated the possibility that the controlling mechanism on the morphology in the upper and inner estuary was a combination of high spring flows and high fluvial events. Varying degrees of impact along the intertidal foreshore were predicted in the different options tested.

[21] Details from abpmer.co.uk

Based on the analysis of the results, several points were raised and recommendations made, notably that the construction of a bridge with a significant number of footings in the estuary should be avoided and the careful placement of bridge piers outside of the existing channels may assist performance in the short-term. However, in the longer-term, movement of the position of the channels may make such decisions irrelevant. The study did not investigate the effect of storm surge events and high fluvial flow events, which may be important in determining the long-term changes in the upper estuary, particularly on a flooding spring tide. An overall assessment of the various options tested, enabled a recommendation for a route which appeared to have the least impact on the existing estuary dynamics.

This work is ongoing and includes detailed bathymetric, hydrogaphic, chemical and biological surveys. These investigations are providing very useful information for the area above the EMS (P.D. Jones EA, *pers comm.*)

Several modelling exercises were carried out in relation to the proposed Mersey Barrage, the majority focussing on hydrodynamic aspects e.g. MBC, (1991); Wilson & Porter (1992): Towner & Wilson, (1992); Austin, (1990). Austin, (1996) applied a model in an attempt to predict the impact to bird populations on Mersey after the construction of a barrage.

## 9. CONCLUDING REMARKS AND RECOMMENDATIONS

The principal objective, to determine whether prevailing conditions in the Mersey impact on the interest features of the site (namely qualifying birds) cannot be answered satisfactorily at present as studies addressing this issue directly have not been carried out. It is only possible to point out the current level of knowledge regarding biological and chemical status for the Estuary and extrapolate to risks for the bird population. Often this information relates to sites outside the EMS. In this section we appraise the general status of the Estuary, based on best available knowledge, and make suggestions as to how best to remedy the lack of relevant information.

### 9.1 Biological Status

According to some sources, meiofauna and fish communities in the Mersey Estuary are reported to show lower diversity and abundance in comparison to most other estuaries in the UK, despite recent improvements in water quality. Other opinions suggest that the current fish inventory is fairly typical of the estuary type, though fluctuations in abundance and diversity are high. Unfortunately long-term fish records suffer from inconsistent design, methodology and sampling effort, making comparisons difficult. Likewise, there are few standardised long-term studies of benthic invertebrates in the estuary; reports suggest that communities in the inner and upper Estuary and possibly the Narrows have been impoverished due to pollution. However, the diversity of invertebrates is thought to have substantially increased in the post industrial-era, although it appears that the nature of the sediment coupled with strong tidal flows across much of the estuary may still result in a naturally impoverished fauna in many areas. Where reaches of mud and muddy sand exist, productivity is high and these generally support invertebrates such as *Nereis, Arenicola*, *Macoma*, *Cerastoderma*, *Corophium* and *Hydrobia* which form the main dietary items for the large populations of wintering and passage waterfowl. High densities of oligochaetes in the inner and upper estuary are consistent with organic enrichment.

Quantitative diversity indices are increasingly used to assess the effects of environmental degradation on the biodiversity of natural assemblages of benthic organisms. Several indices, which help to put biological status into perspective, have been applied to NMMP sites in the area (though not within the EMS). Results have confirmed that near the estuary mouth, and at Seacombe, communities exhibit a degree of alteration to the expected, though pollution stress is considered low and the physical characteristics of sediment, salinity and tidal flow, rather than contamination, appear to be the major determinands of macrofaunal community patterns. However, abundance of specimens at Seacombe was extremely low by UK standards. To assist in long-term assessment of condition at the EMS, upstream, it may be useful to apply a selection of these quantitative techniques as part of a future monitoring strategy (see Annex 6).

Within the estuary, in the late 1990s there were indications that ranges of sensitive clam species (*Scrobicularia* and *Macoma*) were extending upstream, coinciding with water quality improvements (Pope *et al*., 1998). *Hydrobia* and *Corophium* also appear to be recovering from suspected pollution impacts of the past. It is important to regularly re-evaluate these trends, not only to monitor continuing improvement, but also to check that this does not lead to unacceptably high levels of contaminants in tissues in newly colonized sites in the upper reaches of the Mersey Estuary EMS. Bioaccumulated residues could unexpectedly be passed on to higher organisms in the food chain, notably bird species.

Regarding bird populations, the most recent BTO WeBS report (MacClean, *et al.*, 2004) has shown that the number of species for which Alerts are issued is increasing since the first BTO WeBS report was published. Numbers of Golden Plover, an Annex 1 species, have declined and triggered a Medium Alert, and the internationally important Shelduck and Pintail have declined sufficiently to trigger both High and Medium Alerts.

High Alerts were also triggered for Great crested Grebe, Wigeon, Grey Plover, and Black-tailed Godwit, and Medium Alerts triggered for Shelduck, Pintail, and Lapwing.

Numbers of Great Crested Grebe have declined to less than 5 birds in 2003/04 and the site no longer supports nationally important numbers of this species. This contrasts with both regional and national trends, which have shown a general increase, and suggests that local, rather than larger-scale factors, are influencing the numbers of Great Crested Grebe over-wintering at the Mersey Estuary SPA.

These findings raise significant cause for concern, as many of these species have not declined in either England or Great Britain as a whole. The BTO report suggested that further investigation into these declines is warranted. Findings of a recent level 2 review (Armitage *et al.,* 2004) suggested that several factors may have influenced some of the bird population declines. Of these factors, poor water quality (effluents/pollution) and changes to waste water treatment may be directly related to EA consents.

A recent development in the diagnosis of water quality impacts is the deployment of biomarkers. A number of sub-lethal biological effects on individuals have been observed in the estuary including; impoverishment of benthic communities, low scope for growth, high incidence of lipid peroxidation and DNA strand breaks in mussels, endocrine disruption (vitellogenin induction and intersex in male fish), DNA adducts, EROD induction, metallothionein induction, ChE inhibition, disease and histopathological lesions in fish.

Toxic effects have been observed during bioassays; *Crassostrea* oyster embryo water bioassays, *Tisbe* bioassay of water extracts, and *Arenicola* and *Corophium* sediment bioassay.

Further deployment of these sub-lethal indices would be of value in future assessment of the EMS.

## 9.2 Chemical Status

There is substantial evidence that the numerous initiatives set up in recent years under the Mersey Basin Clean-Up Campaign, coupled with changing industrial practices, have led to improved water quality. However, given the long-term legacy of pollution in the Mersey, and the repository held in fine sediments, it is not surprising that chemical impacts and resultant biological effects are still detectable. The Estuary remains one of the most contaminated estuaries in the UK, though establishing links between cause and effects is made difficult because of the shared gradients of many chemicals present.

The improvements in water quality suggest that acute toxicity from individual chemicals is a thing of the past and resulting modifications to biota of the European Marine Site would not be expected to occur. The potential *combined* threat from multiple inputs of nutrients, selected metals, residual TBT and other organics is probably of most concern. However, the available evidence on biological effects from both toxic and non-toxic contaminants is patchy. To address this issue in the future a more subtle, targeted assessment of impact will be required in order to establish cause and effect (discussed in greater detail later in this section). Until more appropriate, integrated monitoring is put in place it is only possible to assess, subjectively, individual contaminants, or groups of contaminants that could, in theory, impinge on sensitive species and benthic communities: a much abbreviated summary is also provided in table 23.

*1) Organotins (TBT)*

Results of TBT analyses from the Mersey Estuary in recent years indicate there may still be threats to the condition of the site from these compounds. The main risk to the bird features of the SPA are likely to be indirect, through effects on abundance of dietary invertebrates (particularly molluscs).

Between 2002 and 2004 the EQS benchmark for tidal waters (2 ng $l^{-1}$), set as a Maximum Allowable Concentration, was exceeded at all sites. Highest values were recorded upstream at Monks Hall, at the head of the tidal waterway, implying inputs from the river Mersey itself; however, elevated values were indicated at a number of sites along the tideway on different occasions. There are probably a number of point-source and diffuse inputs in the catchment, including from the MSC, WwTWs, landfill leachates, various docks, and fairly widespread contamination in sediments. EA, for example has identified the Cammel Laird shipyard as a priority for further investigation under the stage 3 review of consents. Past uses of triorganotins have also included various biocidal applications and wood preservation; diorganotins have been used as stabilizers in plastics and as catalysts.

The persistence of sediment-bound TBT is also, potentially, a source of long-term chronic impact in poorly flushed areas and could be exacerbated by dredging activities. There are a number of hotspots at various points along the estuary, consistent with multiple localized sources. Generally, however, inter-tidal sediments throughout most of the EMS do not contain exceptionally high TBT levels.

Near boatyards and in docks TBT levels can exceed provisional (though perhaps overcautious) ecotoxicological guidelines set by OSPAR and also action levels instigated by CEFAS. A precautionary approach may be needed if such areas are to be dredged. Processes including physical resuspension and bioturbation could remobilise these sinks. Furthermore, TBT in such contaminated sediments is likely to be bioavailable, and potentially harmful, to deposit-feeders and infauna (many of which are important dietary items for birds).

There are few systematic studies on bioaccumulation of TBT though it is likely that inorganic Sn (measured in MBA surveys) is a useful surrogate for organotins (>85% total Sn). Most invertebrates showed an increase in concentrations upstream and may be of significance for biota of the EMS.

Where speciation has been performed, total concentrations of BTs were generally highest in sediment-dwelling fauna, particularly bivalves, and indicate bioaccumulation relative to sediments. TBT concentrations in mussels from the Mersey Estuary are not exceptional by global standards but are consistently higher than OSPAR ecotoxicological assessment criteria. Triphenyltin (TPT) compounds were not found in mussels; however TPT residues were determined in eels from the Weston canal. The presence in eels from the Weston Canal may be associated with use as a fungicide, or even manufacturing. In addition, docks, industry and shipping associated with the MSC may also be substantial sources of biologically available organotins in the Mersey Estuary.

There are no rigorous TBT time series for the EMS and further sampling is recommended to monitor progress towards recovery. The tin situation in the Mersey estuary warrants further investigations on sources, bioaccumulation and biological impacts to re-assess the situation.

*2) Metals*

The Agency has highlighted metals as priority for near field assessment in the case of several WwTWs (Sandon, Birkenhead, Bromborough, Warrington North and Widnes), the Power Station at Fiddlers Ferry (Hg, Cd), and a number of other inputs (annex 7). During tidal waters monitoring between 2002-2004 greatest concerns over EQS excedences (based on annual averages, mainly) were for Hg, Cu, Zn. These merit further investigation at sites within the EMS, for which there is little data.

Metal concentrations in sediments are considered fairly elevated for estuaries bordering the Irish Sea. Cr, Zn, As, Pb, Cd, Sn and Hg show most anthropogenic enrichment. Most sediment metals exceeded ISQG/TEL guidelines extensively, and Hg, Zn and Pb were above sediment 'probable effects levels' at several sites. On this basis, according to the guideline criteria, chronic effects cannot be excluded and in some cases seem likely to effect sensitive species.

Land-based industrial and urban sources (run-off and WwTWs) within the catchment influence distributions of pollutant metals. In the past there may also have been a contribution from sewage sludge dumping in Liverpool Bay. It is likely that the widespread dispersal of fines (and relative abundance of organic and oxyhydroxide coatings) govern sediment metal loadings and distributions.

Concentrations of several pollutant metals in sediments declined substantially at the commencement of clean up though levels have changed far less in recent years and at depth may contain reservoirs that could reverse trends if remobilised. Continuing re-survey is seen as a particularly important issue in terms of meeting standstill requirements for sediments under the Dangerous Substances Directive and attainment of Favourable Conservation status under the Habitats Directive.

Bioaccumulation surveys conducted from the 1980s onwards by MBA indicated elevation of body burdens for many pollutant metals. Enrichment in *Nereis diversicolor*, for example, decreases in the order Pb>Ag>Hg = Cd>Cr>Mn>Sn>As = Ni>Cu>Fe=Zn.

The main area of concern regarding metal bioaccumulation can be sourced to mid-upper estuary with concentrations decreasing downstream. Patterns of metal bioavailability point to some interesting if transient anomalies such as elevated levels in the outer estuary (eg Southport and Blundellsands); At Egremont, Ag, Hg and Cu concentrations in clams have been shown to fluctuate dramatically in response to sediment conditions (perhaps redox) coinciding with population response. These observations illustrate that site-specific changes in environmental characteristics can drastically affect bioavailability of contaminants even though overall loadings may not change. This may be an important issue to consider when making assessment of the condition of Mersey estuary SPA given its legacy of sediment-bound contaminants.

Body burdens, overall, have declined in line with sediment trends and were beginning to herald biological recovery. Updated studies, focusing on infaunal species such as worms and clams are recommended.

Based on comparisons with OSPAR reference criteria, metals in mussels from the estuary are enriched by UK standards. Applying these criteria to the 1997 MBA data average values exceed the upper reference by almost an order of magnitude for Hg and Pb, but by a small margin for Cu and Zn. However, partial regulation of Cu and Zn may mean that mussels underestimate contamination of these essential metals.

Hg in muscle of fish caught in Liverpool Bay display similar trends to those in invertebrates, with major losses in the early 1980s and more or less constant values in recent years. The average value in 2002 was within the OSPAR JMP 'medium' category for contamination. In UK comparisons of flatfish highest concentrations occurred in the Mersey Estuary and Liverpool Bay – both significantly above the range of the relevant OSPAR background concentration range. Pb concentrations were also elevated in dab and flounder from the Mersey.

Acute ecotoxicological impact due to metal contamination is not anticipated throughout the site as a whole, but it is possible that a degree of anthropogenic enrichment, coupled with conditions in sediments (particularly anoxia), could increase the bioavailability of several metals. There is scope for more research to establish the physiological and ecological significance of metal body burdens. Sub-lethal biomarkers, notably metallothionein induction, provide sensitive and selective measures of metal stress and can help map affected areas, as well as monitoring temporal trends.

**Table 23. A Summary of Water and Sediment Quality issues in the Mersey Estuary EMS** (Findings for each of the numbered 'contaminant categories' are explained in more detail in the accompanying text).

| 'contaminant' | Area | Potential Sources | Most vulnerable features/biota |
|---|---|---|---|
| 1) Organotins (TBT, TPT) | Highest levels in water at the head of estuary – may reflect high suspended solids loads.<br><br>Persistent in sediments throughout the estuary, with localised hotspots. | Probably multiple sources of TBT including docks (nb Birkenhead), Manchester Ship Canal, Chemical industry, WwTWs.<br><br>TPT found in eels from Weston Canal (sources agricultural or manufacturing?) | Molluscs, particularly gastropods |
| 2) Metals | No acute problems identified but Hg, Zn and Cu considered risks, especially upstream. Sediment widely above ISQG/TEL and sometimes above PEL at upper Estuary sites: reflected in bioavailability. | WwTWs, industry, urban run-off, shipping.<br>Sediments principal sink for most metals: Modified conditions at some sites could increase bioavailability | Invertebrates (primarily molluscs and crustaceans), larval fish.<br><br>Bioaccumulation in birds not evaluated but potential risks eg from organometals (alkyl Hg and Pb) |
| 3) Nutrients | Especially toward freshwater inputs. Widnes, Eastham Locks | Freshwater and point source inputs including the Manchester Ship Canal. WwTWs discharges also important<br>Possibly sediments – (phosphate, ammonia) | Invertebrates, fish (esp. early life stages), birds, General diversity |
| 4) Hydrocarbons, PAHs | Poorly defined, due to lack of sampling but evidence of enrichment in sediments, notably Seacombe Ferry | Mixed petrogenic inputs from numerous discharges. Incomplete combustion of fossil fuels, refineries, run-off, boats and ships aircraft. Sediments main reservoir | Benthic invertebrates and fish (NB those in contact with sediment). No bioaccumulation data. |
| 5) Pesticides, herbicides and other organics | Estuarine sediments an important reservoir but little information on spatial distributions within the EMS. Direct toxicity improbable, though sublethal manifestations including endocrine disruption have been demonstrated | Not quantified due to insufficient data but probably includes a significant component from industry, sewage discharges and agricultural and urban run-off.<br><br>In depositional areas, sediment subsurface maxima reflect historical inputs | Invertebrates (esp. crustacea), fish<br><br>The region is still a hotspot for bioaccumulation of PCBs and a number of OC pesticides: very few bioaccumulation data in EMS itself<br><br>Extent of endocrine disruption not fully tested, particularly in invertebrates. |

The main risk to the bird features of the SPA are likely to be through bioaccumulation of some 'pollutant' type metals, particularly those with toxicologically important forms such as Hg and Pb and also Cd which is irreversibly accumulated in the kidney. The threat from Se should also be assessed since there is a fine distinction between levels considered essential and those causing adverse effects e.g. on reproduction. Other effects are likely to be indirect, through effects on the abundance of dietary invertebrates; particularly the settlement and survival of vulnerable larval and juvenile stages.

*3) Nutrients*

Nutrient-associated water quality problems within the Mersey Estuary have been alleviated somewhat over recent years by improvements in the estuary, which include the establishment of new sewage works and the restriction of industrial discharges. The former resulted in a dramatic reduction in organic load and improvements in levels of dissolved oxygen. However, the estuary is reported to still receive an elevated nutrient load, and this is reflected in high concentrations of N and P downstream of Howley Weir. There are for example elevated concentrations at Eastham Ferry - close to Eastham Locks, where the Manchester Ship Canal joins the Estuary, Mount Manisty and Widnes. Unfortunately, data was not supplied for concentrations in freshwater inputs, WwTWs or industrial discharges; therefore these 'hotspots' cannot be attributed to specific sources.

In the long term, concentrations of ammonia in the upper estuary have been reduced dramatically, although there is evidence that the trend for concentrations between 2002 and 2004 was reversed. Again, highest concentrations occur in the inner estuarine areas.

Effects of high levels of nutrients on individual species are in the EMS are largely unresearched, and if they do occur, are likely to be 'knock-on effects'. In view of the conservation importance of the site, 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.

The main risk to the bird features of the SPA are likely to be indirect, through effects on the abundance of dietary invertebrates; particularly the settlement and survival of vulnerable larval and juvenile stages. These would be impacted by ammonia and dissolved oxygen levels primarily. Overall biomass and secondary production of the benthos and hence food availability to bird populations, will also be a function of nutrient levels, as mediated through primary production (phytoplankton, benthic diatoms) though the precise nature of this function has not been adequately described for the Mersey. Intuitively it is anticipated that reduced nutrient levels might lead to reduced food availability and hence fewer bird numbers. Undoubtedly however there are a myriad of other factors which may confound such a direct relationship.

*4) Hydrocarbons, PAHs*

High levels of total hydrocarbons and PAHs in tidal waters have been reported over recent years which indicate continuing inputs. These inputs probably maintain the existing high background levels of hydrocarbons reported in the sediments of the Mersey due to chronic oil contamination.

PAH enrichment in sediments of the Estuary is consistent with an anthropogenic origin. The sources of these PAHs include mixed petrogenic inputs, probably from numerous discharges, although without information for contaminant levels in discharge effluents it is difficult to pinpoint specific discharges. Other sources include, spills, particulates derived from combustion products, urban run-off, various trade and domestic inputs, and shipping activity.

PAH concentrations in the EMS are not as high as those recorded in some highly industrialised estuaries, although the reported levels represent a threat of harmful effects to benthic organisms, notably at Eastham Lock. Exposure pathways to most biota probably consist of both water and dietary sources including sediments. Feeding habit and lifestyle will be significant factors in modifying the bioavailability of PAHs, as with most contaminants. Because of their stronger affinity for sediments, high molecular weight PAHs are thought to be accumulated more strongly by deposit-feeders, rather than by those types which process overlying waters.

Reported PAH concentrations in sediments of the Mersey are above the proposed Threshold Effect Levels for ΣPAHs, but below the Probable Effects Level, and almost all individual PAHs are above proposed TELs. These concentrations in sediments are sufficiently high to generate sub-lethal effects in fish and fish larvae, i.e. EROD induction, which has been reported in various fish species caught in the Estuary.

Considering the presence of the petrochemical industry around the Mersey, and the potential for spillage, leakage etc., there appears to be little information on current levels of PAH contamination in the estuary. Recent monitoring data (EA/NMMP) appears to be limited to only one site within the actual EMS; spatial distributions of PAHs must be assessed from published literature and the somewhat limited CEFAS monitoring data for 2001.

Further work will be needed to assess the actual biological consequences of PAHs for the marine site: the presence of elevated levels of other contaminants is a complicating feature and demonstrates the need to integrate biological and chemical monitoring. As higher organisms usually have more active detoxification sytems than invertebrates the main threat from hydrocarbons to the bird features of the SPA (other than through major oil spillage) is likely to come from effects of PAH's on the recruitment and abundance of dietary invertebrates. However more specific information on bioaccumulation of PAHs in wading birds of the estuary is needed to assess direct risks.

*5) Pesticides, herbicides and other organics*

There are very few values for pesticides (or other POPs) in Mersey water samples which exceed the detection limits and the assessment of risk of EQS excedence is predominantly 'low'. Because of the limited number of pesticide values it is not possible to discuss spatial or temporal trends. The only information is for op TDE which, as expected, increases upstream. Sources are not known.

Information on pesticides in surface sediments is also insufficient to give a realistic impression of distribution and sources of contamination for benthic fauna of the Estuary. A small *ad hoc* sampling programme should be considered, incorporating some of the priority compounds such as lindane ($\gamma$-HCH), DDT isomers, 'drins', and perhaps other compounds including PCB's.

In the NMP surveys of PCBs in sediments at UK sites. Mersey samples were second highest to the Thames. However considerable variation is observed in Mersey samples which may reflect granulometry. In the early 1990s total PCB in sediment samples from Liverpool Bay were significantly correlated with the amount of fine particles and with the organic carbon content. Lowest concentrations were found in the sandy southern area towards the North Wales coast and highest values were found in muddy deposits where spoil particles are likely to accumulate, particularly near the River Mersey in the Burbo Bight area, implying the estuary is a net exporter of PCBs, both directly and via dumping activities. The quality guideline (TEL) for total PCB was sometimes exceeded though not the probable effect level and ranges of sediment values are consistent with other industrialized areas. In more recent transects from Liverpool Bay in to the narrows section of the Estuary, values rarely exceeded the TEL. The situation for sediments in the SPA is not known since sites here were not sampled, though, on the evidence presented, impact is not expected

Sediment chronologies in cores from Ince Banks and Widnes show that ΣDDT concentrations start to increase ~1945s, reflecting the start of local production (Manchester), and peak in the 1960s, declining to low levels in surface sediments following regulation.. PCBs follow a similar pattern but decline at relatively slow rates presumably because of persistence and residual inputs. Historical deposits of organic contaminants could become an issue during periods of erosion.

Surveys of PCBs, DDT dieldrin, $\gamma$-HCH and HCB, in flatfish confirm that the Mersey and Liverpool Bay are still amongst the most contaminated areas monitored in the UK. Concentration ranges of POPs tend to be higher in invertebrates and PCBs are above the lower Ecotoxicological Assessment Criteria (EAC) set by OSPAR. Organochlorine (DDT, dieldrin, HCB, $\alpha$-MHCH and PCB) concentrations increase in mussels upstream through the Narrows, presumably reflecting sources in the mid-upper Mersey.

There have been substantive reductions in body burdens of organochlorines in mussels from the outer estuary in recent years. Nevertheless for some persistent compounds (e.g. highly chlorinated PCB congeners) it may be decades before the legacy of contamination disappears. The issue of bioavailability of sediment contaminants within the EMS still needs to be addressed – by incorporating infaunal types in surveillance programmes. Soft-substrate habitats occupy most of the SPA and are becoming increasingly important, relatively, as diffuse sources, Many infaunal species are important prey items for predators including the birds for which the SPA is designated. The risks to the qualifying features may therefore be anticipated to arise primarily as a result of consumption of contaminated prey items, though the likelihood of this needs to be assessed through direct measurement of relevant samples (historically, biomagnification of organochlorines such as DDT and PCB have been associated with eggshell thining and reproductive failure in birds). Also, indirect risks, caused by deleterious effects of synthetic organics on invertebrates, algae and plants (n.b. from hebicides) are possible, but require testing as part of a wider biomonitoring investigation across the site.

At upstream sites above Runcorn nonylphenol, a potential endocrine disrupting chemical, sometimes exceeds the EQS (MAC). Risk declines to 'medium' at Randalls Sluices and thereafter to 'low' at more seaward sites. Concentrations in sediments mirror these trends with values in the inner estuary higher than most proposed PNECs, declining seawards. Sources of NP to the Mersey requires further investigation as do concentrations in sediments of the EMS.

It seems unlikely that volatile organics represent a significant threat to the European Marine Site, though confirmation of sources of trichloromethane and to a lesser extent trichloroethene in the inner estuary (above Runcorn) would seem important to establish.

## 9.3 Future Research Requirements

Risks to qualifying bird features of the Mersey Estuary European Marine Site from water and sediment quality are two-fold. Firstly, from bioaccumulation and toxicological effects of contaminants, directly, and secondly from indirect effects of water quality on dietary components. To address the first issue requires analysis of bird tissues in relation to food items (perhaps before and after overwintering periods), coupled with diagnostic biological effects markers such as metallothionein and EROD induction, oxyradical scavangeing capacity, immune function and comet assay as well as more general condition indices. To address indirect effects, on dietary organisms, requires a wider understanding of ecosystem health, as discussed below, and might be applied to sites within the EMS and, equally to sites throughout the estuary, depending on the requirements for assessment.

Better integrated information on environmental chemistry, 'health' and biodiversity are obvious top-level needs to address the 'quality' of the Mersey Estuary (including the European Marine Site), just as rigorous monitoring of habitats will be needed to provide estimates of their 'quantity' and extent.

With regard to the latter, an appropriate surveillance strategy should be adopted to quantify the nature and extent of biotopes in order to fulfil Favourable Conservation Status[22] as encompassed in the Habitats Directive. Monitoring techniques are

[22] Favourable Conservation Status (FCS) for a given habitat/species requires that it's condition has to be characterised and, if considered necessary, brought up to a level where the habitat/species is sustainable in the long term. Under the Habitats Directive, Member States must report on the progress towards FCS for all nominated sites. English Nature has produced Favourable Condition tables to aid

described in detail by Davison and Hughes (1998) in relation to surveillance of *Zostera* beds but are equally applicable to biotope monitoring in a broader context. These fall into four categories: *aerial remote sensing*; *sublittoral remote sensing*; *underwater video*; *conventional benthic sampling*. (e.g. grabs and cores and observations arising from inter-tidal surveys and diving). The first three options have potential for large-scale generalised mapping of distribution and extent, whilst the fourth provides a more detailed synthesis of biotope structure and condition. Ideally, the preferred monitoring scheme would probably consist of a blend of these approaches taking in to account questions of scientific objectives, practicality and cost. (Davison and Hughes, 1998).

In view of the sensitivity of the site to the possible effects of eutrophication it is recommended that monitoring of both phytoplankton and benthic macroalgae is undertaken, alongside nutrient determination. More work is needed to construct spatial and seasonal models of nutrient sources and fluxes and should also include the role of sediments. Further hydrodynamic modelling and simulation of nutrient distributions would be a useful supplement.

The requirement to fulfil FCS and other drivers relating to toxic contaminants and water and sediment quality (such as the 'standstill' provision under the Dangerous Substances Directive) may be difficult to monitor. The fragmented nature of much of the available environmental quality data prevents all but a first approximation of the status of the site for many contaminants. This needs to be addressed if we are to progress our understanding of how environmental quality, and in particular anthropogenic inputs, are affecting the status of the European marine site.

A major issue central to the current project is how to monitor the health of the environment within the site i.e. to ensure that conditions are favourable for the survival of biota and, if they are not, to establish any cause and effect relationships.

Some of the classes of contaminants which, in our opinion, should be prioritised in future surveys have been discussed above. Traditionally, surveillance of chemical parameters in water has often been carried out by the EA for the purposes of compliance monitoring and is not necessarily intended for survey purposes (or for the type of characterisation being undertaken here). This should perhaps be reviewed in future to maximise the value of the information.

Thus, in addition to nutrients, accurate, up-to-date chemical data on e.g. metals, PAHs, organotins, PCBs and some pesticides and herbicides, are needed to give better impressions of fluxes from rivers and discharges, and to provide details of their current distribution, sources and sinks within the EMS. It is particularly important that future sampling programmes incorporate more information on sediment contaminants and their role as diffuse sources within the site itself. Bioindicator organisms should be collected from the site, concurrently, to try to link sediment loadings with their biological consequences. This should incorporate infauna, particularly bivalves and polychaetes, which are capable of reflecting sediment-bound contamination. Surveys should be repeated at intervals in the future, to ensure that bioavailability does not

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this process, which encompasses a number of attributes, including the extent and biological quality of the interest features (summarised in Annex 1 and 2 for the Mersey Estuary EMS).

increase. Furthermore, many sediment-dwelling organisms are essential food items for the important bird species and assemblages for which the site is designated. The threat posed by bioaccumulation and food chain transfer of priority contaminants needs to be qualified in these species, requiring a much more extensive data set.

Biotope mapping and biodiversity indices are important components of the site assessments but may not be sufficiently sensitive to quantify subtle threats, or predict future change. In recent years, a range of biomarker and bioassay techniques have been developed to assess sub-lethal biological impact in greater detail, and would allow targeted biological-effects screening of the EMS, including possible problem discharges. Also, they can be used to assess the risk from diffuse sources. Current sediment quality criteria are useful initial guidelines to scale threats, but may not be entirely appropriate for all species or sediment types. Individual site conditions are likely to modify threats considerably, therefore accurate assessments need to be customised to the habitat in question. By selection of an appropriate suite of indicators/biomarkers[23], a sampling strategy could be tailor-made to establish the causes and extent of damage (if any), or improvement, in the EMS with greater certainty. This would ideally include; conventional quantitative ecological survey (for identifying changes in the abundance and diversity of species), targeted chemical and biomonitoring procedures as outlined above (for determining the concentrations and bioavailability of anthropogenic contaminants), and biochemical, physiological and behavioural biomarkers which signal exposure to, and in some cases, adverse effects of, pollution. Some examples of biological effects techniques are summarised in Annex 6.

When such procedures are used in combination in well-designed survey programmes, they can provide insights into which pollutants are responsible for environmental degradation. They may also be useful in addressing the long-standing problem of additivity/ synergism. A major criticism of many current statutory monitoring assessments, whether using comparisons with EQS values, sediment quality guidelines, or some other marker, is that they address only single contaminants at a time. Even if individual chemicals do comply with limit values (as many appear to do in the Mersey) it does not necessarily mean the environment is healthy. Biological effects may occur if several contaminants act together. The majority of outfalls and sediments contain a particular cocktail of chemicals whose true impact can usually only be assessed through a site-specific evaluation, taking into consideration the interactions that occur between different components and also the local environment.

By incorporating biological-effects monitoring, alongside chemical surveillance (and modelling outputs), it may be possible to make substantial progress towards understanding and managing these complex environmental issues and would provide more reliable and objective site characterisations in the future. If such an integrated approach were put in place at an early stage, to provide baselines, it would clearly be amenable for measuring long-term trends.

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[23] Examples of biological effects techniques from which a selection could be chosen to assess condition are shown in annex 8. Note also that a trial project on the value of such techniques in assessing the condition of EMS is currently being undertaken by PMSP (University of Plymouth and MBA); EN project FST 20-18-028.

In the absence of specific information on discharges it is not possible to comment on the arguments for and against more rigorous regulatory action on individual consents. Presumably EA will be assessing loadings from these sources as part of the Review of Consents process. Review of the available chemical data for tidal sections of the Mersey Estuary rarely raises concerns over acute toxicity within the EMS, though the possibility that combined pressures might impair performance of sensitive species and communities cannot be ruled out.

There is no doubt that the investment in waste treatment and disposal undertaken in the Mersey Basin clean-up campaign has produced substantial improvements over the last 25 years. In the absence of specific information on individual discharges the evidence presented here is insufficient to justify further expensive remedial action on particular sources. However, there is sufficient uncertainty to justify a more targeted and detailed programme of research and surveillance to measure actual biological impacts at a variety of levels (e.g. biochemistry, bioaccumulation, biomarkers, community structure) at sites within the EMS and near priority discharges. If results indicate deleterious effects, which can be attributed to known causes, then the case for remedial action against key sources (which may include multiple inputs) would be placed on a stronger, scientifically-sound basis. At the very least, such a program would provide a benchmark for assessing future changes in the condition of the site, and likely contributions from water quality.

Glossary and Definition of terms

**Hypernutrification** – any measurable increase in the concentration of a dissolved nutrients (ICES, 1984*). Hypernutrification is deemed to exist where winter nutrient concentrations "significantly" exceed 12 mM DAIN $m^{-3}$ [>12 μM $l^{-1}$ or 168 μg $l^{-1}$ N] in the presence of at least 0.2 mM DAIP m -3 [≥0.2 μM $l^{-1}$ or 6.2 μg $l^{-1}$ P] (EC, 1999**).

**Eutrophication** –Any measurable increase in primary production resulting from hypernutrification (ICES, 1984*). "The enrichment of water by nutrients, especially compounds of nitrogen and/or phosphorus, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance[24] to the balance of organisms present in the water and to the quality of the water concerned" (EC, 1999**).

*International Council for the Exploration of the Sea. I.C.E.S., 1984. (E:12). General Secretary, I.C.E.S., Palaegade 2-4, DK 1261, Copenhagen K, Denmark.

**European Commission Directorate General XI (1999).Verification of Vulnerable Zones Identified under the Nitrate Directive and Sensitive Areas Identified under the Urban Waste Water Treatment Directive. Environmental Resources Management London United Kingdom

[24] The "undesirable disturbance" aspect is used more and more by EA to decide on whether action should be taken

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## 11. ANNEXES

### Annex 1. Summary of the interest features and conservation objectives

### Summary of the interest features and conservation objectives (adapted from English Nature, 2001)

Interest features under the EU Birds Directive:

**Internationally important populations of regularly occurring migratory species**:

Dunlin (*Calidris alpina*), Redshank (*Tringa totanus*), Pintail (*Anas acuta*), Ringed plover (*Charadrius hiaticula*), Shelduck (*Tadorna tadorna*), Teal (*Anas crecca*), Redshank (*Tringa totanus*)

Conservation objectives focus on maintaining habitats for these species in favourable condition subject to natural change. In particular:-

- Intertidal sediments
- Rocky shores
- Saltmarsh

**• Internationally important assemblage of waterfowl:**

The Mersey Estuary supports large populations of wintering waterfowl. 78,015 individual birds (47,714 waders and 30,301 wildfowl). The Mersey alsop supports nationally important populations of Wigeon (*Anas penelope*), Grey plover (*Pluvialis squatarola*), Black-tailed godwit (*Limosa limosa*), Curlew (*Numenius arquata*), Redshank (*Tringa totanus*)[1], Dunlin (Calidris alpina)[2]

Conservation objectives focus on maintaining habitats for these species in favourable condition subject to natural change. In particular:-

- Intertidal sediments
- Rocky shores
- Saltmarsh

[1] Spring passage i.e. not component of wintering assemblage
[2] Autumn passage i.e. not component of wintering assemblage

## 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] | None mentioned with regard to the annual mean. |

| | | | |
|---|---|---|---|
| | | 20 MAC[4] | |
| 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
(from Cole *et al.,* 1999)

| Parameter | Unit | G | I |
|---|---|---|---|
| **A. GENERAL PHYSIO-CHEMICAL PARAMETERS** | | | |
| Colour | | | [(a)] |
| Dissolved oxygen | % sat | >80 T95 | >70 TAA[(b)] |
| pH | | | 7-9 T75 |
| Salinity | g/kg | 12-38 T95 | 40 T95[(c)] |
| Suspended solids | | | [(d)] |
| Tainting substances | | | [(e)] |
| Temperature | | [(f)] | |
| **B. METALS AND INORGANIC ANIONS** | | | |
| Arsenic | | [(g)] | [(h)] |
| Cadmium | | [(g)] | [(h)] |
| Chromium | | [(g)] | [(h)] |
| Copper | | [(g)] | [(h)] |
| Lead | | [(g)] | [(h)] |
| Mercury | | [(g)] | [(h)] |
| Nickel | | [(g)] | [(h)] |
| Silver | | [(g)] | [(h)] |
| Zinc | | [(g)] | [(h)] |
| **C. ORGANIC SUBSTANCES** | | | |
| Hydrocarbons | | | [(i)] |
| Organohalogens | | [(g)] | [(h)] |
| **D. MICROBIOLOGICAL PARAMETER** | | | |
| Faecal coliforms | per 100 ml | 300 T75[(j)] | |

## Notes:

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

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

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

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

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

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

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

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

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

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

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

## Annex 4. Bathing Waters Quality Standards

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

| Parameter | Unit | G | I |
|---|---|---|---|
| **A. INORGANIC SUBSTANCES AND GENERAL PHYSICO-CHEMICAL PARAMETERS** | | | |
| Colour | | | (a, b) |
| Copper | mgCu/l | | |
| Dissolved oxygen | % saturation | 80-120 T90 | |
| pH | | | 6-9 T95(b) |
| Turbidity | Secchi depth m | >2 T90 | >1 T95(b) |
| **B. ORGANIC SUBSTANCES** | | | |
| Floating waste(c) | | (d) | |
| Hydrocarbons | µg l-1 | 300 T90(e) | (f) |
| Phenols | 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 |

### Notes

G guide value

I imperative (mandatory) value

T total concentration (ie without filtration)80 standard defined as 80-percentile*

90 standard defined as 90-percentile*

95 standard defined as 95-percentile*

It is further stipulated that of the 20, 10 or 5% of samples from designated waters which exceed the standard, none should do so by more than 50% (except for microbiological parameters, pH and dissolved oxygen) and that "consecutive water samples taken at statistically suitable intervals do not deviate from the relevant parametric values" (Article 5 of CEC 1976).

[a]No abnormal change in colour

[b]May be waived in the event of exceptional weather or geographical conditions

[c]Defined as wood, plastic articles, bottles, containers of glass, plastic, rubber or any other substance

[d]Should be absent.

[e]Applies to non-routine sampling prompted by visual or olfactory evidence of the presence of he substance

[f]There should be no film visible on the surface and no odour

[g]Reacting with methylene blue

[k]There should be no lasting foam

## Annex 5. Sediment Quality Guidelines

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

| Substance | ISQG | PEL |
|---|---|---|
| | | |
| **Inorganic ($mgkg^{-1}$)** | | |
| | | |
| Arsenic | 7.24 | 41.6 |
| Cadmium | 0.7 | 4.2 |
| Chromium | 52.3 | 160 |
| Copper | 18.7 | 108 |
| Lead | 30.2 | 112 |
| Mercury | 0.13 | 0.70 |
| Zinc | 124 | 271 |
| | | |
| **Organic ($\mu gkg^{-1}$)** | | |
| | | |
| 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 Assays** – these assay measures the immunocompetence of haemocytes from invertebrates, reflecting both the extent of exposure to immunotoxins and the general well-being of the test organism. Various immunological parameters (e.g. cell counts, generation and release of superoxide anions, phagocytosis, lysosomal enzyme activity) have proved useful in monitoring the status of shellfish in response to oil pollution and PAHs (Pipe *et al*, 2000; Raftos and Hutchinson, 1995; Dyrynda *et al*., 1998).

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

**Metallothionein** (MT) induction and associated changes in metal metabolism are specifically induced by metals and are sufficiently sensitive to be used to detect elevated levels of bioavailable metal in the field or arising from metals in discharges (e.g. Langston *et al*., 2002). The induction of MT protein, and associated metal-binding patterns can therefore be used to map spatial and temporal trends in biological respones to metals. Examples of the application of this assay, in relation to eels from the Weston Canal, are illustrated in section 7.2.

**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

**Annex 6 (cont.)**

sediment bioassays to look at growth and survival of juvenile bivalves. Compare responses in Mersey biota with those elsewhere to look for signs of adaptation.

**Biodiversity indices: quantitative techniques to assess community-level response to environmental degradation** - *Species richness* - an indication of the number of taxa per unit area; -*Shannon-Weiner diversity index* ($H^1$) - expresses the relationships between the occurrence of species and the apportioning of individuals among those species (relative dominance); -*Pielou's evenness index (J)* compares the diversity of the data with its theoretical maximum, where all species would be equally abundant. Lower values would be associated with samples from sites numerically dominated by only one or two species, which is generally indicative of stressed communities; -*The Simpson index* relates the contribution made by each species to the total population. Although observing similar aspects of the dataset, this index is unrelated to the Shannon-Weiner diversity index. Higher values in the Simpson index equate to the presence of a few dominant species in the assemblage; -*Taxonomic distinctness* This index, which captures phylogenetic diversity rather than simple species richness, is more linked to functional diversity. Clarke and Warwick (2001) have refined and developed this index to pick out degraded locations; -*Abundance Biomass Comparison* - can be used 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.

Various forms of multivariate statistical analysis of benthic communities and associated environmental variables are useful in examining spatial and temporal trends in communities in relation to contaminants (Warwick *et al.,* 1998).

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

## Annex 7. EA current priority discharges for assessment

| | HIGHLIGHTED OUTFALLS TOP PRIORITY FOR NEAR FIELD ASSESSMENT | | | | |
|---|---|---|---|---|---|
| | MODEL EASTING | MODEL NORTHING | TITLE | Exact NGR | Comments |
| | | | | | |
| | | | | | |
| X | 359700 | 388000 | Ineos Silicas Ltd | | u/s SPA |
| 10 | 333290 | 387300 | Shell UK Ltd (1) | SJ33298730 | Temperature only |
| 10 | 333500 | 387200 | Shell UK Ltd (2) | SJ33508720 | Temperature only |
| X | 335200 | 384300 | Lubrizol Ltd | | BOD/ss only |
| X | 336100 | 382900 | FMC Chemicals Ltd | | BOD/ss only |
| 8 | 332800 | 387500 | Cammel Laird | SJ 328 875 | d/s SPA, organnotin |
| X | 353100 | 386400 | Croda Colloids (1) | | u/s SPA |
| X | 352800 | 385500 | Clariant UK Ltd | | u/s SPA |
| 9 | 354300 | 386500 | AEP Energy Ltd (1) | SJ 543 865 | close to SPA and big! T, Hg, Cd |
| 9 | 354300 | 386500 | AEP Energy Ltd (2) | SJ 543 865 | close to SPA and big! |
| X | 332400 | 396200 | Cargills | | outside SPA |
| X | 338700 | 378950 | Bridgewater Paper | | via tidal Brook |
| | 342900 | 376100 | Cleanaway Incinerator | | via tidal Brook |
| X | 343060 | 374980 | Shell Stanlow (1) | | via tidal Brook |
| X | 343010 | 376600 | Shell Stanlow (2) | | via tidal Brook |
| 6 | 350300 | 384000 | Granox | SJ 503 840 | borders SPA |
| 7 | 349300 | 383800 | Croda Colloids (2) | SJ 493 838 | in SPA, Cr |
| X | 352900 | 385400 | Pilkington Sullivan | | close to SPA but small |
| X | 334450 | 384480 | Unichema | | to tidal Dibbinsdale |
| X | 360130 | 386430 | Solvay Interox | | u/s SPA |
| X | 359460 | 387960 | Crosfields (1) | | u/s SPA |
| X | 359870 | 387770 | Crosfields (2) | | u/s SPA |
| X | 342580 | 375930 | Castrol | | to tidal Gowy |
| X | 359600 | 386000 | Solvay Interox (2) | | u/s SPA |
| X | 333000 | 387100 | Shell UK Ltd (3) | | consider with Shell (2) |
| X | 352900 | 385400 | Saffil Ltd | | close to SPA but small |
| X | 359500 | 387600 | Vinamul Ltd (1) | | u/s SPA |
| X | 359800 | 387500 | Vinamul Ltd (2) | | u/s SPA |
| 5 | 333210 | 392640 | Sandon Dock STW | SJ 3321 9264 | all metals |
| 4 | 332730 | 389390 | Birkenhead STW | SJ 3292 8949 | all metals |
| 3 | 335410 | 384410 | Bromborough STW | SJ 3471 8564 | all metals |
| 2 | 358110 | 386960 | Warrington North STW | SJ 5811 8696 | all metals |
| 1 | 348510 | 382920 | Widnes STW | SJ 4851 8292 | all metals |

## 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).

Characterisation of European Marine Sites: **Essex Estuaries EMS**. Marine Biological Association of the United Kingdom occasional publication No 17 (In press)

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