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A Survey of Trace Metals in Biota of the Mersey Estuary - 1993

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Abstract

The biological availability of metals along the length of the Mersey estuary has been re-evaluated using macro algae, *Fucus vesiculosus*, gastropods *Littorina littorea*, polychaetes *Nereis diversicolor*, suspension-feeding bivalves *Mytilus edulis*, *Mya arenaria* and *Cerastoderma edule* and deposit-feeding bivalves *Scrobicularia plana* and *Macoma balthica*. In the current survey, conducted in May 1993, concentrations of Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn and Zn have been measured in sediments and biota and the results compared with data for similar Mersey surveys carried out since 1980. Observations of long-term trends in contamination, species distribution, and abundance are discussed and comparisons are made with conditions found in other UK estuaries. The results will assist in the general quality assessment of the Mersey estuary.

Contents

Summary

Concentrations of 13 metals (Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn, Zn) have been measured in various biological indicator species collected at sites along the Mersey estuary during May 1993 and the results compared with those of previous surveys dating back to 1980. The species used include the brown alga *Fucus vesiculosus*, the gastropod *Littorina littorea*, the polychaete *Nereis diversicolor*, suspension feeding bivalves *Mytilus edulis*, *Mya arenaria* and *Cerastoderma edule*, and the deposit feeding bivalves *Scrobicularia plana* and *Macoma balthica*, as a means of assessing contamination in different phases of the environment (e.g. water, sediment, suspended solids). In addition to determining spatial and temporal trends in metal burdens in Mersey biota, comparisons have also been made with other UK estuaries in order to place in context the degree of contamination present.

The distribution of organisms was generally similar in the 1993 survey to that found in previous years (although some species were recovered from further upstream than in the 1991 survey) and was characterised by a limited diversity of fauna and flora in the upper Mersey. Of the above species only *Nereis* was present in this region. The use of the NRA's hover craft enabled a thorough sampling exercise, and sites along the Ince/Stanlow banks were sampled again to enable comparisons with 1991 data to be made.

A much greater variety of species was encountered towards the mouth of the estuary. The abundance of most organisms compared favourably with observations made in earlier studies, though densities of sediment-dwelling bivalves seemed lower than in recent surveys. At Egremont, where declining clam populations and increasing metal bioavailability have been a consistent feature, no *Scrobicularia plana* or *Macoma balthica* could be found.

The benefits of using several species in the assessment of metal contamination and bioavailability in the Mersey estuary are demonstrated in this report. *Nereis* is generally the most useful indicator of metals along the length of the estuary due to its widespread occurrence. However it is a relatively poor accumulator of metals compared with most molluscs and displays the ability to regulate Zn and Fe. Results for *Nereis* show that, as in previous surveys, contamination/bioavailability is highest in the mid-upper portion of the estuary for most metals, and decreases downstream. Although most other organisms are confined to the lower estuary, the majority generally reflect this latter spatial pattern in contamination. For some species-metal combinations, however, there are clearly exceptions and in spite of the general correlation between tissue metal concentrations and trends in sediment (and water) contamination, there are a number of examples where bioavailability may be modified considerably by factors other than total metal loading in the environment. These factors include salinity, redox conditions and the presence of sewage (especially at Blundellsands) and interactions with competing ligands in sediments.

Concentrations of Hg remain similar to those measured in 1991 and indicate a continuation of 'steady- state' conditions following the significant reductions of the early 1980's. The latter improvement coincided with the introduction of clean-up procedures introduced by major industrial users during the late 1970's and early 1980's. Similar observations generally apply to Pb. For some metals however, particularly silver and chromium in sediments throughout the estuary, and most metals at the mid-estuarine sites of Garston and Eastham Lockgates, together with Blundellsands in the outer estuary, metal concentrations in biota remain elevated and in some instances have increased. Therefore, despite the earlier success of control measures, concern over many metals, particularly of organic forms (alkyl leads, methyl mercury) is still warranted in view of their potential toxicity.

Zinc concentrations, which twelve years ago were extremely high in non- regulating species such as *Fucus* and *Scrobicularia*, have followed a similar pattern to Hg and Pb and suggest a considerable reduction in inputs of the metal. Since 1991 however there have been no further changes recorded.

Between 1984 and 1989 significant decreases in arsenic concentrations in biota were a consistent feature at sites in the middle and upper estuary, though the sources of As and the cause of the improvements were not known. Since 1991 however, arsenic concentrations in most indicator species have increased, and while the cause remains uncertain, it may be speculated to be in part related to the reduction in phosphate levels (phosphate competes with arsenate for uptake) within the Mersey.

For the remaining metals surveyed, mean concentrations (all sites) generally fall within the ranges encountered previously and do not as yet constitute evidence of long-term changes in bioavailability or inputs to the estuary. However, at certain sites significant changes do appear to have occurred, most notably the increase in all metal concentrations measured (except Cd, Ni and Se) in sediments and *Nereis diversicolor* from Hale, and continued high bioavailability of all metals (with the exception of Se) to molluscs from Eastham Lockgates, and Blundellsands. Increased inputs of dissolved metals via the Manchester Ship Canal and changing conditions in sediments (possibly related to amounts of sewage/redox potentials), may be responsible for the increase in bioavailability at these sites.

It is difficult to generalise about the state of pollution in the Mersey estuary as a whole because of these spatial and temporal variations, and also because bioaccumulation potential can vary significantly between different organisms. Nevertheless, comparisons have been made with similar data derived from more than 100 estuaries in the UK, collected during the last 20 years. These data confirm a degree of contamination in the Mersey (above baseline values) for all the metals studied: Mean metal concentrations in Mersey biota fall within a factor of about 10x baseline levels, but for all metals (except As, Cu and Ni), this enrichment level is exceeded (up to a maximum of 123x for Cr in *Nereis diversicolor* at certain locations.

Indeed, Cr, Fe and Mn concentrations in biota from some sites coincide with worst-case UK conditions. However, for the majority of metals it still remains appropriate, to describe the Mersey estuary as being 'moderately' contaminated.

Introduction

The concept of using biological samples as indicators of metal contamination is now widely regarded as an essential component of monitoring schemes to complement the traditional methods of assessment provided by water and sediment analyses (Phillips, 1980; Bryan et al, 1985). The major argument supporting the inclusion of indicator organisms in such schemes is that they reflect and integrate only the biologically available forms of metals. In contrast, analyses of water and sediment usually provides information concerning the total concentration of the contaminant in the environment without defining its accumulation potential and thus its biological impact. Since Environmental Quality Targets are most frequently aimed at the protection of biological resources, the use of indicator organisms which reflect the presence of bioavailable metals is therefore often a preferable means of assessing contamination.

Choice of indicator organisms

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 seaweeds, *Fucus vesiculosus*, gastropods, *Littorina littorea*, suspension feeding bivalves *Mytilus edulis*, *Mya arenaria*, *Cerastoderma edule*, and deposit feeding clams *Macoma balthica*, *Scrobicularia plana*, as well as *Nereis diversicolor*, and their relative merits as indicators of metal contamination have been described in a previous study (Langston 1988), and in a variety of more detailed papers (see for example Bryan et al 1983, 1985; Davies and Pirie, 1980; Foster, 1976; Langston, 1982; Luoma et al, 1982).

Previous Research

Prior to the present survey, conducted in May 1993, sampling had been carried out in the Mersey estuary by MBA/PML staff on 10 occasions since 1980. Early surveys were largely supported by DOE funding as part of larger studies on metal bioavailability in UK estuaries. Examination of these results suggested surveys of a similar nature might be usefully repeated at 2-yearly intervals in order to monitor bioavailability of metals of concern (Langston, 1986). Thus it was observed that although metal concentrations rarely approached those encountered in estuaries in mineralised regions of SW England, the Mersey was unusual in being moderately contaminated with such a wide range of metals. The exception to this general observation was mercury which was consistently high in Mersey biota compared with other estuaries in the UK. Concern has also focused on bioavailability of lead in the estuary following suspected environmental damage caused by discharges of alkyl lead in the late 1970's and early 1980's.

The NWWA commissioned a similar survey of the Mersey estuary in 1987, results of which indicate the approach of 'steady state' conditions for Hg and Pb concentrations in biota, following the significant reductions observed during the early part of the decade. Consistent long term trends were not observed for other metals (Langston, 1988).

Following the transfer of environmental responsibility to the NRA, further surveys were conducted on their behalf in June 1989, May 1991, and most recently in May 1993. The results of this latest survey form the basis of the current report.

Objectives and Benefits of Present Research

Having made a preliminary assessment of the organisms which provide the most useful comparative information on environmental quality, the aims of the present study are:

1. To evaluate temporal and spatial trends in metal (Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn, and Zn) bioavailability in the estuary (by incorporating results for similar surveys carried out since 1980).

2. To assemble further data to assist in the identification of factors which promote or inhibit metal bioavailability.

3. To compare metal concentrations in biota from the Mersey estuary with data for similar species in other UK estuaries.

4. By determining the current status of metal contamination in the Mersey estuary, to assess the effectiveness of pollution control measures already taken and to establish information as a platform for future controls which may be required to improve environmental quality.

5. Through a combination of the above to assist in decisions regarding selection of the most suitable location, composition and quantity of metallic waste discharges with a view to minimising their impact.

6. To provide background information relating to proposals to include sediments as part of the requirements for General Quality Assessment of estuaries.

Materials and Methods

Sampling Sites, Collection and Distribution of Indicator Organisms

Seventeen inter-tidal sites were sampled along the length of the estuary during the period 24 - 27th May 1993. The sites were distributed over 50km between Fiddlers Ferry (the furthest upstream location) and Hoylake and Hightown at the seaward end, on the Wirral and Formby shores of Liverpool Bay respectively (Figure 1, Table 1). These sites were identical to those visited in 1991 and incorporated all those sampled in previous surveys.

The occurrence of indicator organisms collected in the present study, together with Ordnance Survey grid references of sampling sites and distances downstream from Fiddlers Ferry are presented in Table 1. *Nereis diversicolor* remains the most valuable indicator species due to its extensive distribution throughout the estuary (Widnes - Hoylake), although it is absent from New Brighton and Blundellsands due to the coarse nature of the sediments at those sites. For sites upstream of Garston, *Nereis diversicolor* is the only indicator organism available, and therefore, due to the absence of other macro fauna it is an important component of the diet of several species of wading birds. Consequently, *Nereis diversicolor* is thought to be significant in the transfer of metals through the food chain, but it should be noted that compared to the majority of molluscan species, *Nereis* is a poor accumulator of many metals.

The increased availability and abundance of additional indicator organisms occurring downstream of Garston, due partly to more widespread sampling using the hover craft, improves the monitoring capabilities in the lower part of the estuary. As a result, in comparison to the 1991 survey, there has been an apparent increase in the number of different species collected at many sites, as shown in Table 1. This is most noticeable at Garston and Eastham Lockgates, which now represent the new upstream limits of occurrence for the majority of species other than *Nereis diversicolor*. For example, the bivalves *Cerastoderma edule*, *Mytilus edulis*, *Scrobicularia plana* and *Mya arenaria* were found only as far upstream as Rock Ferry in 1991, while in 1993 all were found at Eastham Lockgates, and only *Cerastoderma edule* could not be found at Garston. This increase in distribution has improved monitoring capabilities compared to previous years, but it would be premature to relate this to improved conditions within the estuary.

Although biological sampling in the current survey was not quantitative, comparisons with previous surveys suggest moderate stability within the communities sampled at the different sites, with some exceptions. As already mentioned, some species were found further upstream, though this may in part be due to greater sampling effort at these sites, combined with searches over a greater area. The absence of substantial numbers of large *Macoma balthica* at New Brighton, and of any at all at Hightown, is as stated in the previous report (1991), probably a reflection of natural variability in populations of this species. The inability to find any *Scrobicularia plana* or *Macoma balthica* at Egremont however, is thought to be due to a more

Figure 1. Mersey 1993 - Sampling Sites

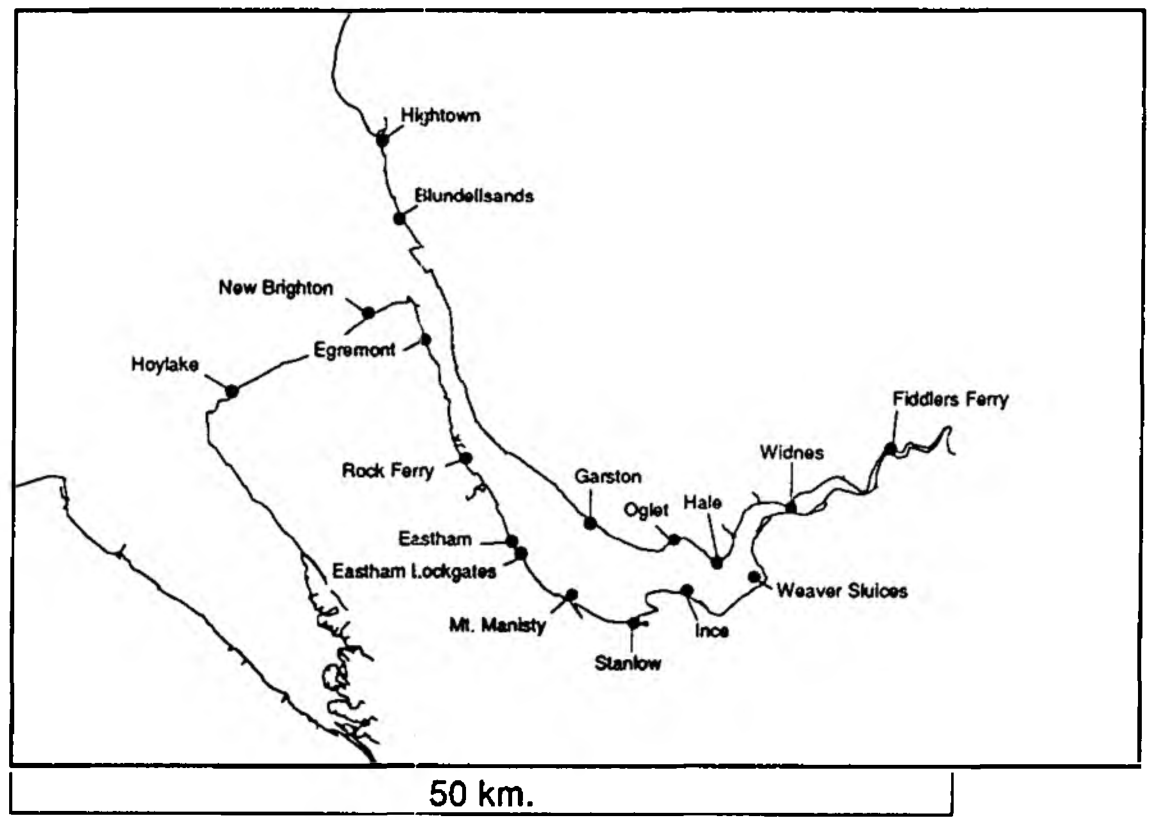


Table 1. Sampling Sites and Occurrence of Indicator Species, Mersey Estuary, May 1993.

Site	Map reference	Distance km.	*Fucus vesiculosus*	*Cerastoderma edule*	*Mytilus edulis*	*Littorina littorea*	*Mya arenaria*	*Macoma balthica*	*Scrobicularia plana*	*Nereis diversicolor*
Fiddlers Ferry	SJ566867	0.0								
Widnes	SJ514837	7.0								*
Weaver Sluices	SJ494800	10.0								*
Hale	SJ483816	11.0								*
Ince	SJ458793	12.0								*
Oglet	SJ451819	16.0								*
Stanlow	SJ430777	17.5								*
Mount Manisty	SJ397791	20.0								*
Garston	SJ406828	21.5	*		#		#	*	*	*
Eastham Lockgates	SJ370812	23.0	*	#	#	*	#	#	#	#
Eastham	SJ365819	23.5	*							*
Rock Ferry	SJ340862	28.5	*	*	*	*	*	*	*	*
Egremont	SJ319924	34.5	*	*	*	*	#			*
New Brighton	SJ288938	39.5	*	*	*	*		*		
Blundellsands	SJ304988	41.5		*	*	*		#		
Hightown	SD295030	45.5							*	*
Hoylake	SJ216897	48.0		#				*	*	*

- Indicates new records of occurence in 1993.

general decline in numbers at this site since surveys began in 1980. Finally, populations of *Nereis diversicolor* at some sites in the upper estuary, particularly at Widnes and Hale, appear to be less abundant than in 1991.

Pre treatment and Analysis of Samples

Full details of methods of pre-treatment and analysis have been documented in earlier publications (Langston 1980, 1986, 1988; Bryan *et al* 1985). Briefly, all organisms were transported live to the laboratory and allowed to depurate in clean sea water in order to eliminate possible contamination from sediment bound metals. Suitable numbers of individuals of each species were subsequently pooled, and sub-samples digested with either HNO_3 (Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn); $HNO_3/H_2SO_4/H_2O_2$ (Hg, Se); or dry ashed with a mixture of MgO + $Mg(NO_3)_2$ as an ashing aid (As, Sn). The first of these groups of metals (Ag - Zn) were analysed by Flame Atomic Absorption (FAA), or, where concentrations were low, by Graphite Furnace Atomic Absorption (GFAA). Arsenic, tin and selenium were measured using hydride generation / flameless AA, and mercury by cold vapour / flameless AA. Metal concentrations in organisms are expressed as µg/g (ppm) on a dry weight basis unless stated otherwise. Sediments were digested with hot nitric acid to provide estimates of total metals, or extracted with 1N HCl for 2 hours as an estimate of the bioavailable metal fraction.

Data Processing and Analysis

Data from the analyses described above were input to Microsoft Excel v4.0 spreadsheets, interlinked to output the calculations performed into both Excel databases and another, larger database (dBase III) holding data for most UK estuaries.

In order to make comparisons with other UK estuaries the averaged data for all Mersey sites for each species and each metal is compared to baseline UK data in a manner similar to the previous survey. However, with the establishment in recent years of our computer database, for levels of metals in estuarine biota, it has now become possible to update the baseline data. Briefly, the UK minimum and UK maximum values, as presented in the appendices of this report, refer to the mean of the lowest ten and highest ten values recorded for each species, and each metal in the database. The use of these mean data are justified on the grounds that the influence of exceptionally high and low individual values on baseline levels is reduced, thus presenting more generally applicable values for comparison with other data. There may be instances however, where averaged data for the Mersey estuary exceeds the mean of the current top ten values, thus placing the Mersey within that group. When such instances occur it may become necessary to compare the data on a site by site basis using the extreme values recorded in the database, together with further discussion on the interpretation of such results.

Relative Contamination Indices have been used in previous reports (Langston *et al*, 1990; 1992) as a simplified means of comparison between the Mersey and other UK estuaries. Since the UK minimum and maximum levels for metals in different species have been updated for this report, values for RCI's have been calculated based on this new data. In addition, RCI's for 1989 and 1991 data have been re-calculated using these new lower and upper limits in order that comparisons with the latest survey can be made. It is useful at this point to review how the RCI values are generated, and their limitations. Briefly, by condensing the range of concentrations of a metal in organisms from UK estuaries to a scale of 0 - 100 (0 representing the UK baseline level, 100 = UK maximum, as described above) it is possible to place mean Mersey levels at a point on this scale (an example of this calculation is shown below), and thus provide some idea of the relative degree of contamination in biota from the Mersey estuary.

Maximum value (mean of 10 highest recorded) = 4.888 µg/g Cd

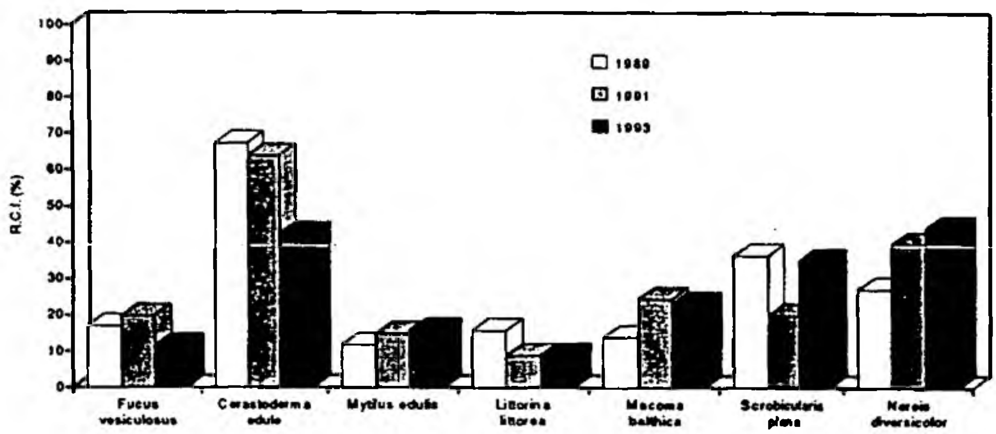
Minimum value (mean of 10 lowest recorded) = 0.032 µg/g Cd

Mersey 1993 mean for *Nereis diversicolor* = 0.348 µg/g Cd

$$1993\ \text{R.C.I. for Cd in } \textit{Nereis diversicolor} = \frac{(0.348 - 0.032)}{4.888} * 100 = 6.46$$

For every metal analysed, these indices are presented as shown in the diagram below:

Relative Contamination Indices for a metal in Mersey Biota



These figures are essentially an oversimplification of the current pollution status of the Mersey for several reasons:

- The data for other UK estuaries has been compiled over more than 20 years, and conditions at some sites will probably now be different.
- For some metals e.g. mercury and chromium, some of the highest values recorded were Mersey samples collected at earlier dates.
- The mean data for different estuaries is based on variable numbers of samples, or even single samples in some cases, due to restricted occurrence or sampling.

Despite these difficulties in interpretation, the RCI figures nevertheless provide a broad impression of the scale and biological significance of metal contamination in the Mersey estuary.

Results

Silver

Data for silver in 1993 samples are presented in Appendix 1.

Spatial Trends

Total silver concentrations in Mersey sediments were found to vary only slightly (1 - 2.5 µg/g) across the entire area surveyed in 1993, as shown in Figure 2A. Within this distribution, the highest levels are seen in the mid-estuarine regions of Mount Manisty, Eastham and Rock Ferry, and again at Hightown towards the seaward end.

The profile of silver concentrations in *Nereis diversicolor* (Figure 2B) however, is noticeably different to the sediment profile and may provide more information about the bioavailability of silver in the Mersey sediments. The pattern is similar to that seen in previous years, with a peak in the upper/middle region of the estuary, this time centred at Stanlow, and there is again a slight increase in silver concentrations towards the mouth of the estuary at Hoylake, but this is less pronounced than in the previous survey.

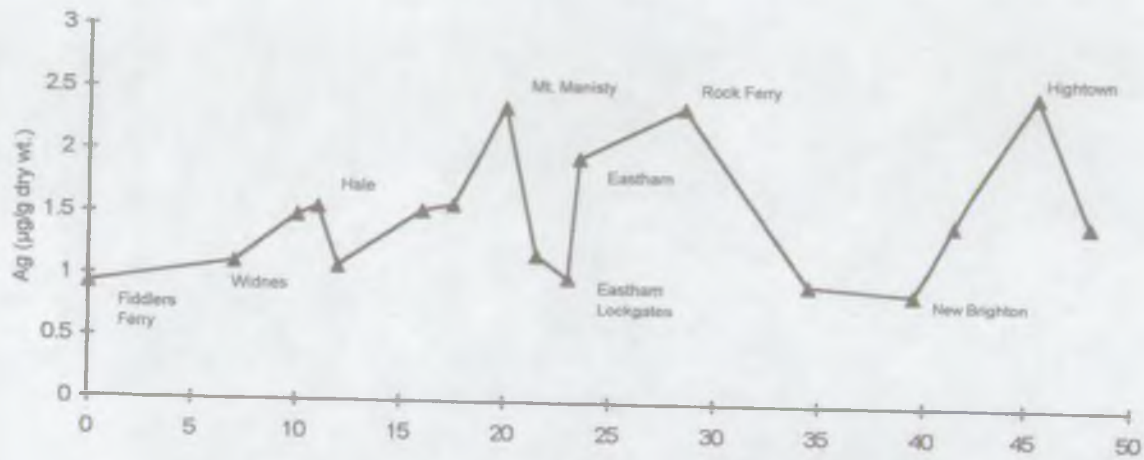
The deposit-feeding bivalves *Scrobicularia plana* and *Macoma balthica* are not as widely distributed within the estuary as *Nereis*, but within their limited distributions some interesting and consistent patterns can be seen, as shown in Figure 2C. Here there is an increase in silver concentrations between Eastham Lockgates and Rock Ferry, followed by a decline towards the mouth of the estuary, however, no clams were found at Egremont this year. A quite similar distribution can be seen in the suspension feeding bivalves *Cerastoderma edule* and *Mya arenaria* (Figure 3A), although comparative interpretation must consider the occurrence and distribution of these different species, since not all species occur at all sites. However, both *Mya arenaria* and *Cerastoderma edule* show highest levels at Rock Ferry and decline downstream, (*Cerastoderma edule* exhibiting a slight increase at Blundellsands, similar to *Nereis diversicolor*). Distributions of silver in *Mytilus edulis* and *Littorina littorea* profiles are less well defined and the range of concentrations measured in these two species is small. Levels in *Fucus vesiculosus* however, show a peak at Eastham Lockgates, falling sharply towards Eastham followed by a slight increase seawards (Figure 3B). Since *Fucus* derives most of its metal burden from solution, this may indicate an input of silver in dissolved form from the Manchester Ship Canal.

Temporal Trends

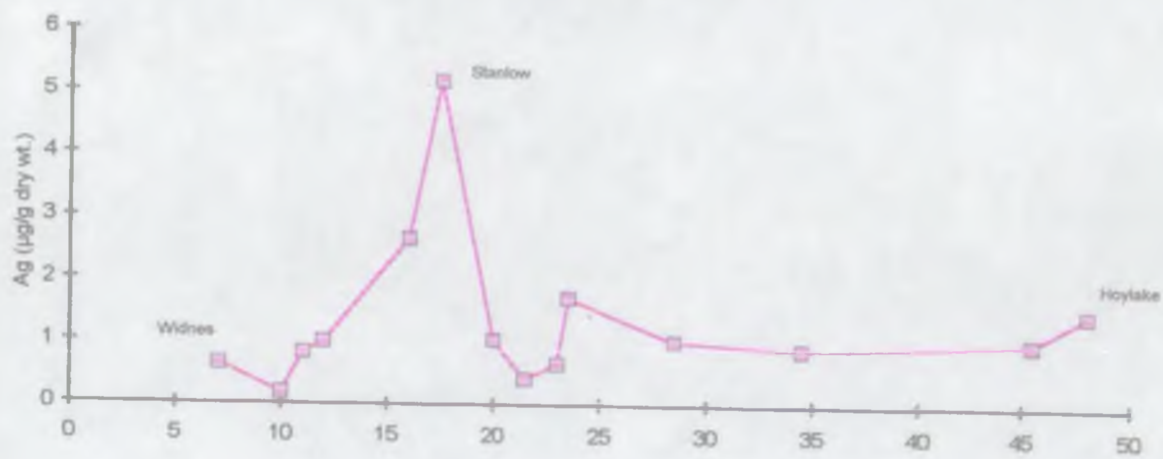
Contrary to the trend for several other metals there has been a statistically significant (ANOVA, $P<0.0001$) increase in mean total silver levels in Mersey sediments in recent years, from average concentrations of 0.56 µg/g in 1989 to 1.07 µg/g in 1991 increasing to 1.51 µg/g in 1993, the highest average silver concentration found so far in the Mersey estuary (Figure 4A) [NOTE - vertical bars on temporal trend charts indicate 95% confidence intervals]. This indicates that inputs of silver into the estuary are continuing, and may be increasing.

Figure 2. Spatial trends for Silver, 1993.

A. Total Silver in Sediments



B. Silver in Nereis diversicolor



C. Silver in Scrobicularia plana and Macoma balthica.

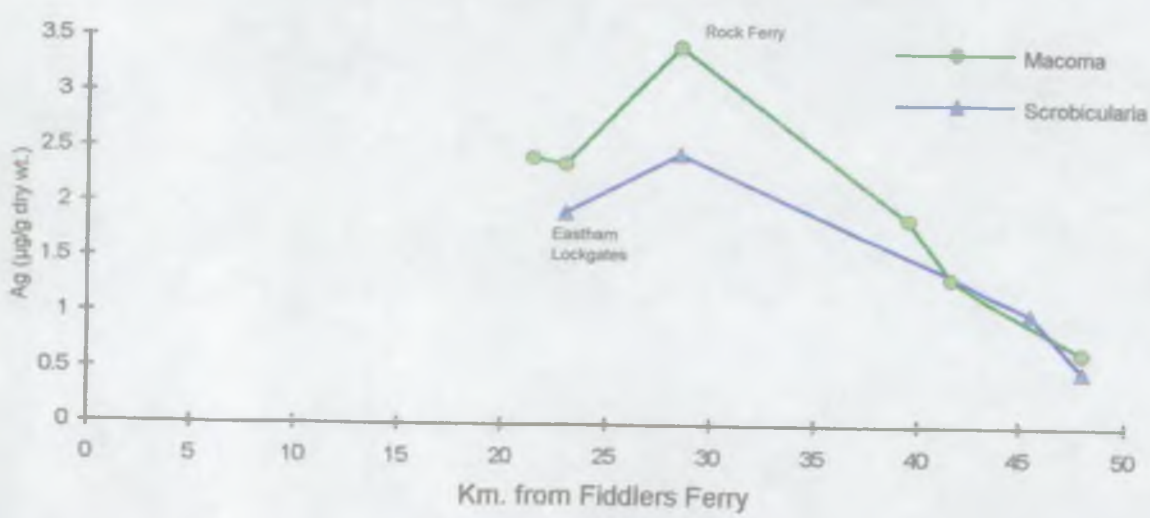
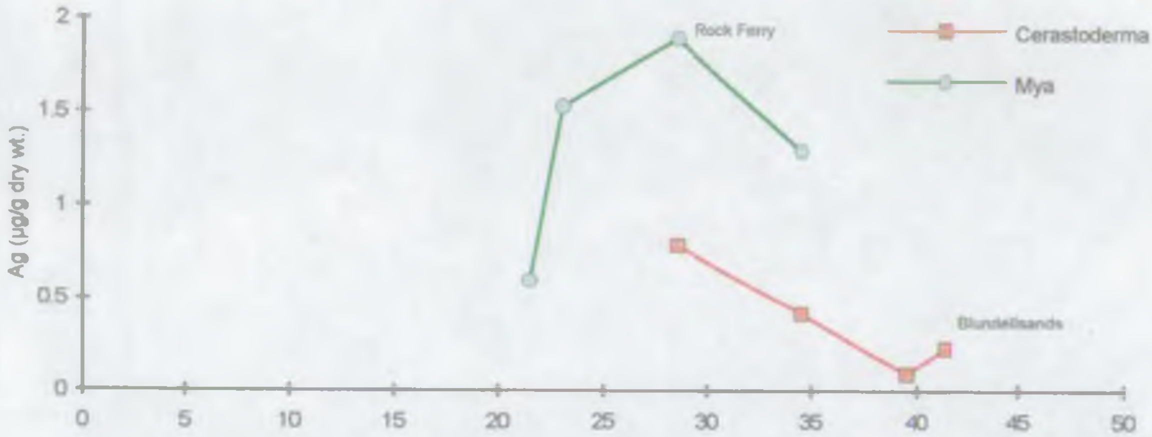


Figure 3. Spatial trends for Silver, 1993.

A. Silver in Cerastoderma edule and Mya arenaria



B. Silver in Fucus vesiculosus

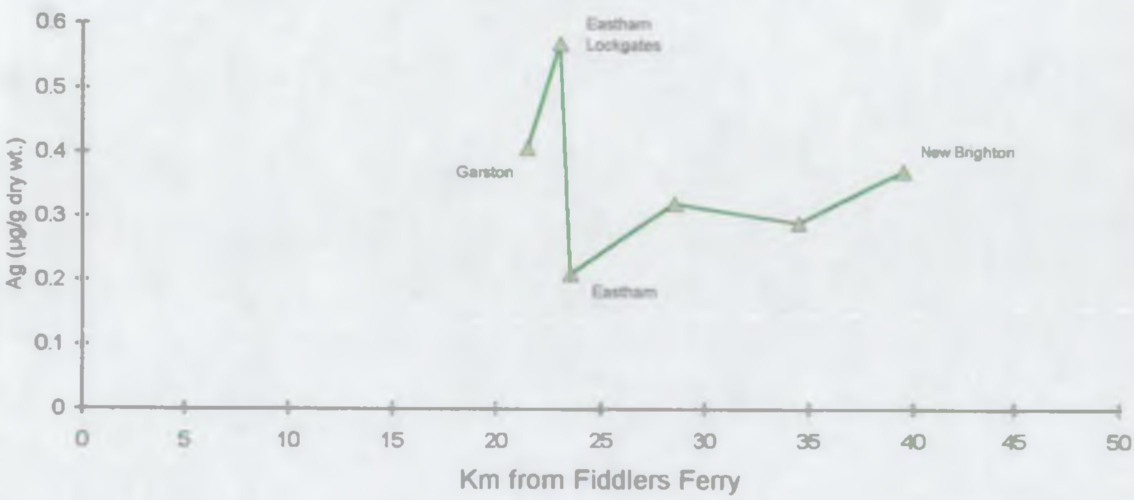
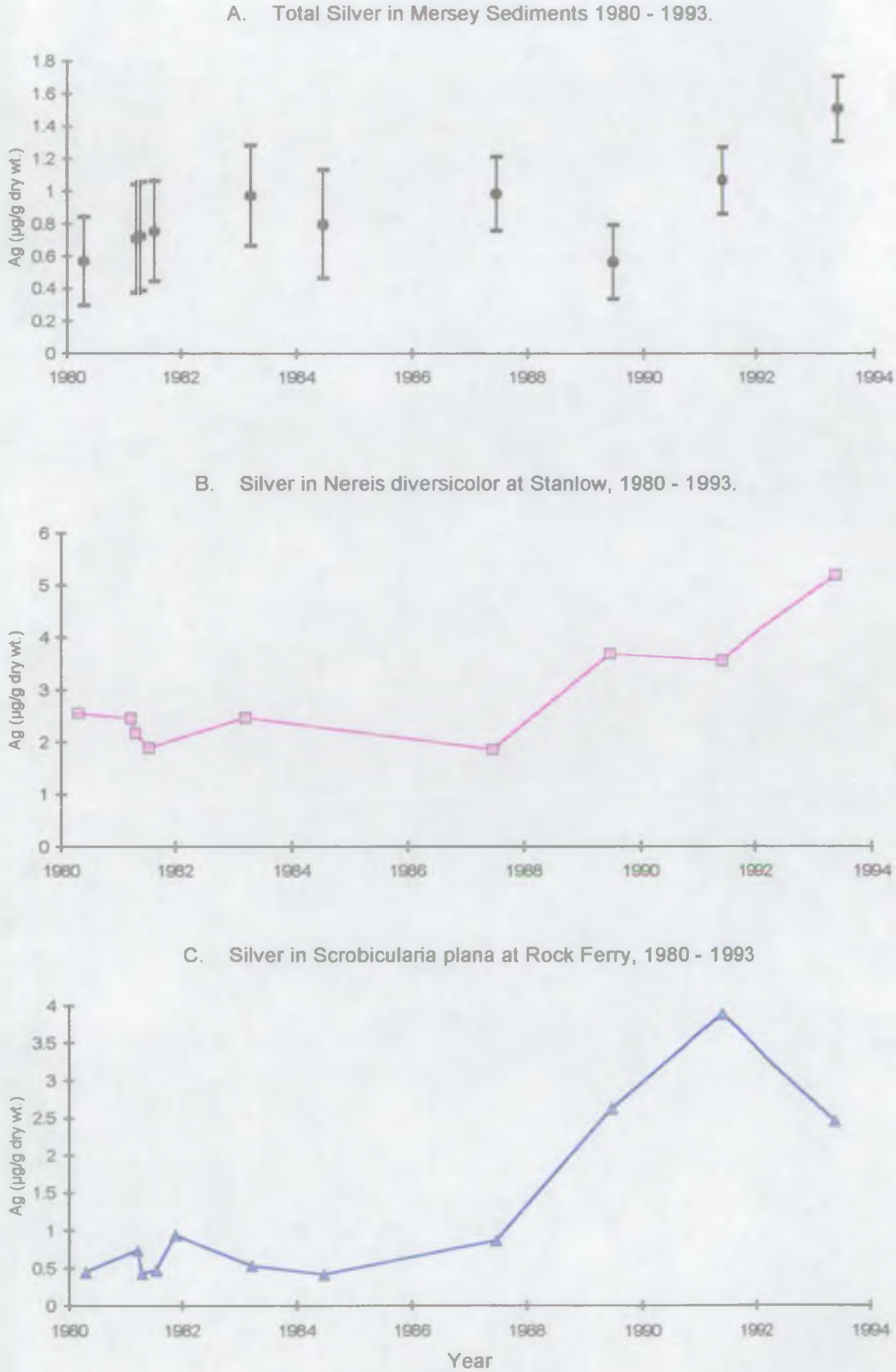


Figure 4. Temporal trends for Silver, 1980 - 1993.



When the mean concentrations of silver in biota found throughout the estuary are compared over the period 1980 - 1993 no statistically significant changes are apparent. However, by making such a comparison, events at particular sites may become obscured. For instance, increasing levels of silver in *Nereis diversicolor* at Stanlow (Figure 4B) and *Scrobicularia plana* at Rock Ferry (Figure 4C) can clearly be seen over this period. It is also important to note that, in the previous report, even more significant increases in silver were a feature of deposit-feeding clams from Egremont. These populations now appear to be extinct, though whether recent increases in metal burdens, including silver, are responsible, has yet to be determined.

Comparisons with other estuaries

From the data presented in Appendix 1 it can be seen that although there are inter-site variations in silver concentrations within each species, the range of levels encountered is relatively narrow, both within and between species, with the possible exception of *Littorina littorea* which tends to accumulate more silver than other species. Such an absence of major spatial variation within each species data set means that comparisons with other estuaries are more realistic than if there was a large variation in concentrations within species.

Using averaged data for samples collected in 1993, enrichment factors for each species (relative to baseline values for UK estuaries as described previously - page 12) are presented in Table 2.

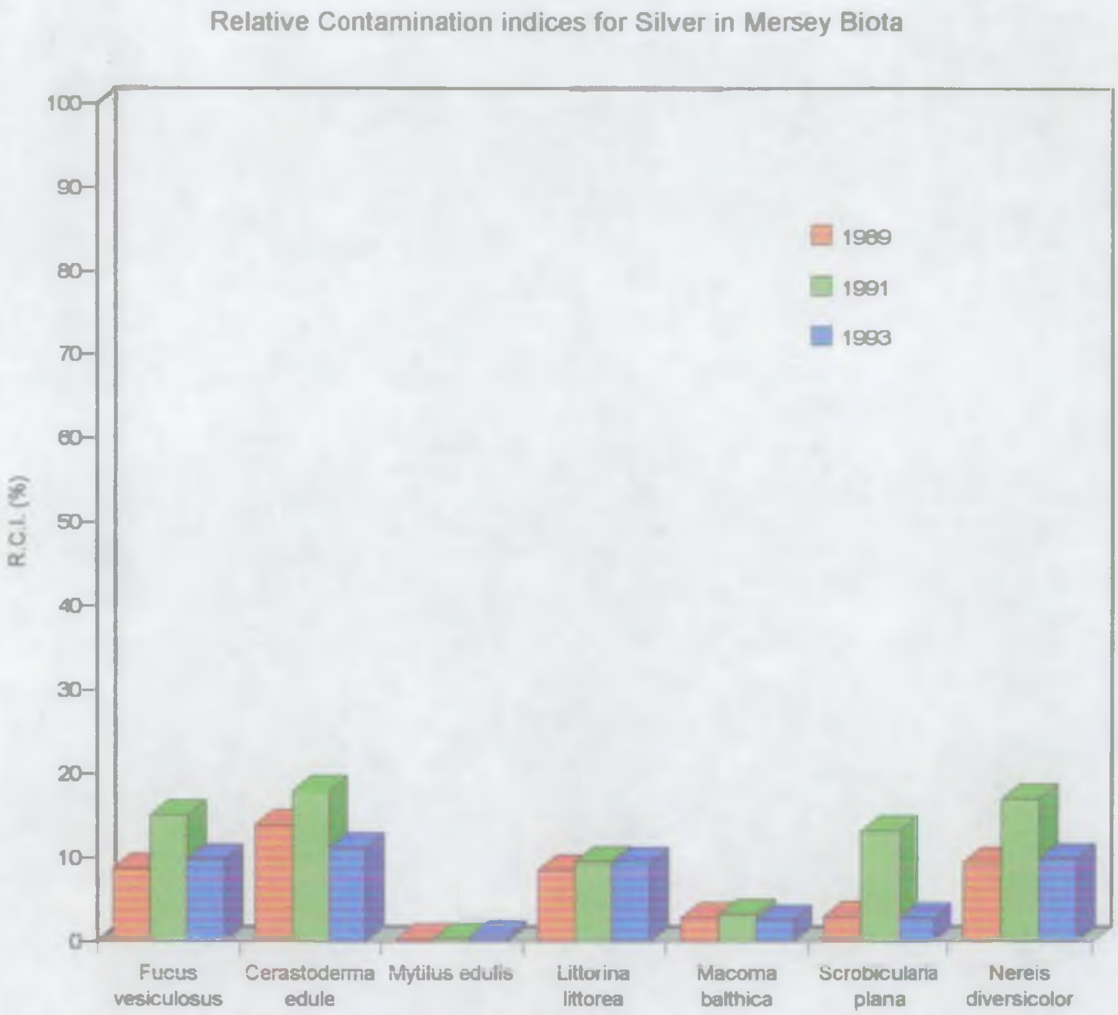
Table 2 Enrichment factors for silver in Mersey 1993 species relative to UK baseline data.

Species	Enrichment Factor*
Fucus vesiculosus	8.39
Cerastoderma edule	11.91
Mytilus edulis	9.08
Littorina littorea	10.70
Macoma balthica	6.11
Scrobicularia plana	14.50
Nereis diversicolor	17.71

* - Mean value for all sites.

Thus in general it can be seen that Mersey species, contain silver burdens which on average are some 10 times higher than UK baseline. However, when this is compared to the upper limits of levels encountered in the UK, all species collected from the Mersey contain less than 20% of the maximum recorded silver concentrations (Figure 5), which are usually associated with metal mining in parts of SW. England.

Figure 5



Relative Contamination indices for Silver in Mersey Biota
R.C.I. (%)
100
90
80
70
60
50
40
30
20
10
0
1989
1991
1993
Fucus vesiculosus
Cerastoderma edule
Mytilus edulis
Littorina littorea
Macoma balthica
Scrobicularia plana
Nereis diversicolor

Arsenic

Data for arsenic in 1993 samples are presented in Appendix 2.

Spatial Trends

The distribution profiles for arsenic in sediments are shown in Figure 6A. The profile for total arsenic is similar to that for many other metals, with peaks at Hale and Stanlow in the upper estuary, and lower concentrations at more seaward sites. The distribution of 1N-HCl-extractable arsenic is different however, with high levels occurring at Stanlow only.

The concentrations of arsenic in *Nereis diversicolor* vary by only a factor of 2 over the whole estuary and do not correlate with either total, or HCl-extractable arsenic in the sediments indicating that the range of bioavailable arsenic does not vary considerably (Figure 6B). The highest levels in this range occur at the mid-estuarine sites suggesting that small inputs may occur in this region. It should be noted however that bioavailability of arsenic can be modified considerably by the presence of competing elements such as sediment iron (Langston, 1980).

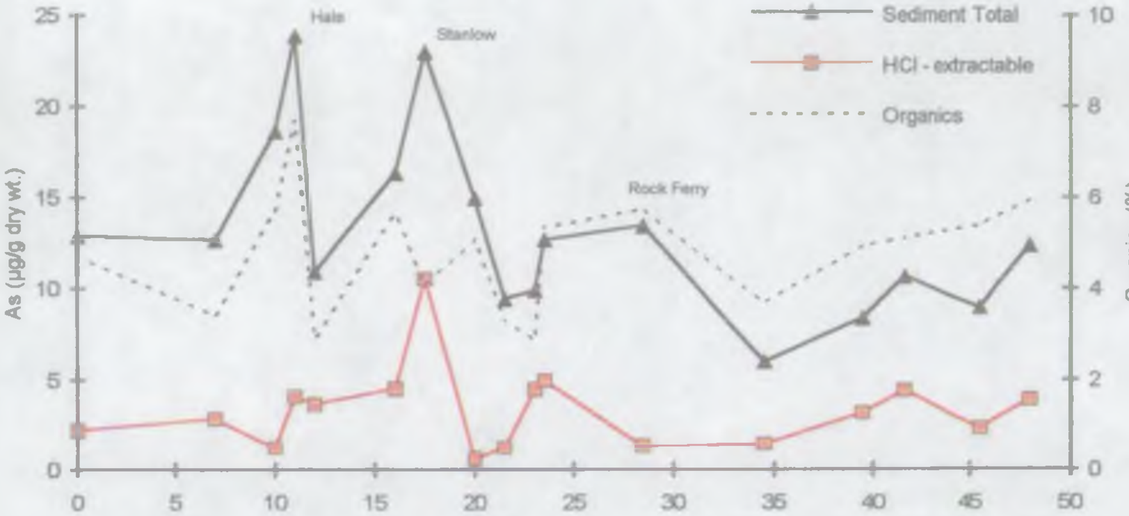
The deposit-feeding bivalves *Scrobicularia plana* and *Macoma balthica* (Figure 7A), together with the suspension feeders *Mya arenaria* and *Cerastoderma edule*, and the filter feeder *Mytilus edulis* (Figure 7B) exhibit some common spatial trends. These consist of a small increase between Garston and Eastham Lockgates (possibly a bank effect), followed by a downstream decline in tissue levels of arsenic. Additionally, whenever any of these species occurs at Blundellsands, a slight increase in concentration is apparent, which may relate to sewage-enhanced arsenic bioavailability at that location.

Temporal Trends

Figure 7C shows that there has been no significant change in total arsenic levels in sediments in recent years. The decline seen in the mid 1980's appears to have stopped at a 'steady-state' mean concentration of about 15 µg/g. The concentrations of arsenic in biota generally reflect this difference in sediment loadings between high levels of the early 1980's, and the lower levels found recently. However, for some species, significant increases in mean tissue arsenic levels have been measured between 1991 and 1993 (Student's t-test). These increases are shown in Table 3, and some examples (*Nereis, Mytilus and Fucus)* are illustrated in Figures 8A, 8B and 8C. The possibility that iron is acting as a modifier of arsenic bioavailability has been investigated, but does not explain these long term changes. Alternatively, phosphate is known to compete with arsenate for uptake in biota (see Langston *et al* 1993) such that reduced levels of phosphate in the estuary could contribute to the apparent increase in tissue arsenic burdens observed in some Mersey biota.

Figure 6. Spatial trends for Arsenic, 1993.

A. Arsenic in Sediments, 1993.



B. Arsenic in Nereis diversicolor, 1993.

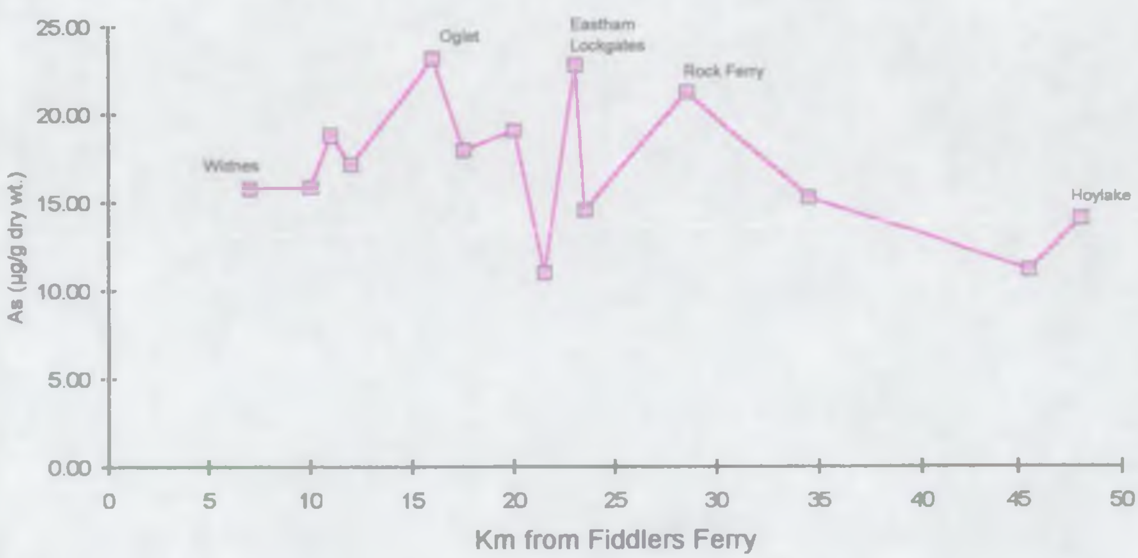
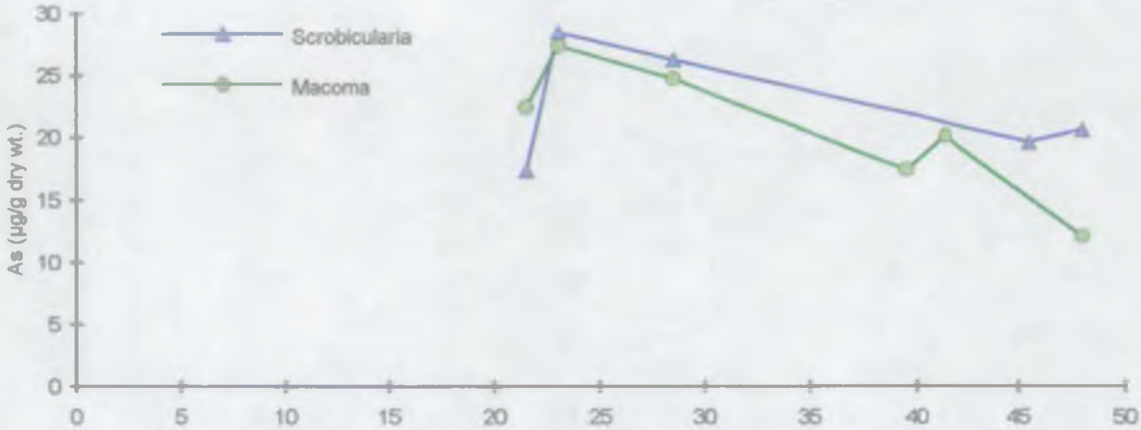
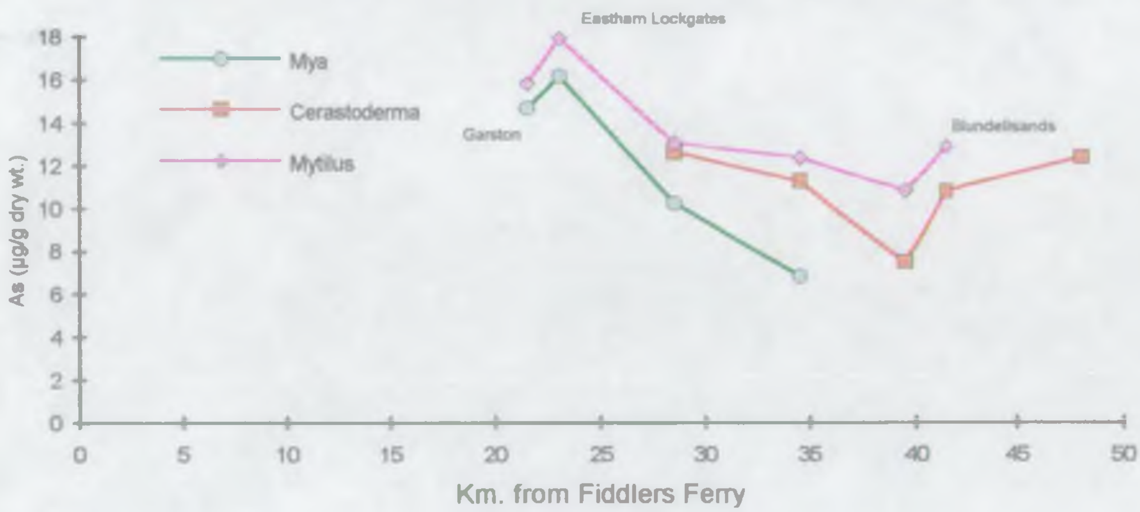


Figure 7. Spatial and Temporal trends for Arsenic.

A. Arsenic in Scrobicularia plana and Macoma balthica, 1993.



B. Arsenic in Mya arenaria, Cerastoderma edule & Mytilus edulis, 1993.



C. Arsenic in Sediments, 1980 - 1993.

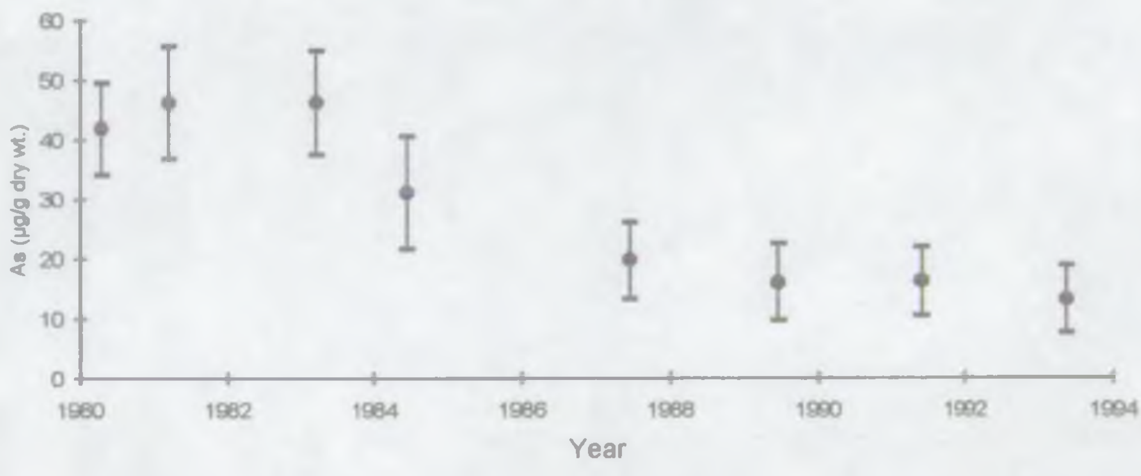
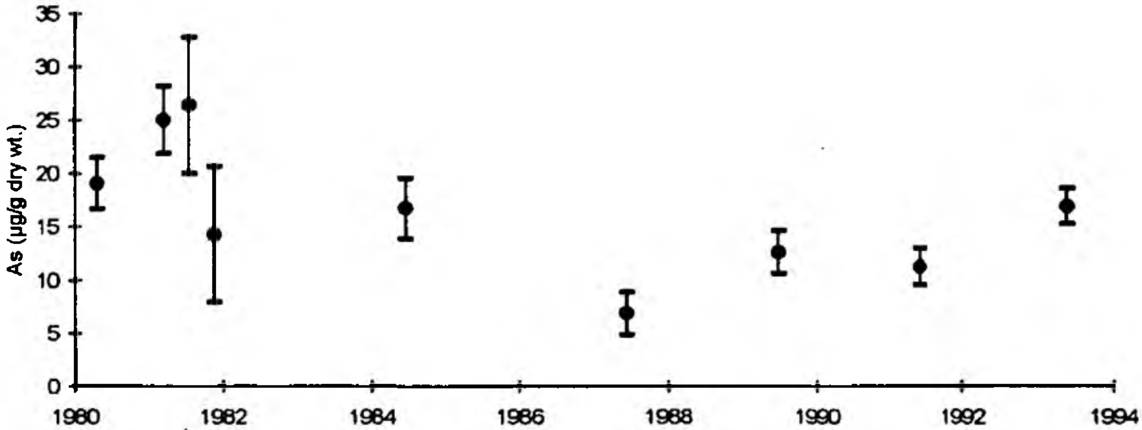
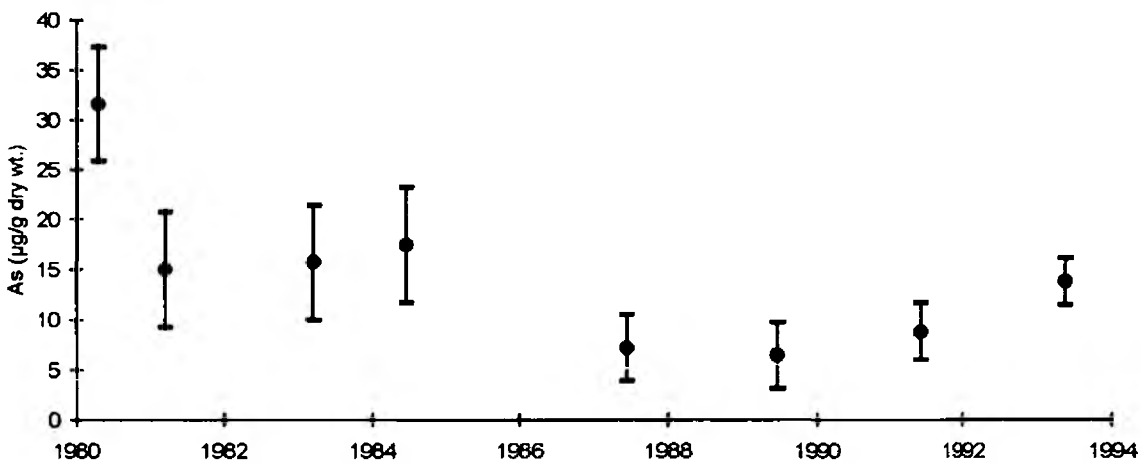


Figure 8. Temporal trends for Arsenic, 1980 - 1993.

A. Arsenic in Nereis diversicolor, 1980 - 1993.



B. Arsenic in Mytilus edulis, 1980 - 1993.



C. Arsenic in Fucus vesiculosus, 1980 - 1993.

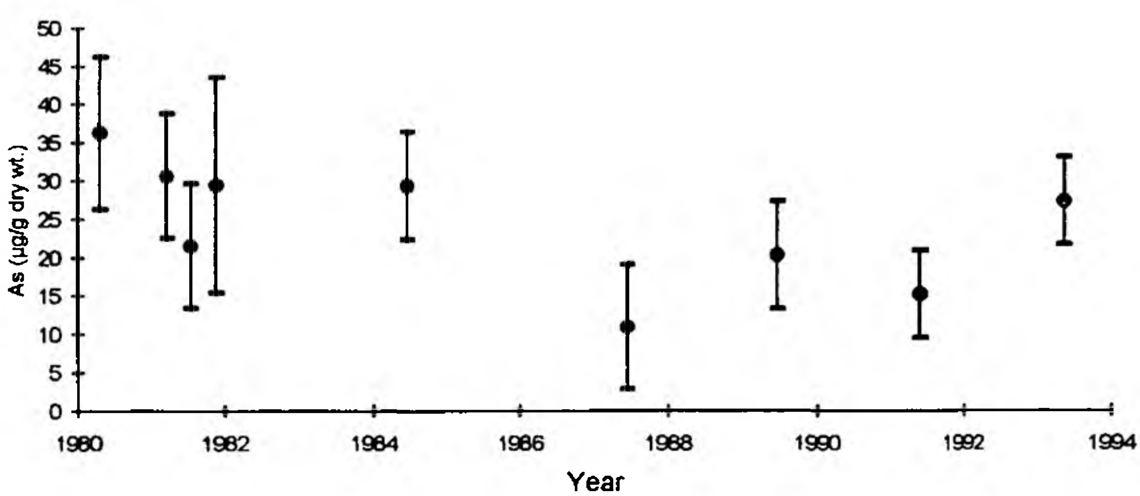


Figure 9.

Relative Contamination Indices for Arsenic in Mersey Biota.

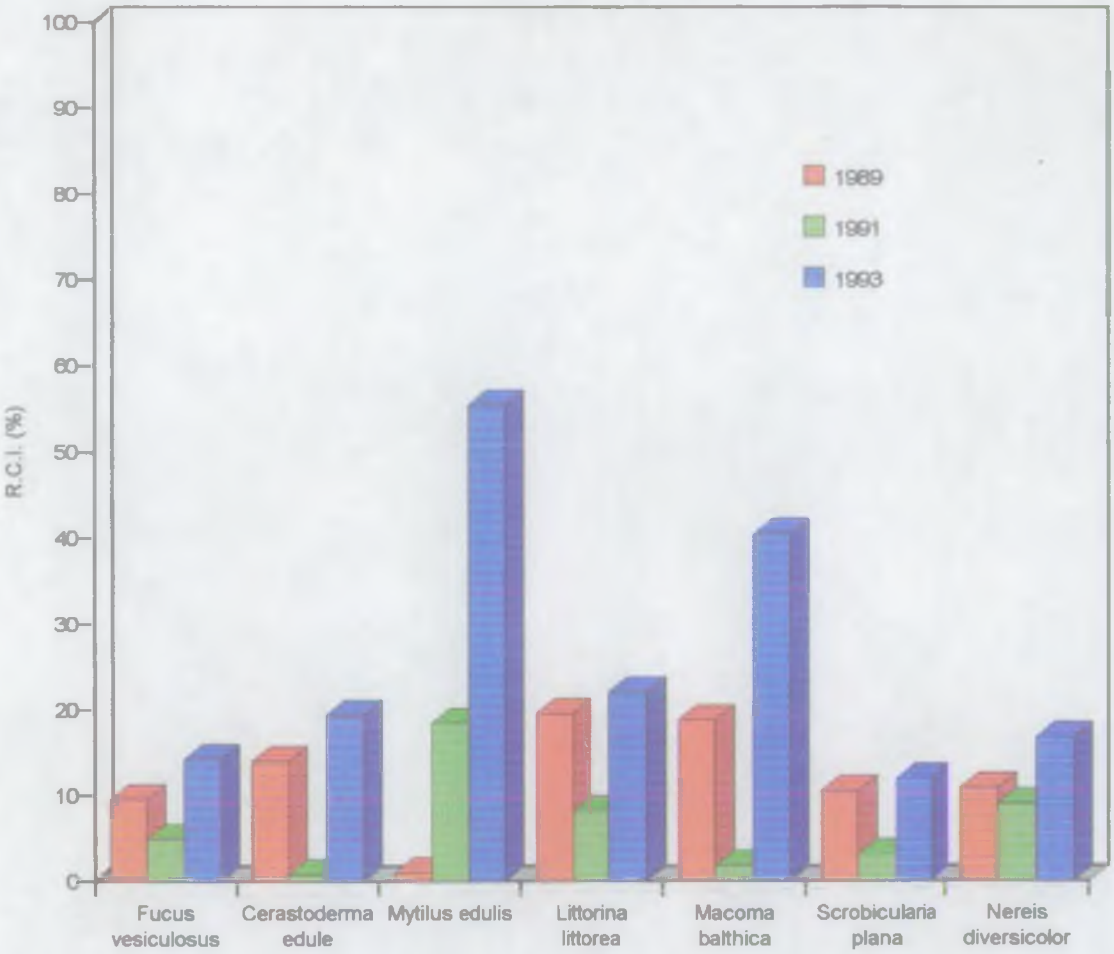


Table 3 Means, and significance level of differences between As levels in Mersey species over the period 1991 - 1993 (Student's t-test).

Species	As µg/g (1991)	As µg/g (1993)	Significance level
Nereis diversicolor	11.30	17.01	P<0.0001
Scrobicularia plana	12.20	22.52	P=0.017
Macoma balthica	9.42	20.72	P=0.001
Mytilus edulis	8.81	13.84	P=0.012
Cerastoderma edule	7.20	10.93	P=0.042
Fucus vesiculosus	15.25	27.47	P<0.0001

Comparisons with other estuaries

The results of the current survey (Appendix 2) show that there are no major species differences in arsenic concentrations among the indicator organisms collected. In addition Table 4 shows that enrichment factors for arsenic in Mersey biota are low with a maximum value of 3.68 (*Nereis diversicolor*). However, the range of arsenic concentrations encountered in many species throughout the UK i.e. the difference between the UK maximum and minimum, is in many instances quite small. Thus, as can be seen in Figure 9, some species such as *Mytilus edulis* and *Macoma balthica* contain arsenic levels which are in the middle range of UK concentrations. This is largely attributable to their absence from heavily polluted sites. Most other species generally show levels within the lower 20% of recorded values. Compared with mineralised estuaries in SW. England, arsenic contamination in the Mersey is relatively low but in some species, increasing.

Table 4 Enrichment factors for arsenic in Mersey 1993 species relative to UK baseline data.

Species	Enrichment Factor
Fucus vesiculosus	3.11
Cerastoderma edule	1.56
Mytilus edulis	2.20
Littorina littorea	2.13
Macoma balthica	2.33
Scrobicularia plana	2.64
Nereis diversicolor	3.68

Cadmium

Data for cadmium in 1993 samples are presented in Appendix 3.

Spatial Trends

The behaviour of cadmium in estuaries is often different to that of many other metals in that it is less readily adsorbed onto sediment particles. For many organisms, dissolved cadmium may therefore represent the major route for uptake.

Concentrations of total and HCl-extractable cadmium in Mersey sediments show a significant decrease downstream through the estuary ($r=-0.81$, $P<0.001$; $r=-0.79$, $P<0.001$ respectively). However, within this distribution there are features common to many other metals, principally the peaks at Hale and Stanlow (Figure 10A).

The pattern of cadmium accumulation in *Nereis diversicolor* is different to the sediment distribution, but in common with many previous surveys highest levels are in the middle section of the estuary at Oglet/Stanlow suggesting a source of bioavailable cadmium (on the south bank) in this region (Figure 10B). Cadmium levels in *Scrobicularia plana* and *Macoma balthica* follow slightly different trends from each other. Cadmium in *Scrobicularia plana* increases sharply between Garston and Eastham Lockgates (bank effect?) followed by a slight decline downstream (Figure 10C). In *Macoma balthica* the bank effect is less, and the decrease in concentrations seawards of Rock Ferry are more pronounced (Figure 11A). *Mya arenaria* and *Mytilus edulis* (Figure 11B) show patterns similar to *Scrobicularia plana* which may imply greater bioavailability of cadmium at Eastham Lockgates, or enhanced dissolved cadmium concentrations which may in turn be related to the proximity of the Manchester Ship Canal. Cadmium levels in *Fucus vesiculosus* exhibit a slight peak at Eastham Lockgates (Figure 11C) which appears to confirm an input of dissolved cadmium at this point. Unusually however, and in contrast to most other species (and earlier surveys) concentrations of cadmium in *Fucus vesiculosus* show a significant increase downstream ($r=0.86$, $P=0.026$).

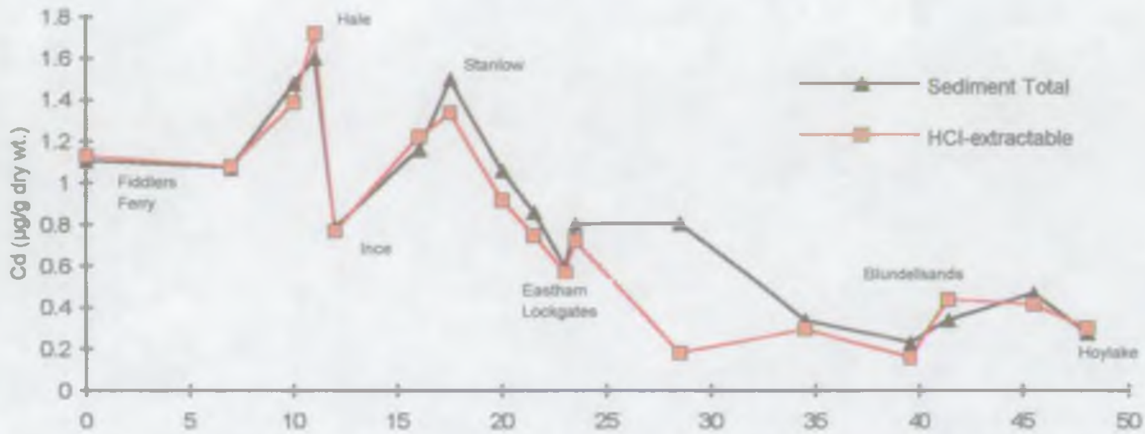
The signals regarding cadmium bioaccumulation along the Mersey estuary are therefore difficult to simplify, and although the position and magnitude of inputs may be important, the latter do not always explain spatial trends in biological contamination. In estuaries modifying factors include:

1. Salinity - increasing chloride-complexation at higher salinities reduces the bioavailability of cadmium by reducing the free ion (Cd^{2+}) concentration.
2. Acid Volatile Sulphides (AVS) - cadmium sulphide is very insoluble and cadmium bioavailability decreases with an increased AVS content in sediments (Di Toro, 1990).

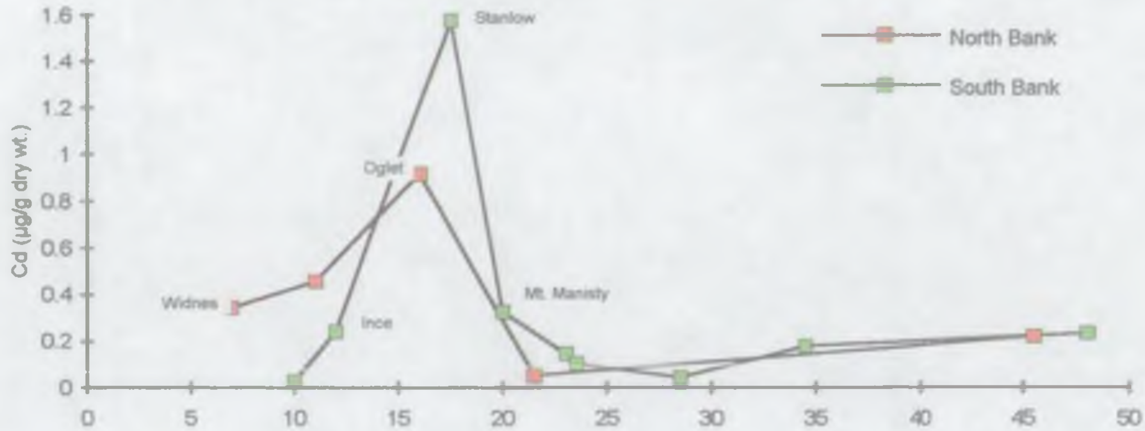
Faced with such variation it is not surprising therefore, that patterns of cadmium accumulation may differ between organisms of different type (i.e. infauna vs. surface dwellers). This illustrates why a multi-species approach is important for comprehensive impact assessment.

Figure 10. Spatial trends for Cadmium, 1993.

A. Cadmium in Sediments, 1993.



B. Cadmium in Nereis diversicolor, 1993.



C. Cadmium in Scrobicularia plana, 1993.

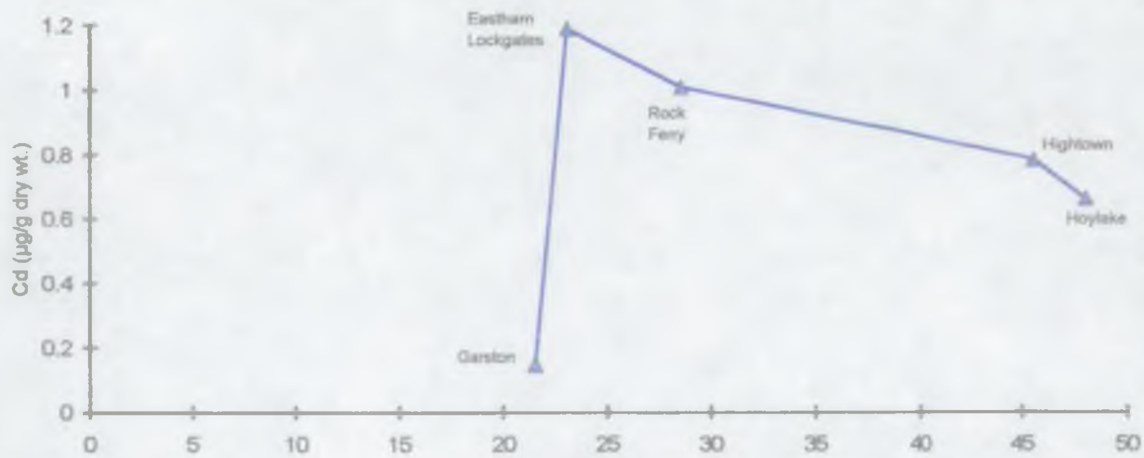
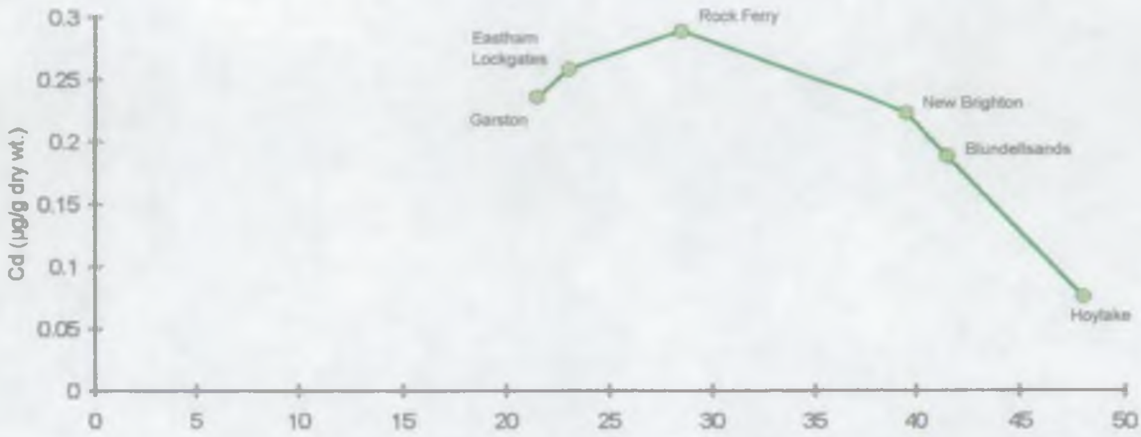
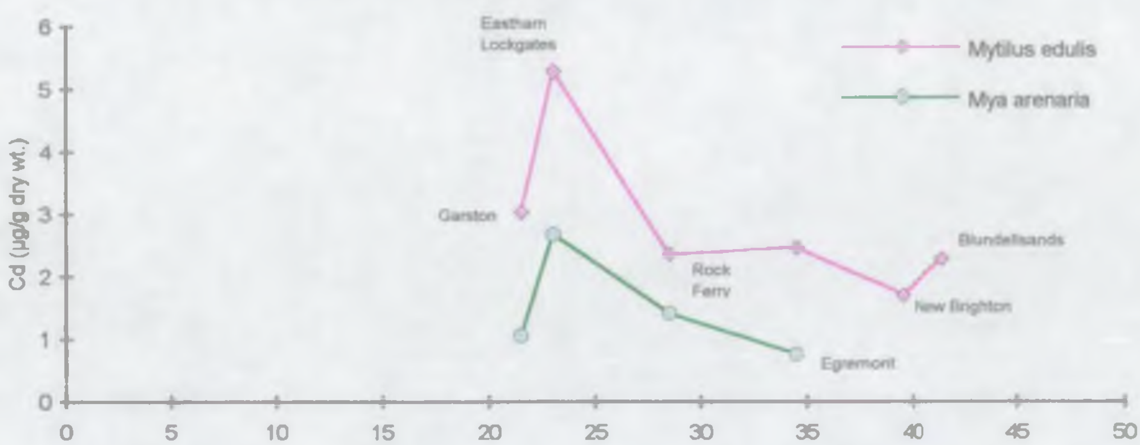


Figure 11. Spatial trends for Cadmium, 1993.

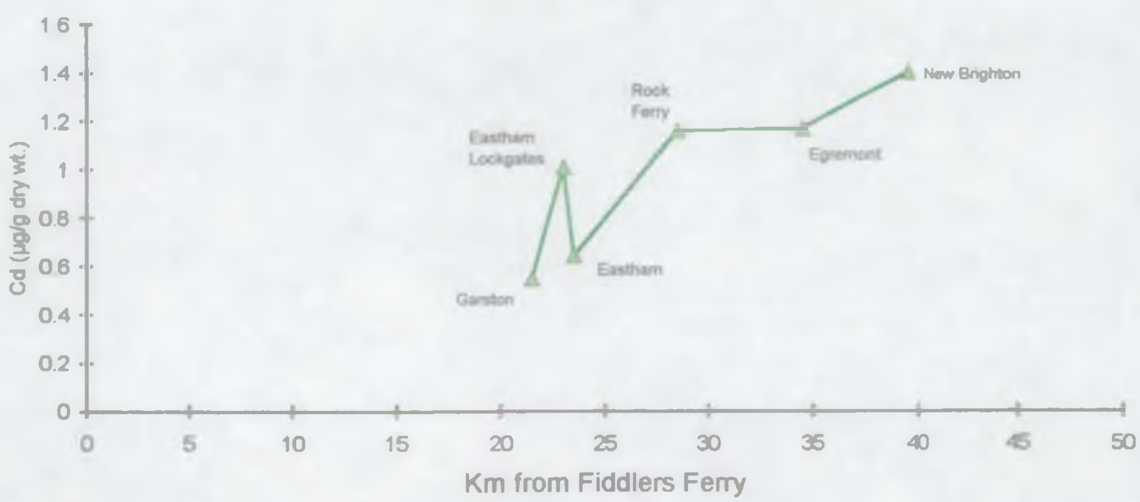
A. Cadmium in Macoma Balthica, 1993.



B. Cadmium in Mytilus edulis and Mya arenaria, 1993.



C. Cadmium in Fucus vesiculosus, 1993.



Temporal Trends

The range of mean cadmium concentrations recorded in Mersey sediments since 1980 varies over a small range of only 0.5 - 2.0 µg/g (Figure 12A). Sediment metal levels may sometimes change as a function of, for example, sediment grain-size, surface area, organic carbon content (and similar parameters which usually co-vary), without having to invoke changes in contaminant inputs. This is not the case with cadmium however, since trends in cadmium and organic content of sediment appears to be different. It seems likely that varying inputs, rather than granulometry, account for these temporal changes. Thus, a trend towards increasing levels of cadmium in sediments in the mid 1980's can be seen, followed by a decline since that period until 1991 when there was a significant increase in cadmium concentrations. The 1993 data shows that mean levels are similar to those of 1989, suggesting that inputs of cadmium may have occurred in the period 1989 - 1991, but have since reduced. A very similar pattern is also seen for HCl-extractable cadmium. Although sediments are not thought to be the major vector for uptake this trend is reflected by significant (Student's t-test) reductions in cadmium burdens of some species since 1991 as shown in Table 5.

Table 5 Means, and significance level of differences between Cd levels in Mersey species over the period 1991 - 1993 (Student's t-test).

Species	Cd µg/g (1991)	Cd µg/g(1993)	Significance level
Nereis diversicolor	1.01	0.35	$P = 0.012$
Macoma balthica	0.402	0.212	$P = 0.002$
Cerastoderma edule	2.365	0.470	$P < 0.0001$
Fucus vesiculosus	1.892	0.989	$P = 0.015$

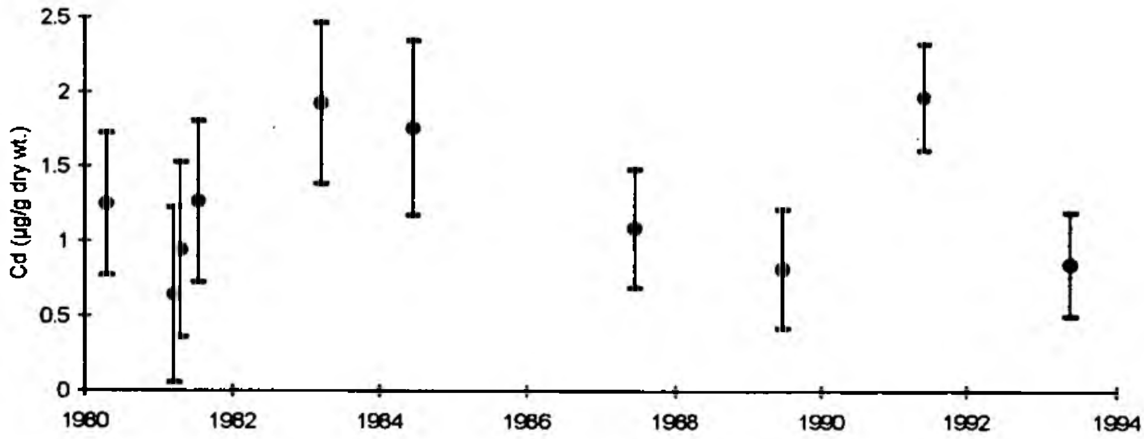
Figures 12B - 13A show the change of mean cadmium concentrations in some of these species since 1980, including the period 1991 - 1993. It must be noted that the 95% confidence intervals shown in these figures refer to ANOVA over the entire period and are therefore not the same as those for the 1991/1993 comparison (Student's t-test).

Comparisons with other estuaries

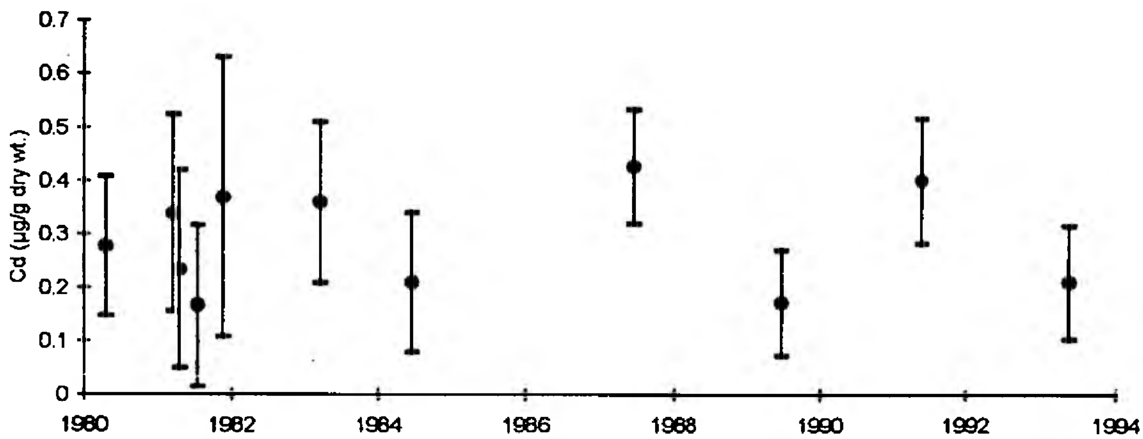
The data in Appendix 3 shows that cadmium concentrations in Mersey biota vary by a factor of 10 or more between, and sometimes within species. Comparisons with other estuaries should therefore consider such variability. Table 6 shows enrichment factors for cadmium in each species relative to UK baseline data.

Figure 12. Temporal trends for Cadmium, 1980 - 1993.

A. Total Cadmium in Sediments, 1980 - 1993.



B. Cadmium in Macoma balthica, 1980 - 1993.



C. Cadmium in Cerastoderma edule, 1980 - 1993.

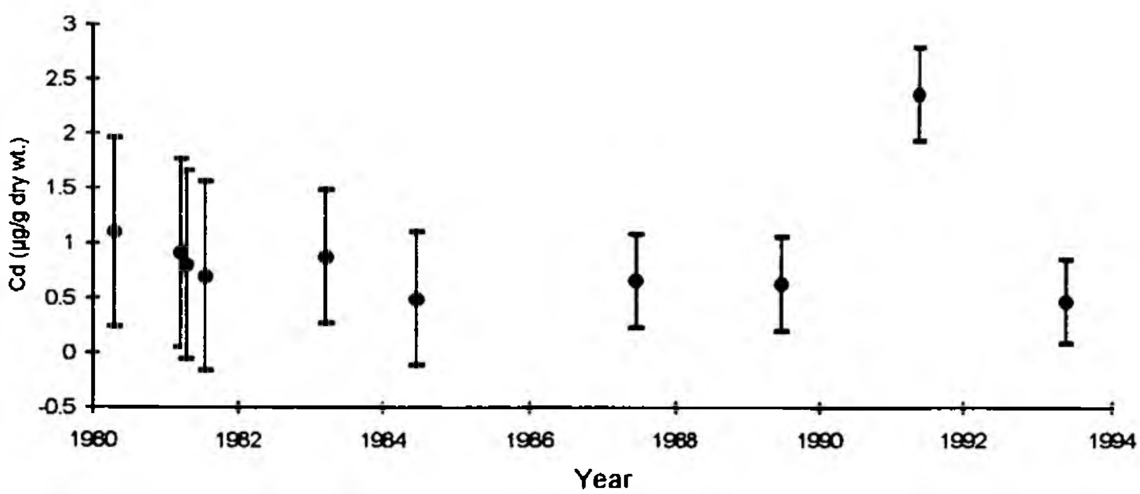
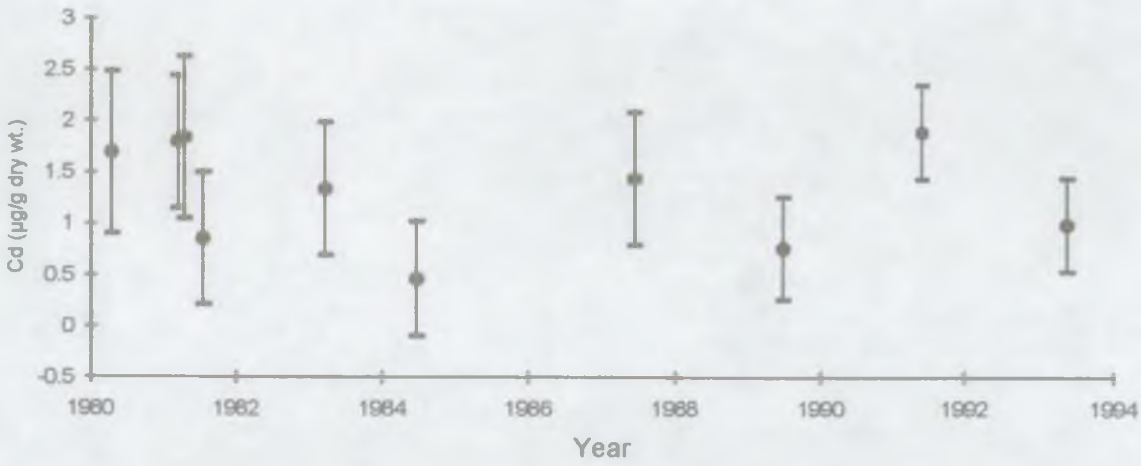


Figure 13

A. Cadmium in Fucus vesiculosus, 1980 - 1993.



B. Relative Contamination Indices for Cadmium in Mersey Biota

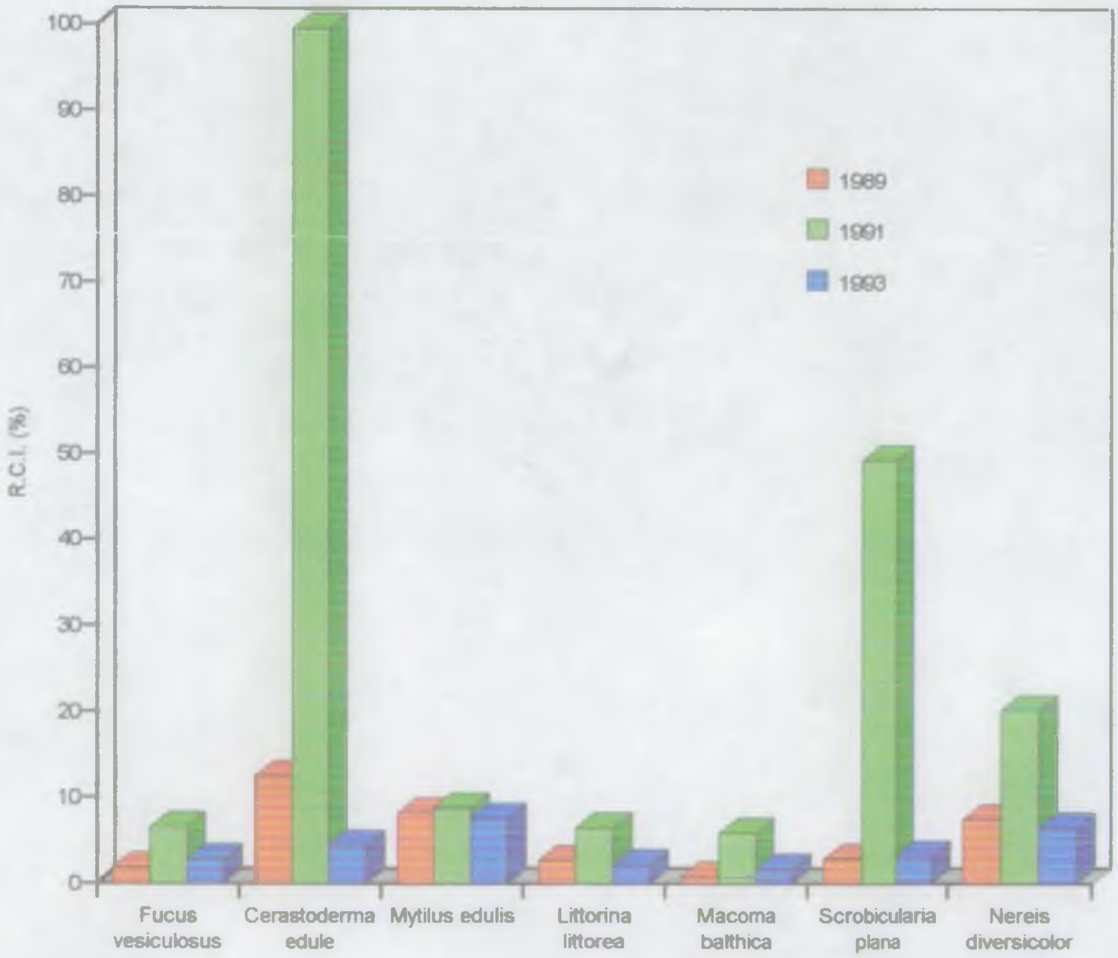


Table 6 Enrichment factors for cadmium in Mersey 1993 species relative to UK baseline data.

Species	Enrichment Factor*
Fucus vesiculosus	3.24
Cerastoderma edule	1.23
Mytilus edulis	3.22
Littorina littorea	2.19
Macoma balthica	1.58
Scrobicularia plana	3.28
Nereis diversicolor	10.88

* - Mean value for all sites.

It can be seen that for most species mean cadmium concentrations are currently (1993) close to UK minimum levels (Figure 13B) However, the lowest cadmium levels recorded this year for *Cerastoderma edule*, *Macoma balthica* , *Scrobicularia plana* and *Nereis diversicolor* all fall below the UK baseline as defined previously, while the highest levels in *Nereis diversicolor* are within a factor of 3.1 of the UK maximum, emphasising the point that within estuary variability must be taken into account when making comparisons of this type. For cadmium concentrations in Mersey biota, variability in space and time seems a particularly outstanding feature.

Chromium

Data for chromium in 1993 samples are presented in Appendix 4.

Spatial Trends

The profiles for the distribution of chromium in total, and HCl-extractable sediment fractions are almost identical in shape and are both significantly correlated with the profile for organic matter in the sediments ($P = 0.0019$ and 0.0088 respectively) as shown in Figure 14A. The bioavailability of chromium is thought to be highly dependent on its oxidation state, which in estuaries consists of the Cr (III) and Cr (VI) species. The trivalent form is rapidly scavenged by particulates and its bioavailability is low compared to the hexavalent form.

The profile for chromium in *Nereis diversicolor* (Figure 14B) is somewhat different to that of the sediments, and shows highest tissue levels at Hale and Rock Ferry, implying that bioavailability of chromium from the sediments is greater at these locations. The profiles for *Scrobicularia plana* and *Macoma balthica* however, do not show increased levels at Rock Ferry, but rather a gradual decline seawards from their upstream limits (Figure 14C). This pattern is also exhibited by *Cerastoderma edule* and *Mytilus edulis* (Figure 15A) which, additionally, like *Macoma balthica* (Figure 14C) show increased levels of chromium in their tissues at Blundellsands, possibly as the result of sewage associated uptake at this site. Concentrations of chromium in *Fucus vesiculosus* show a dramatic fall between Garston and the other downstream sites where it occurs (Figure 15B). Since contamination of the alga by adhering sediment was not evident at this site it would appear that this indicates higher levels of dissolved chromium upstream (in hexavalent form) notably at Garston on the northern shore of the estuary. The fact that this pattern seems to be reflected by most species suggests a predominantly dissolved route of uptake. The exception may be *Nereis diversicolor* which appears to be less permeable to chromium than other invertebrate species judging by the comparatively low concentrations present.

Temporal Trends

Analysis of variance (ANOVA) of data for all samples shows that there have been no significant changes since surveys began in 1980, except in the case of total sediment levels, where the trend for gradual reduction of chromium burdens was reversed in 1993, with a significantly higher ($P = 0.004$) mean level of 92.07 µg/g being recorded compared to 64.09 µg/g in 1991 (Figure 16A).

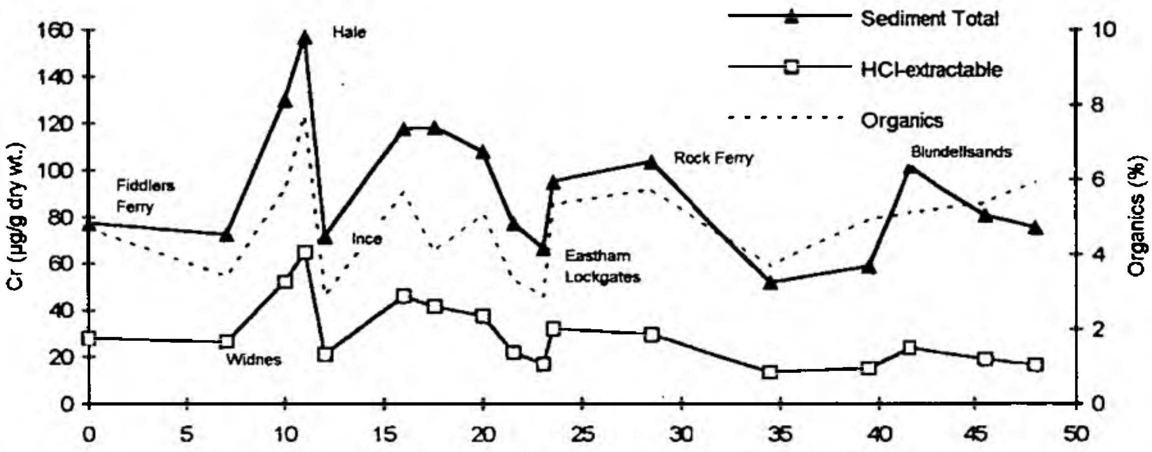
The increase of chromium in *Nereis diversicolor* noted in the last survey has been reversed, and overall there is no longer a significant temporal trend for chromium in *Nereis diversicolor*.

Comparisons with other estuaries

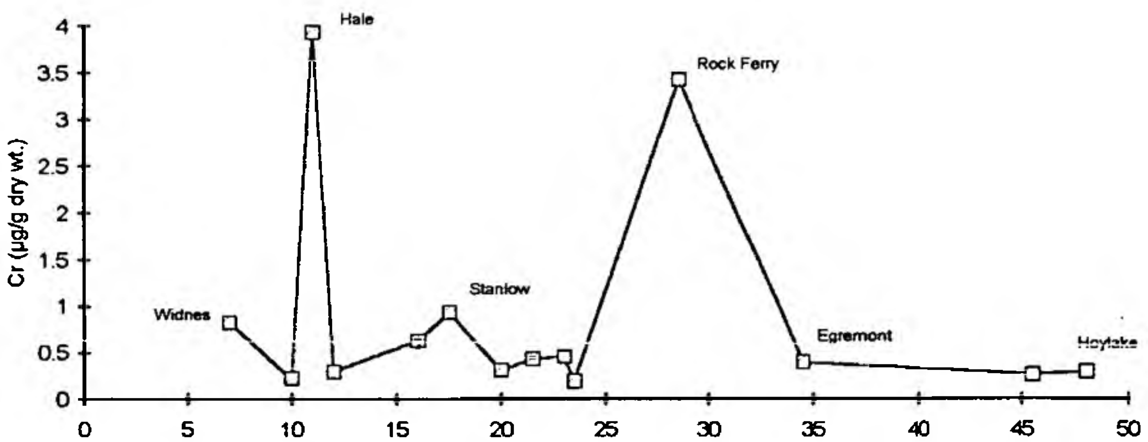
Chromium concentrations in Mersey biota show considerable variations between sites and between species, which, as already discussed, must be considered when making general

Figure 14. Spatial trends for Chromium, 1993.

A. Chromium in Sediment Extracts, 1993.



B. Chromium in Nereis diversicolor, 1993.



C. Chromium in Scrobicularia plana and Macoma balthica, 1993.

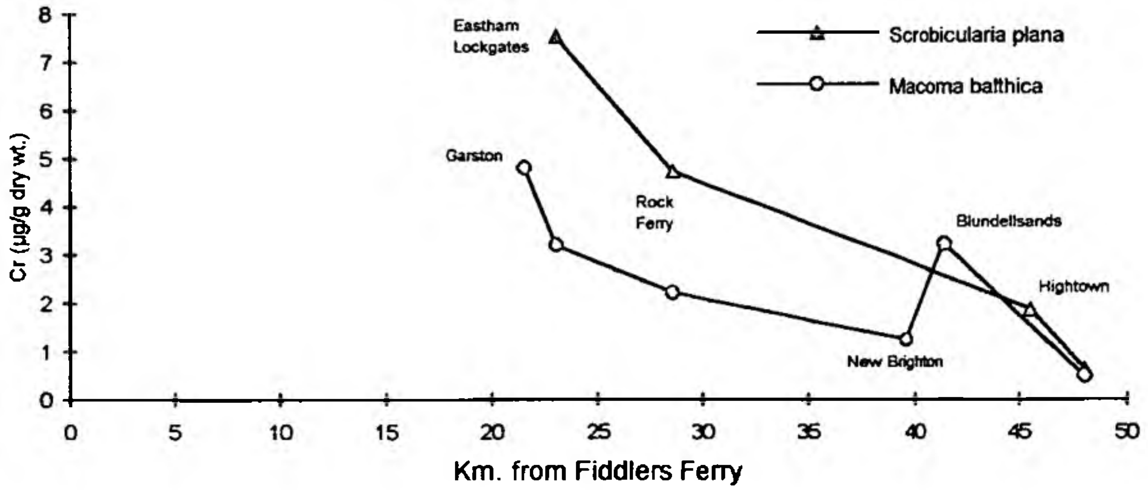
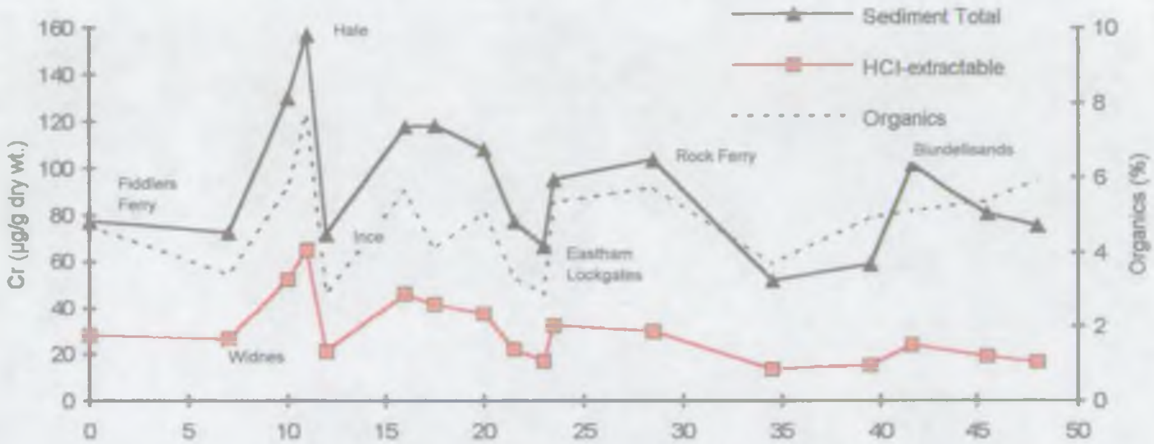
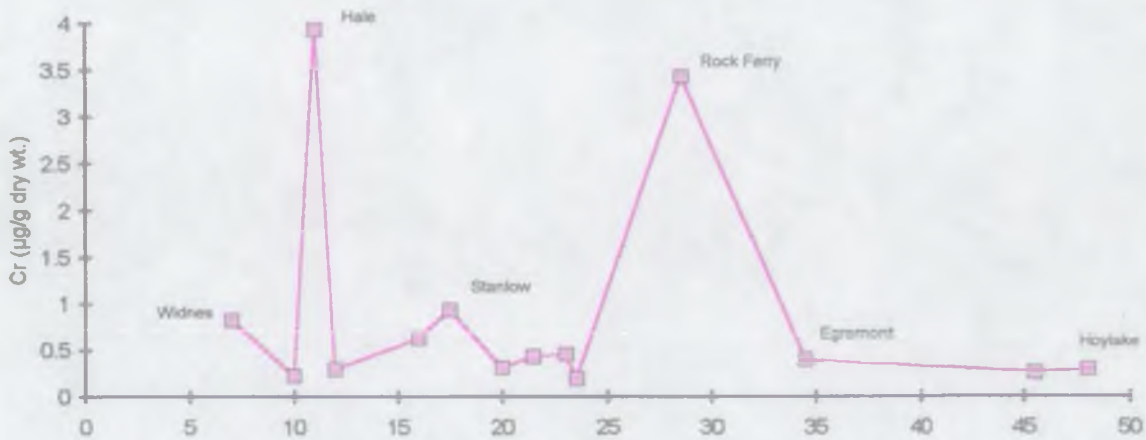


Figure 14. Spatial trends for Chromium, 1993.

A. Chromium in Sediment Extracts, 1993.



B. Chromium in Nereis diversicolor, 1993.



C. Chromium in Scrobicularia plana and Macoma balthica, 1993.

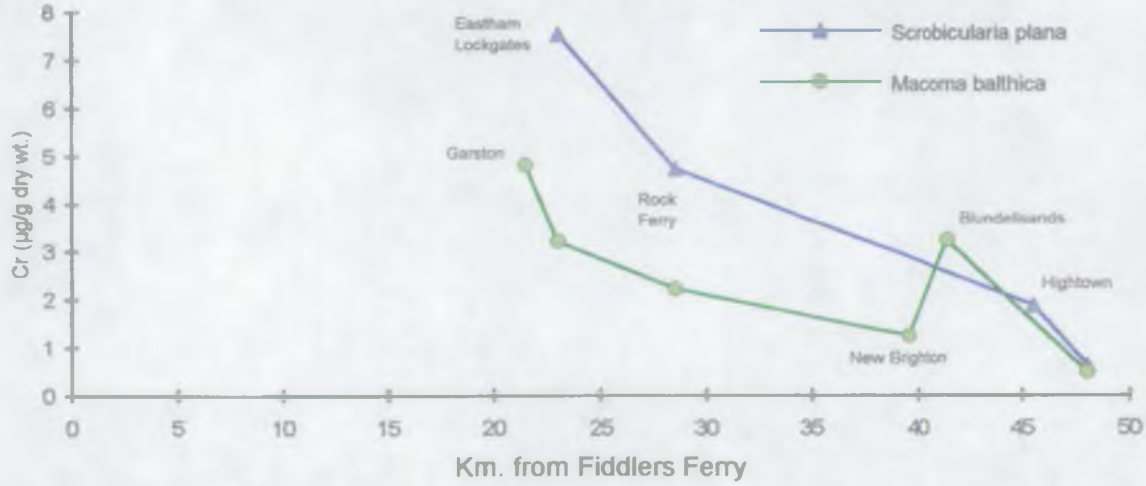
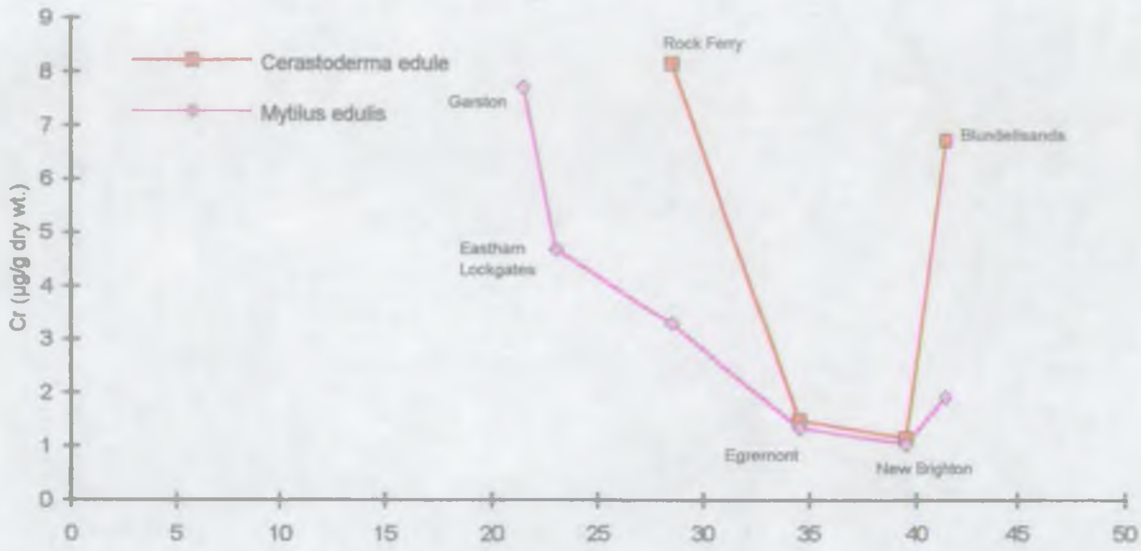
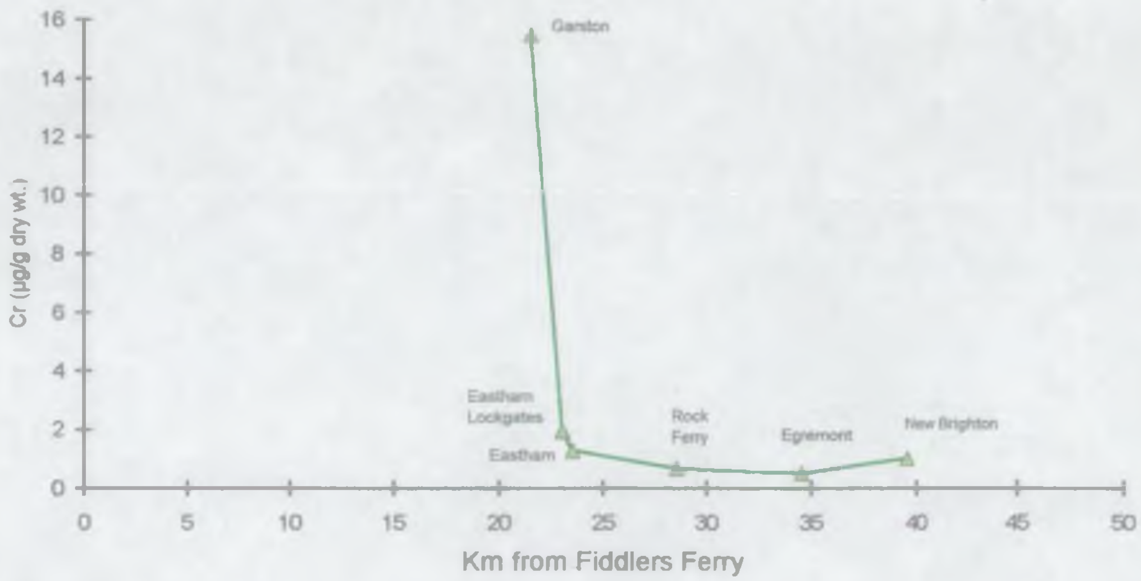


Figure 15. Spatial trends for Chromium, 1993.

A. Chromium in Cerastoderma edule and Mytilus edulis, 1993.



B. Chromium in Fucus vesiculosus, 1993.



comparisons between estuaries. Table 7 shows the enrichment factors for mean chromium levels in Mersey species in 1993.

Table 7 Enrichment factors for chromium in Mersey 1993 species relative to UK baseline data.

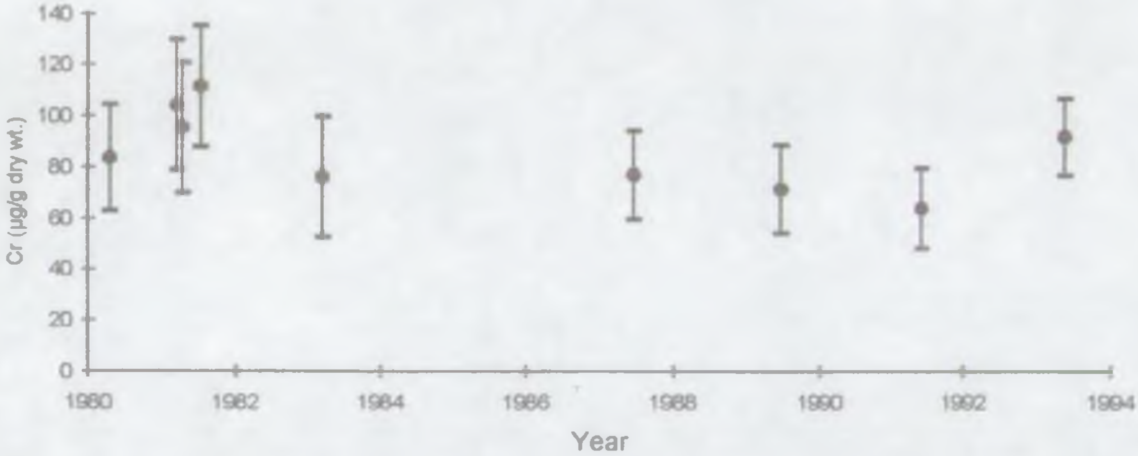
Species	Enrichment Factor*
Fucus vesiculosus	14.80
Cerastoderma edule	4.43
Mytilus edulis	4.89
Littorina littorea	15.43
Macoma balthica	4.03
Scrobicularia plana	6.78
Nereis diversicolor	28.16

* - Mean value for all sites.

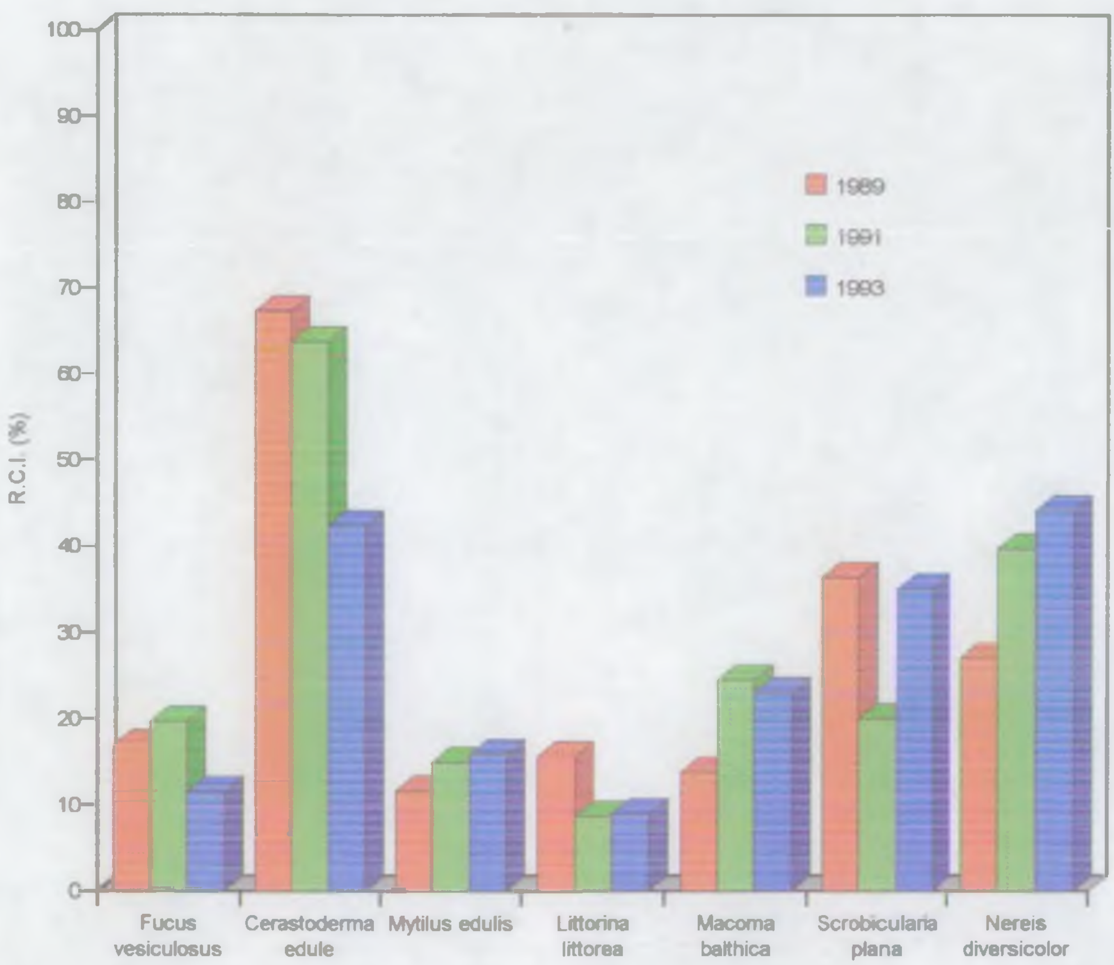
These results, together with the Relative Contamination Indices presented in Figure 16B, show that for several species in the Mersey (*Cerastoderma edule*, *Scrobicularia plana* and *Nereis diversicolor*) mean chromium levels are relatively high compared to new UK baseline data. In addition, data for 1993 (Appendix 4) shows that for *Fucus vesiculosus*, *Cerastoderma edule*, *Scrobicularia plana* and *Nereis diversicolor* the highest levels encountered (at the upper limits of occurrence in most cases) approach, or even exceed the UK maximum level as defined previously, emphasising once again the importance of considering within-estuary variability. At these more contaminated upstream sites, concentrations may exceed baseline values by up to 123 times for species such as *Nereis diversicolor*, confirming the chromium contamination status of the upper estuary.

Figure 16

A. Total Chromium in Mersey Sediments, 1980 - 1993.



B. Relative Contamination Indices for Chromium in Mersey Biota



Copper

Data for copper in 1993 samples are presented in Appendix 5.

Spatial Trends

The spatial distributions of copper in total sediment and HCl extracts are shown in Figure 17A. The correlation between these extracts is highly significant ($P = 0.0005$). Highest levels of copper are found at Hale and Stanlow, and generally decrease in the lower half of the estuary in a profile that is common for many metals in the current survey.

Tissue concentrations of copper in *Nereis diversicolor* are shown in Figure 17B together with those for sediment HCl extracts. The correlation between the two is significant ($r = 0.65$, $P = 0.013$) and is an example of how 1N-HCl extracts can in some instances provide an estimate of the bioavailable fraction of a metal in sediments. Highest levels in *Nereis diversicolor* are found at Hale and Stanlow in the upper estuary, and also at Hoylake towards the seaward end.

The profiles for copper in *Scrobicularia plana* and *Macoma balthica* (Figure 17C) differ from one another, and from the profile for *Nereis diversicolor*. Levels in *Macoma balthica* correlate significantly with total sediment levels in the lower part of the estuary ($r = 0.91$, $P = 0.011$) and reflect the gradual decrease seawards. *Scrobicularia plana* however, shows a marked increase in bioavailability of copper at Garston compared to *Macoma balthica*, which may be due to more anoxic, sulphide rich conditions found in the deeper layers of sediment where *Scrobicularia plana* occurs. The profile for copper in *Cerastoderma edule* shows a decline seawards as far as New Brighton, but an increase at Blundellsands (and Hoylake) is again apparent (Figure 18A). Spatial variations for *Mya arenaria* and *Fucus vesiculosus* show an increase between Garston and Eastham Lockgates, followed by a general decline downstream, (Figure 18B). This may indicate higher levels of dissolved copper in the vicinity of the lockgates, possibly derived from the Manchester Ship Canal.

Temporal Trends

Analysis of variance for sediment totals and HCl extracts for the whole estuary since 1980 show that although significant reductions in sediment copper levels have occurred over the last 12 years (total - $P = 0.0007$; HCl - $P < 0.0001$), there have been no significant changes since the last survey in 1991 or the previous one in 1989 (Figures 19A and 19B). A similar pattern is exhibited by some of the biota. For example, significant changes in copper burdens have occurred in *Nereis diversicolor* ($P < 0.0001$) and *Fucus vesiculosus* ($P < 0.0001$) since surveys began, but there has been no change since 1989/1991 (Figures 19C and 20A). There have been no significant changes with time for any of the other species collected.

Exceptions to these trends were the marked site-specific increases in copper (and other metals) in sediment-dwelling clams from Egremont, and to a lesser extent Rock Ferry reported in recent surveys (Langston *et al* 1992). In 1991, copper in clams at the former site were

Figure 17. Spatial trends for Copper, 1993.

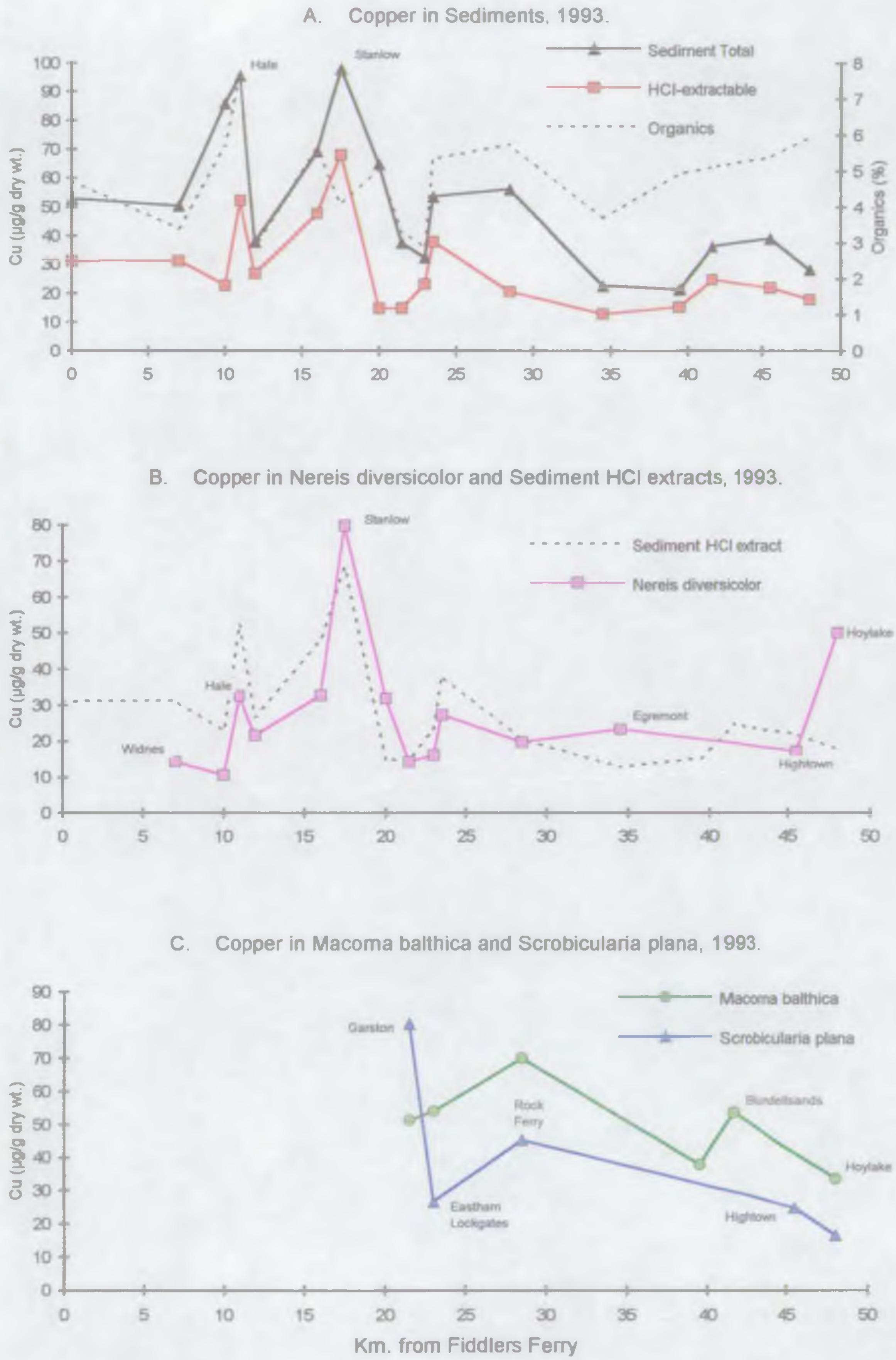
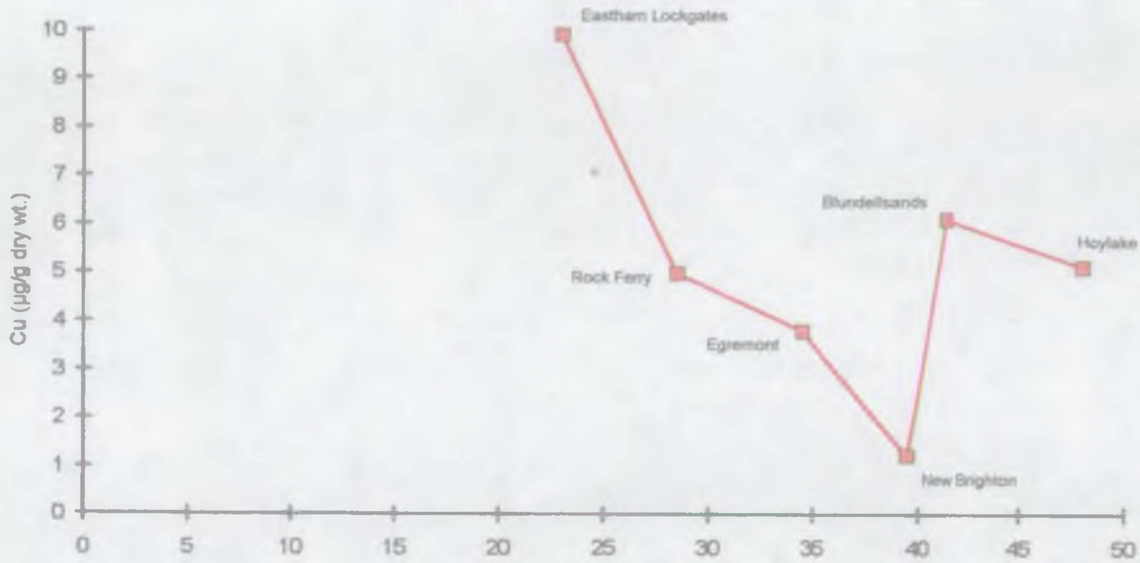


Figure 18. Spatial trends for Copper, 1993.

A. Copper in Cerastoderma edule, 1993.



B. Copper in Fucus vesiculosus and Mya arenaria, 1993.

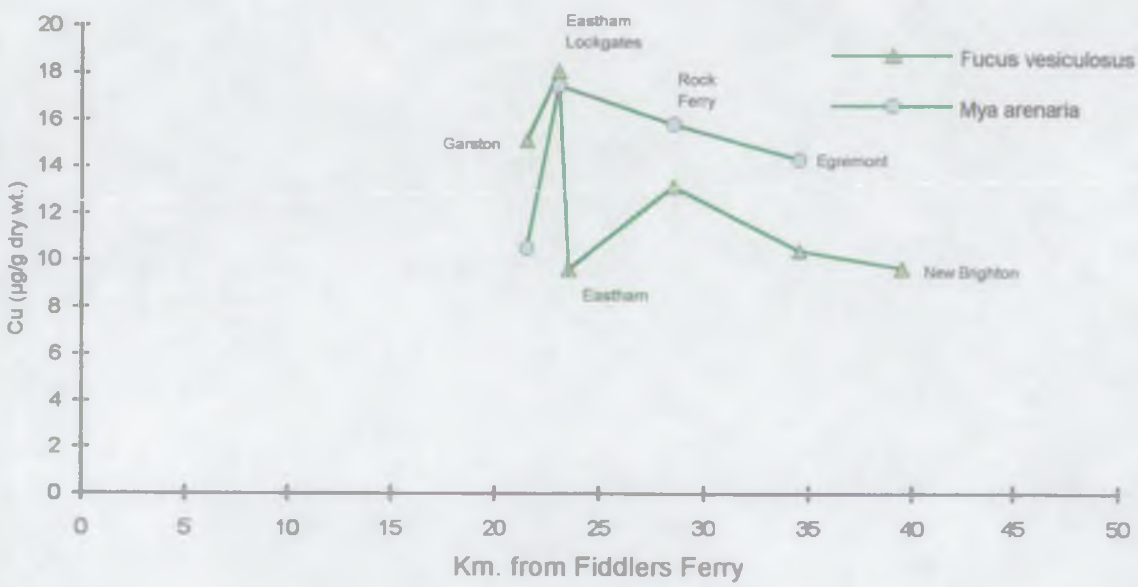
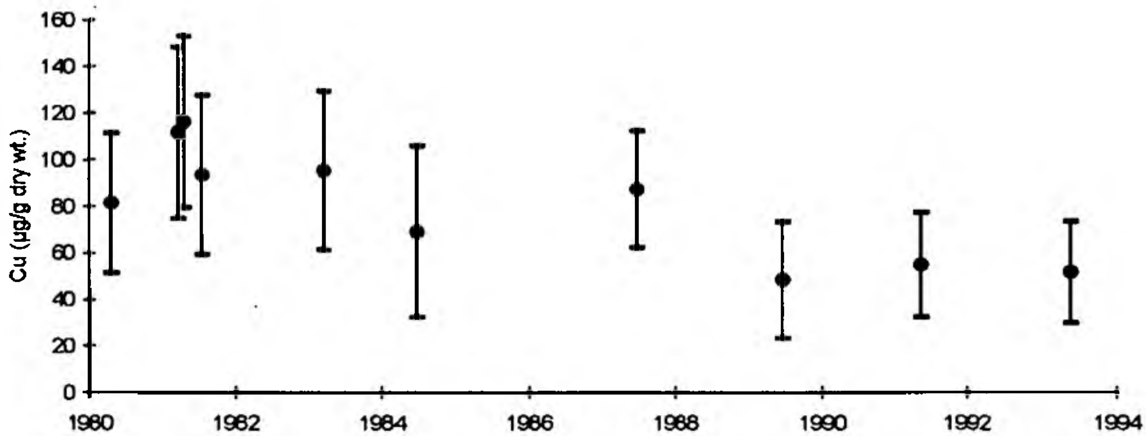
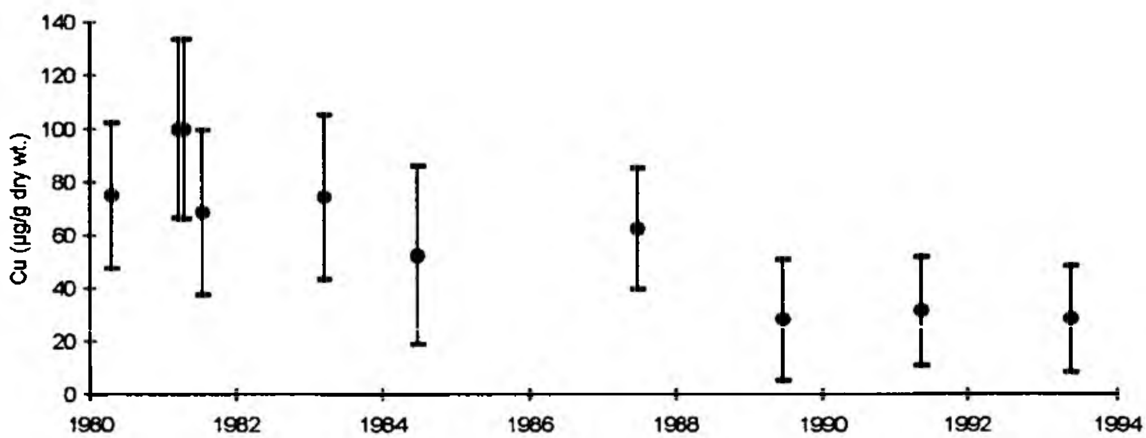


Figure 19. Temporal trends for Copper, 1980 - 1993.

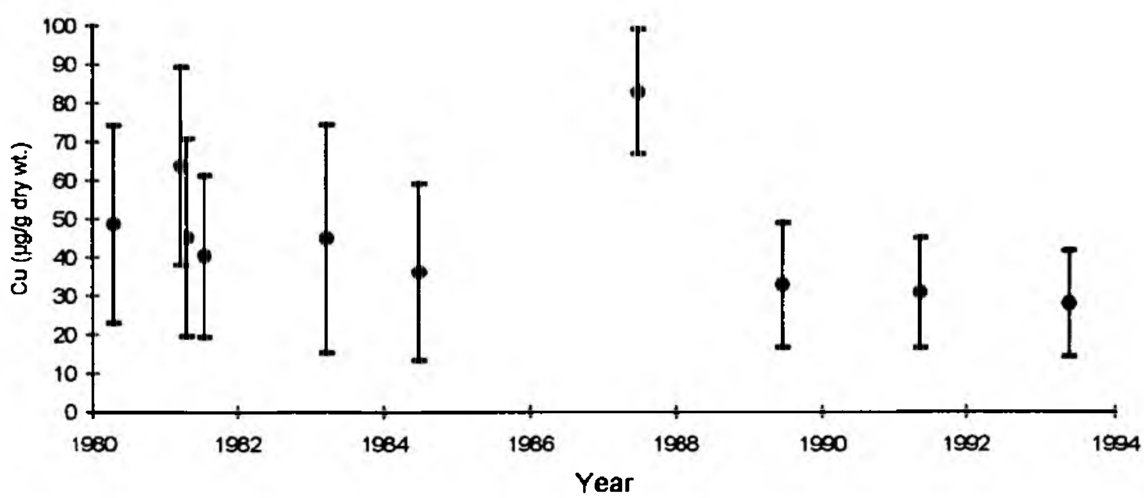
A. Total Copper in Sediments, 1980 - 1993.



B. 1N-HCl Extractable Copper in Sediments, 1980 - 1993



C. Copper in Nereis diversicolor, 1980 - 1993.



approaching similar levels to those found at the most copper-polluted sites in the UK. The elimination of clams from Egremont unfortunately denies us the chance of determining recent trends here and the situation should be studied closely in future surveys.

Comparisons with other estuaries

The results for copper in Mersey biota in 1993 presented in Appendix 5 show that, with some exceptions, variations in copper concentrations tend to be less than those seen for a number of other metals. As a result, general comparisons with other estuaries may be more valid than if greater variation occurred. Table 8 lists enrichment factors for each species relative to the new UK baseline data, and shows that, in general, copper levels in Mersey biota exceed baselines by less than a factor of 4. Furthermore the Relative Contamination Indices for copper (Figure 20B) show all species in 1993 contain average copper concentrations which are less than 20% of recorded maximum values. Nevertheless, at the more contaminated Mersey sites tissue burdens can exceed UK baselines by a factor of 10.

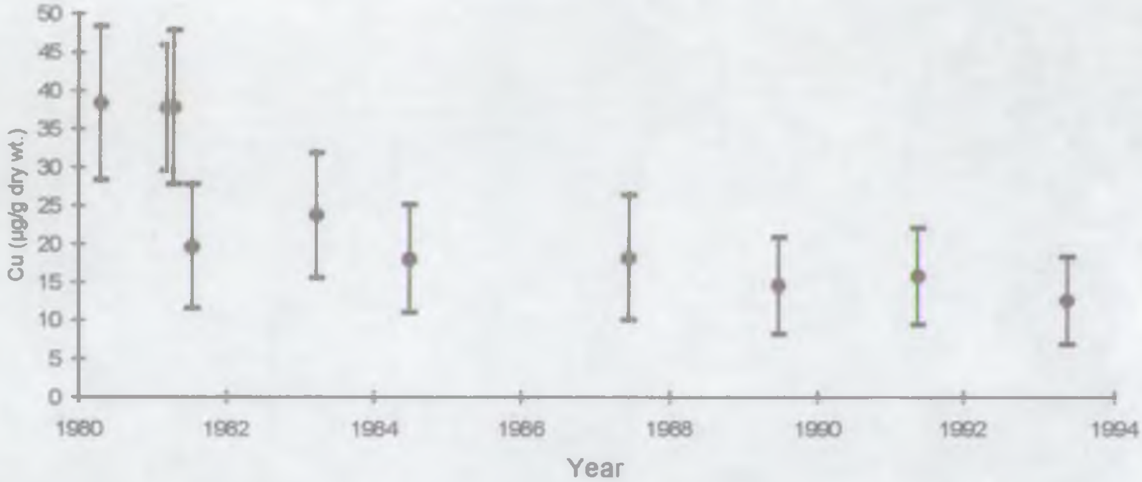
Table 8 Enrichment factors for copper in Mersey 1993 species relative to UK baseline data.

Species	Enrichment Factor*
Fucus vesiculosus	2.92
Cerastoderma edule	1.18
Mytilus edulis	1.51
Littorina littorea	2.94
Macoma balthica	2.26
Scrobicularia plana	3.36
Nereis diversicolor	2.86

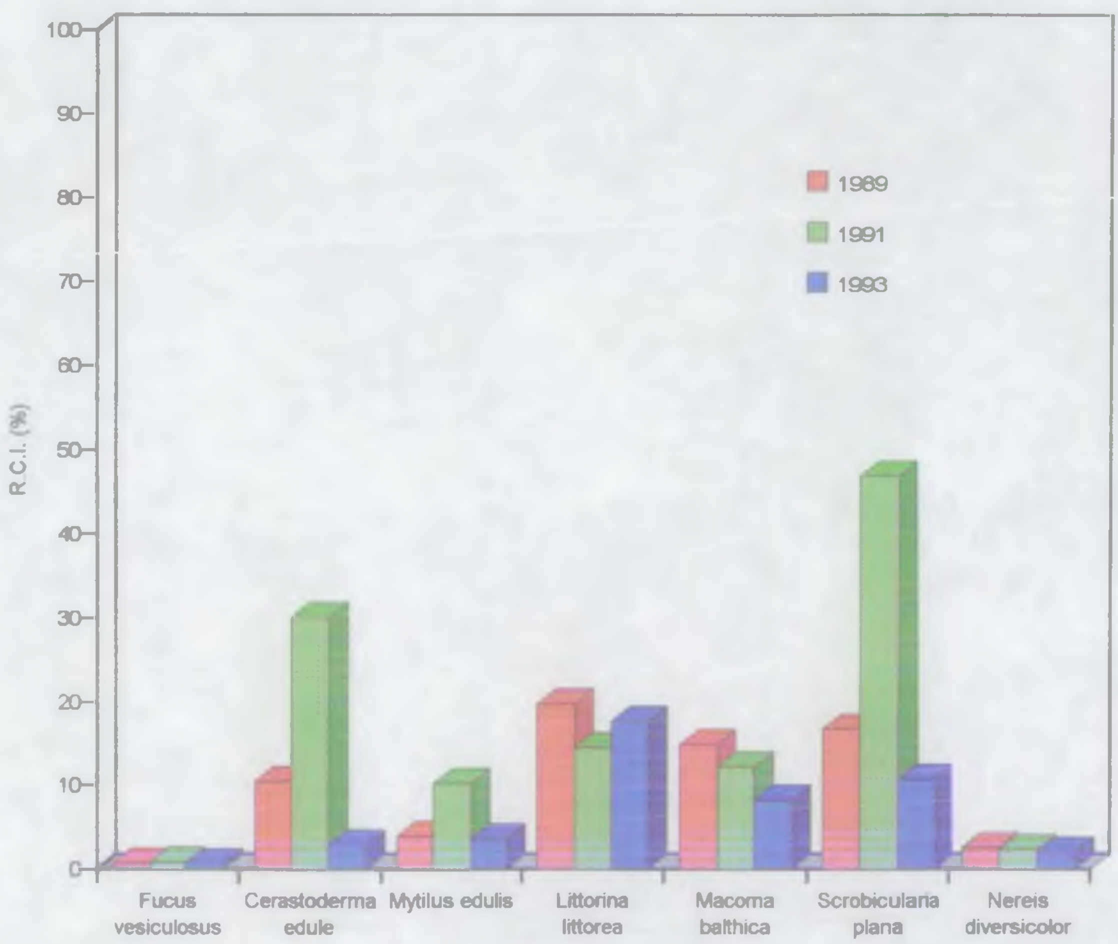
* - Mean value for all sites.

Figure 20

A. Copper in Fucus vesiculosus, 1980 - 1993.



B. Relative Contamination Indices for Copper in Mersey Biota



Iron

Data for iron in 1993 samples are presented in Appendix 6.

Spatial Trends

The spatial profile of iron concentrations in sediment samples (total and HCl-extractable) follow the pattern common to many other metals and are significantly correlated with the organic content of the sediment as shown in Figure 21A (Total: $r = 0.68$, $P = 0.0028$; HCl: $r = 0.78$, $P = 0.0002$). Iron is an essential element for most organisms and is an important component of enzyme systems and respiratory pigments such as haemoglobin. Accumulation is therefore regulated in many instances, and tissue concentrations may not be proportional to environmental levels. Consequently the degree of iron contamination may be underestimated, and clear spatial trends lacking. These factors are demonstrated to some extent in the iron profile for *Nereis diversicolor* where variation is slight, when compared with the sediment profiles, and concentrations are generally much lower in worms than in the surrounding sediment. There are however, considerably elevated tissue levels at Hale and Rock Ferry suggesting that availability may be higher at these locations (Figure 21B), as has been suggested for other elements, and that regulatory mechanisms may be unable to cope with these high levels.

The profile for iron in *Fucus vesiculosus* (Figure 21C) reveals that concentrations increase sharply upstream above Eastham as in previous years, probably indicating relatively higher levels of dissolved iron at these less saline upstream sites. *Littorina littorea* as with *Nereis diversicolor* tends to regulate iron uptake, though tissue concentrations measured in 1993 vary from 250 - 450 µg/g with a trend for decreasing concentrations downstream (Figure 22A). To a limited extent this trend is also exhibited by *Mytilus edulis* and *Scrobicularia plana* (Figure 22B). Once again, and similar to the 1991 survey, the profiles for iron in *Macoma balthica* and *Cerastoderma edule* (Figure 22C) are dominated by very high concentrations at Blundellsands. Since sediment iron levels were not particularly high at that location it seems likely that iron availability may have been enhanced by other environmental factors, possibly the high levels of sewage prevalent in that area.

Temporal Trends

Concentrations of iron in Mersey sediments have varied since surveys began in 1980 to a small degree, (Figure 23A). However, considering the estuary as a whole, trends have not been significant and concentrations have changed little since the last survey in 1991. In view of the regulation of iron by most species it is perhaps not surprising that long-term changes are not apparent in many cases. Some such as *Macoma balthica* and *Littorina littorea* have shown small but significant (*Macoma*, $P = 0.027$; *Littorina*, $P = 0.0012$) changes since the early 1980's when values were somewhat higher, but in recent years (Figures 23B and 23C) mean levels over the whole estuary appear to be in a more or less steady state.

Figure 21. Spatial trends for Iron, 1993.

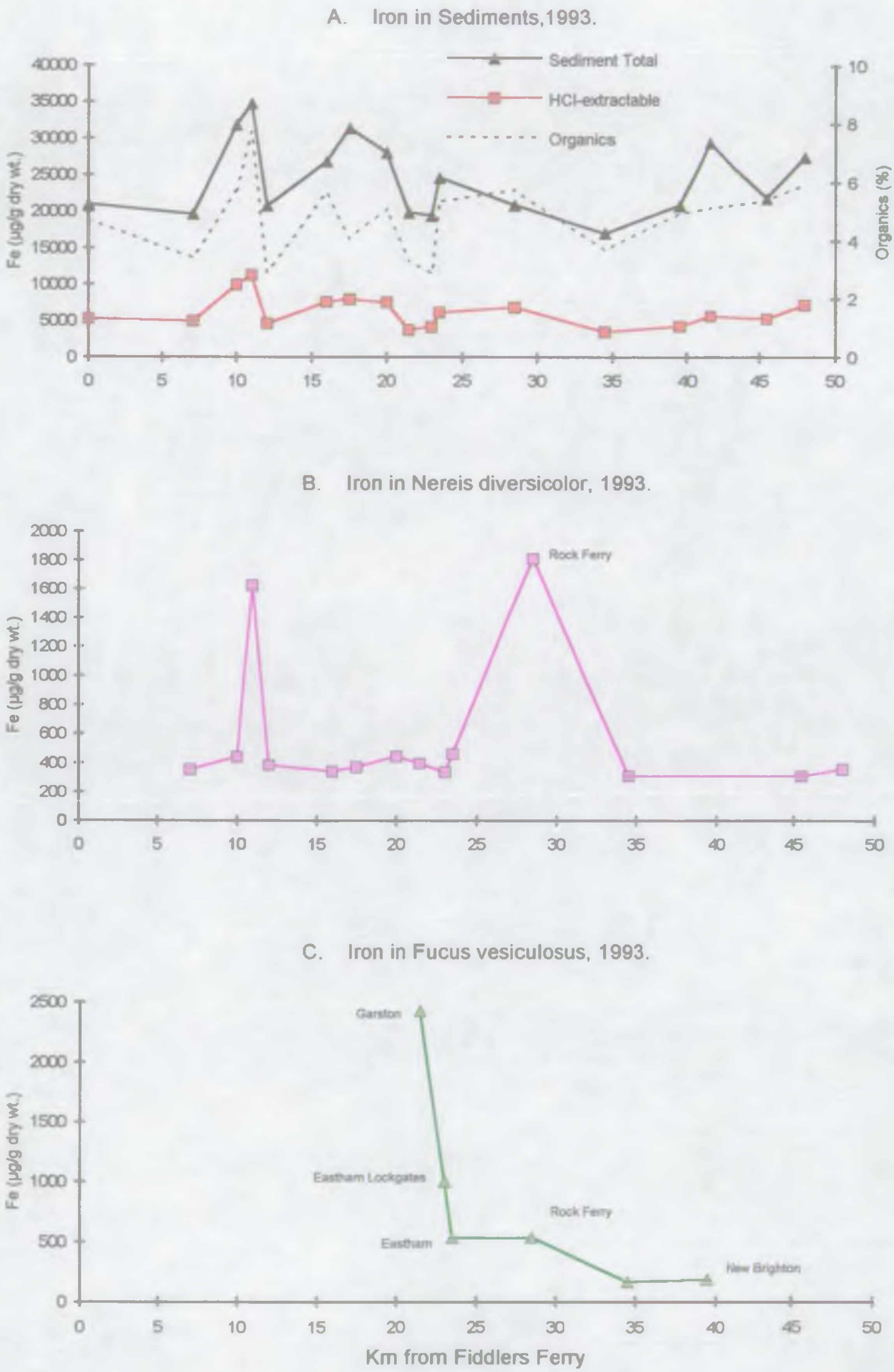
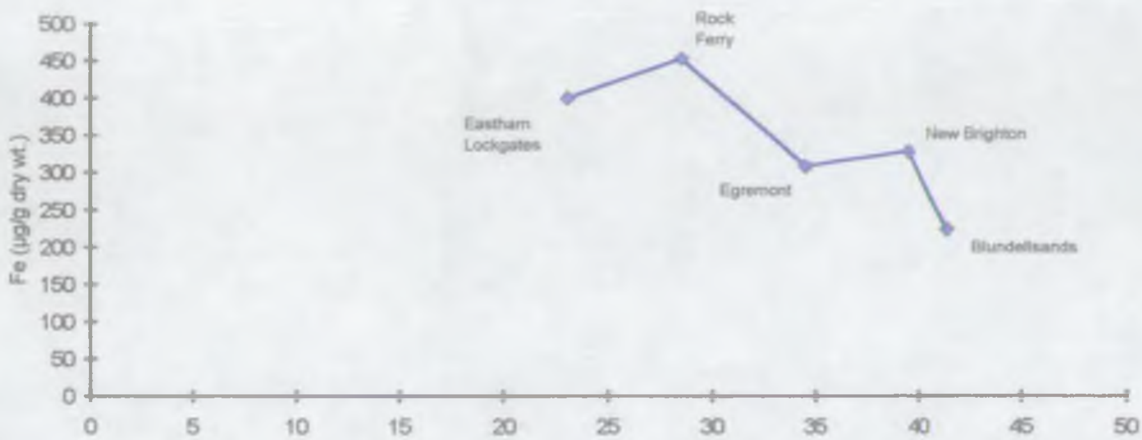
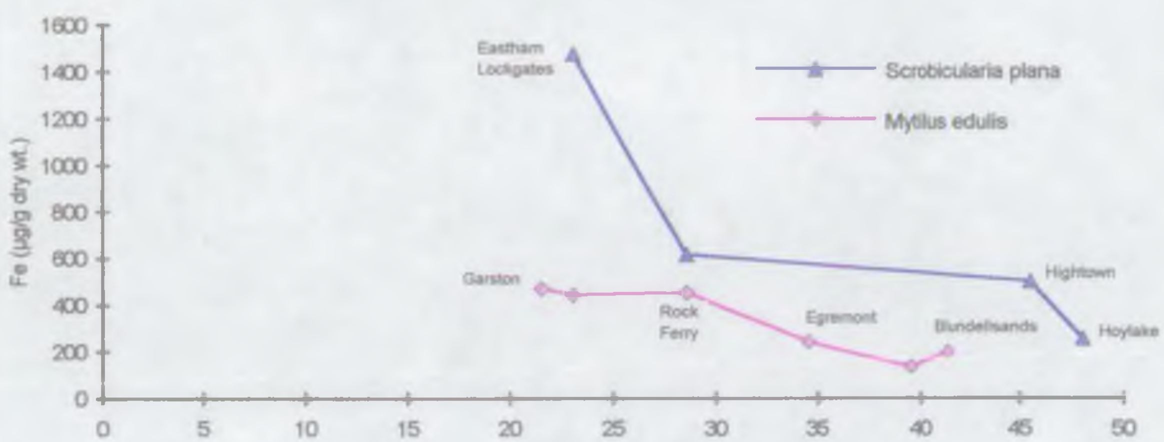


Figure 22. Spatial trends for Iron, 1993.

A. Iron in Littorina littorea, 1993.



B. Iron in Scrobicularia plana and Mytilus edulis,1993.



C. Iron in Cerastoderma edule and Macoma balthica, 1993.

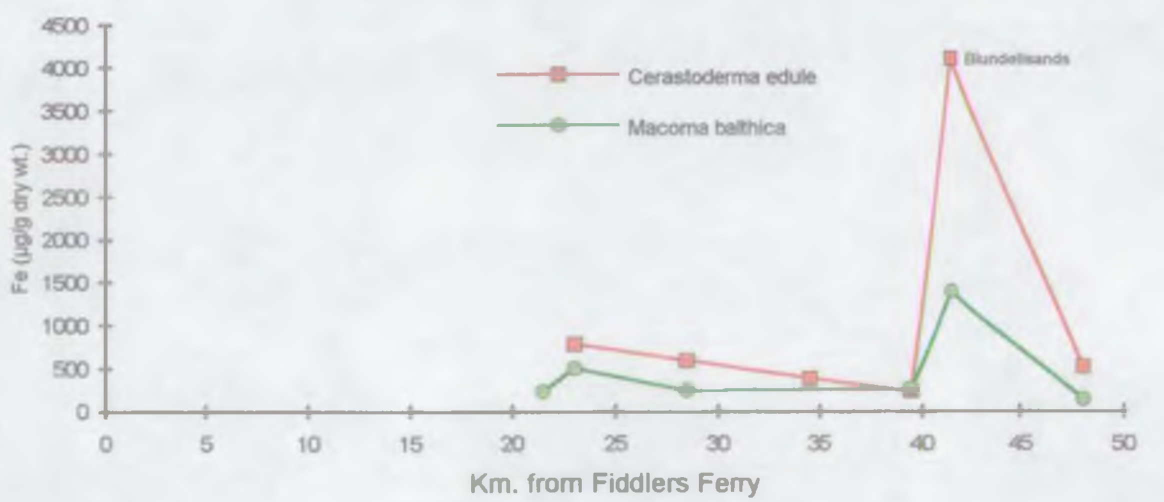
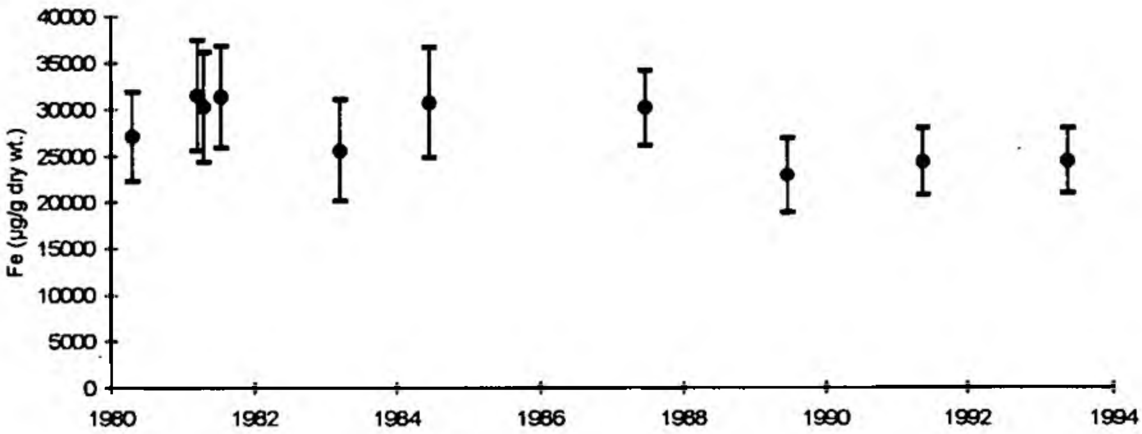
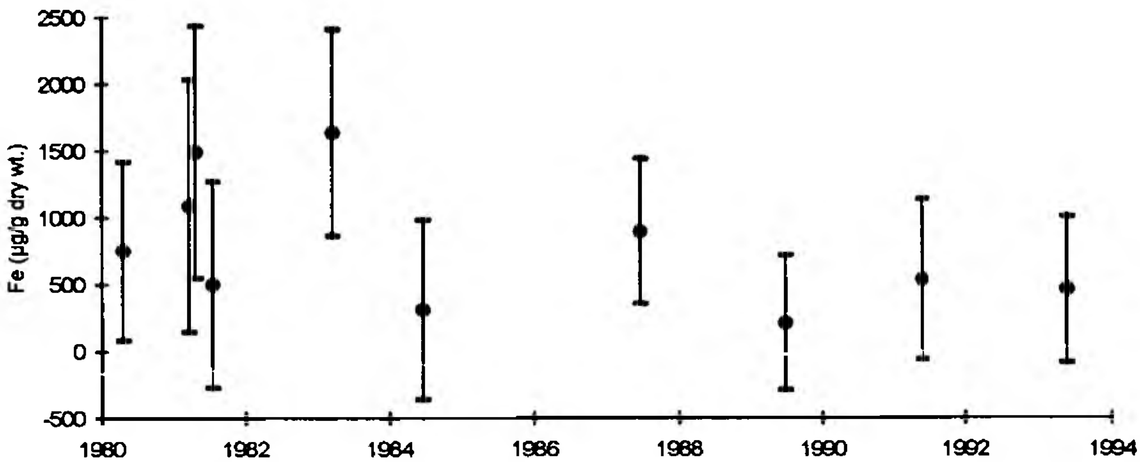


Figure 23. Temporal trends for Iron, 1980 - 1993.

A. Total Iron in Sediments, 1980 - 1993.



B. Iron in Macoma balthica, 1980 - 1993.



C. Iron in Littorina littorea, 1980 - 1993.

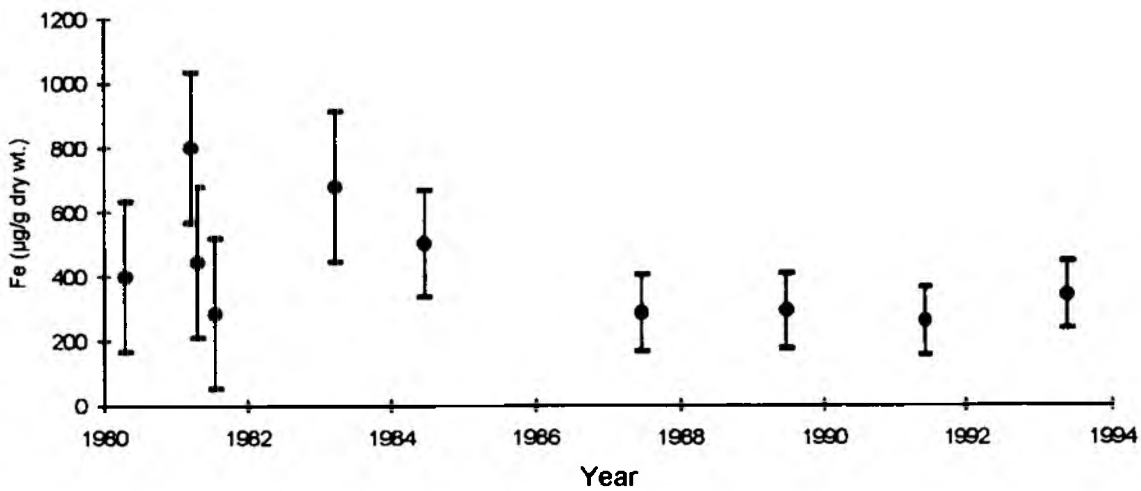
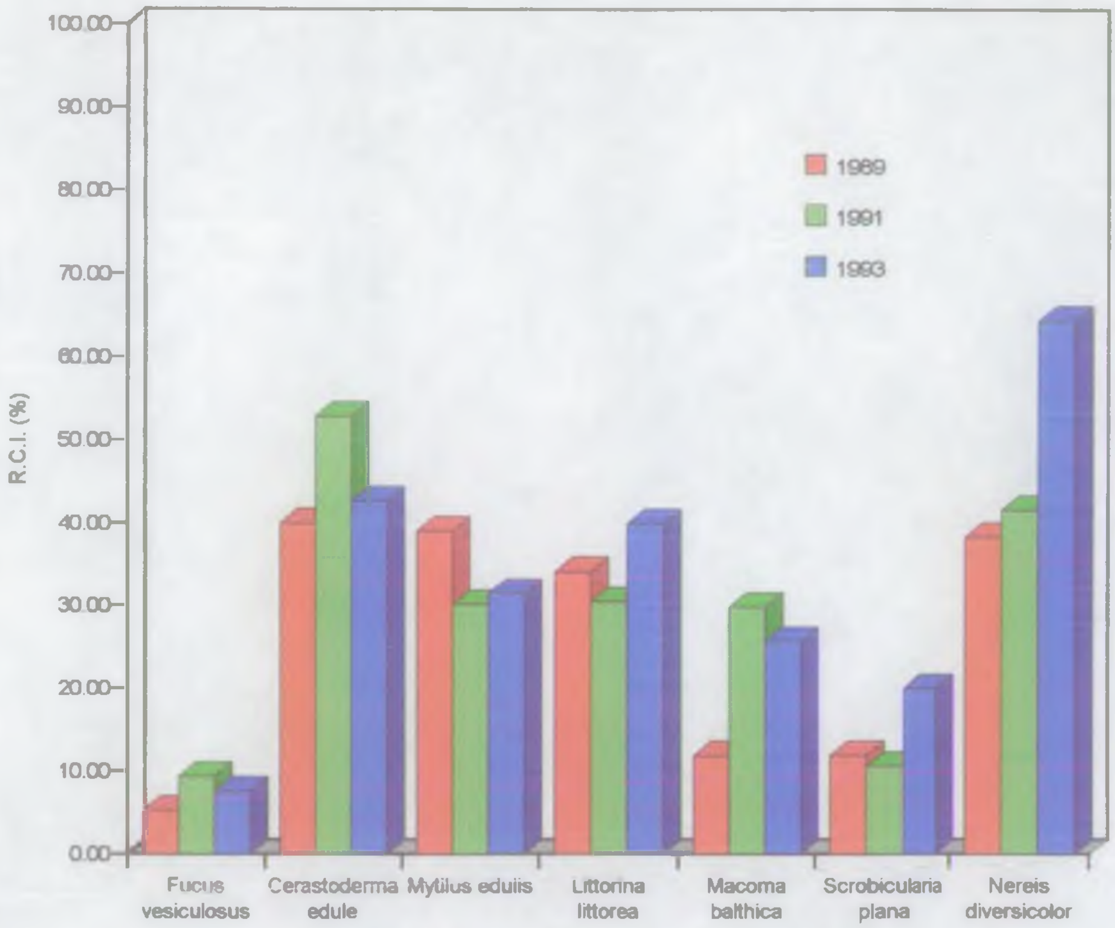


Figure 24

Relative Contamination Indices for Iron in Mersey Biota



Comparisons with other estuaries

Because of the abundance of iron in estuaries, particularly in sediments, and its regulation by most organisms, it is difficult to determine the impact of this element even at heavily polluted sites. Relative contamination indices (Figure 24) suggest a moderate degree of contamination in the Mersey. Similarly, enrichment factors for each species relative to new UK baseline data (Table 9) indicate that in most instances mean Mersey values are within a factor of <3 times the UK baseline. The exception is *Fucus vesiculosus* which exhibits a mean iron level which is over 12 times higher than the UK minimum, while concentrations at individual sites in the upper estuary are up to two orders of magnitude in excess of baseline, probably reflecting the importance of dissolved iron in that part of the estuary.

As for other species, there is also considerable variation in recorded levels between sites. Concentrations in *Cerastoderma edule* at Blundellsands exceed the UK maximum, while iron in *Macoma balthica* at the same site approaches the highest levels recorded for this species. In addition, iron in *Nereis diversicolor* at Hale and Rock Ferry also exceeds the new UK maximum value and in fact are the second and third highest levels of iron in *Nereis diversicolor* recorded in the UK, exceeded only by worms from Devoran in the upper reaches of Restronguet Creek, an area receiving effluent from extensive metal mining operations. The use of estuary wide data for iron (and other metals) can, then, obscure the occurrence of significant levels of localised contamination.

Table 9 Enrichment factors for iron in Mersey 1993 species relative to UK baseline data.

Species	Enrichment Factor*
Fucus vesiculosus	12.27
Cerastoderma edule	2.75
Mytilus edulis	2.94
Littorina littorea	2.10
Macoma balthica	1.45
Scrobicularia plana	1.90
Nereis diversicolor	2.22

* - Mean value for all sites.

Mercury

Data for mercury in 1993 samples are presented in Appendix 7.

Spatial Trends

The profile for total mercury in Mersey sediments is shown in Figure 25A. It can be seen that the pattern is similar to that for many metals, although perhaps not as strongly correlated with the organic content as some others. The trend for a decrease in sediment mercury levels seawards is highly significant ($r = -0.65$, $P = 0.005$) reflecting sources in the upper reaches of the estuary. This is partly corroborated by the results for mercury in *Nereis diversicolor*, the only species to extend into the upper estuary. The *Nereis diversicolor* profile (Figure 25B) correlates significantly with that for the sediments ($r = 0.62$, $P = 0.019$) and is best separated into north and south banks, where it can be seen that generally higher tissue burdens are found in the Weaver Sluice \ Stanlow area, and to a lesser extent Ince bank and Mount Manisty, which may in turn reflect likely regions of mercury input to the estuary, mainly on this southern industrialised shore.

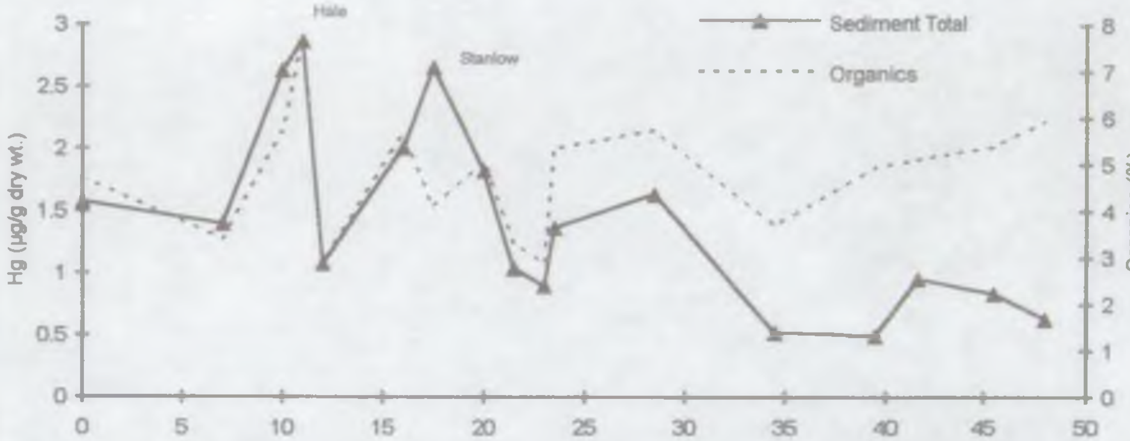
Most other invertebrate species, which occur in the lower half of the estuary, show an overall decline in tissue concentrations downstream, thus reflecting sediment contamination. There are however, some exceptions and additional points of interest. Firstly, whenever a species occurs at both Garston and Eastham Lockgates (situated opposite each other on the north and south banks respectively) there is an increase in mercury concentrations at the latter site e.g. *Scrobicularia plana* (Figure 25C), *Macoma balthica* (Figure 26A), *Mytilus edulis* (Figure 26B) and *Mya arenaria* (Figure 26C). The southern shore has already been shown to be impacted to a greater extent by mercury from the data for *Nereis diversicolor* (a similar bank effect is also described for a number of other metals). Secondly, some species, though not all, show a slight upturn in mercury levels at the mouth of the estuary e.g. *Scrobicularia plana* (figure 25C), *Mytilus edulis* (Figure 26B), *Littorina littorea* (Figure 27A) and *Cerastoderma edule* (Figure 27B). The data for *Fucus vesiculosus* shows a clear increase seawards (Figure 27C), presumably indicating increasing levels of mercury in solution in that direction.

Temporal Trends

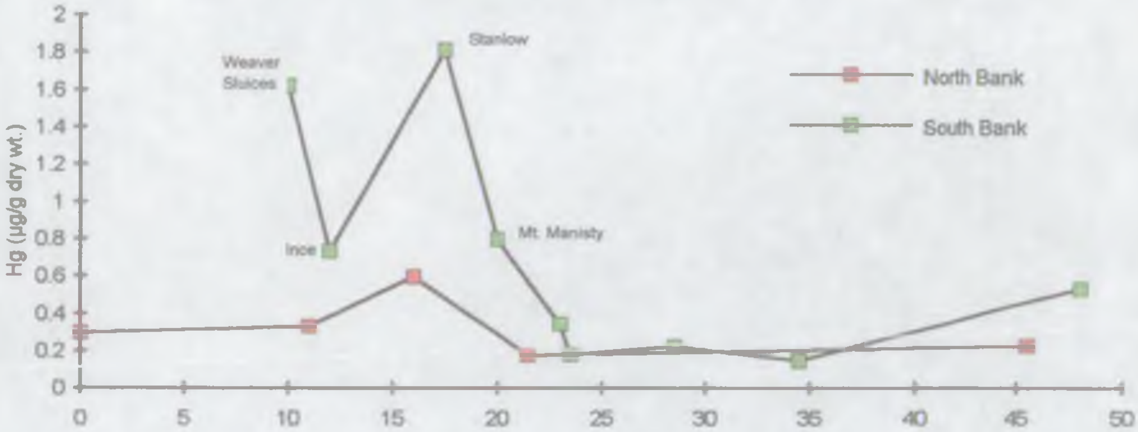
Sediments (Figure 28A) and all species analysed in surveys from 1980 to the present day, with the exception of *Littorina littorea* and *Scrobicularia plana*, show significant (Table 10) decreases in accumulated body burdens of mercury in this period (Figures 28B - 29C). However, it can also be seen that no significant ($P > 0.05$, Student's t-test) changes have occurred since the 1991 survey, or indeed for several years previously in some cases, suggesting that mercury levels have reached a steady state in the estuary as a whole, following the major decreases of the early 1980's.

Figure 25. Spatial trends for Mercury, 1993.

A. Mercury in Sediments, 1993.



B. Mercury in Nereis diversicolor, 1993.



C. Mercury in Scrobicularia plana. 1993.

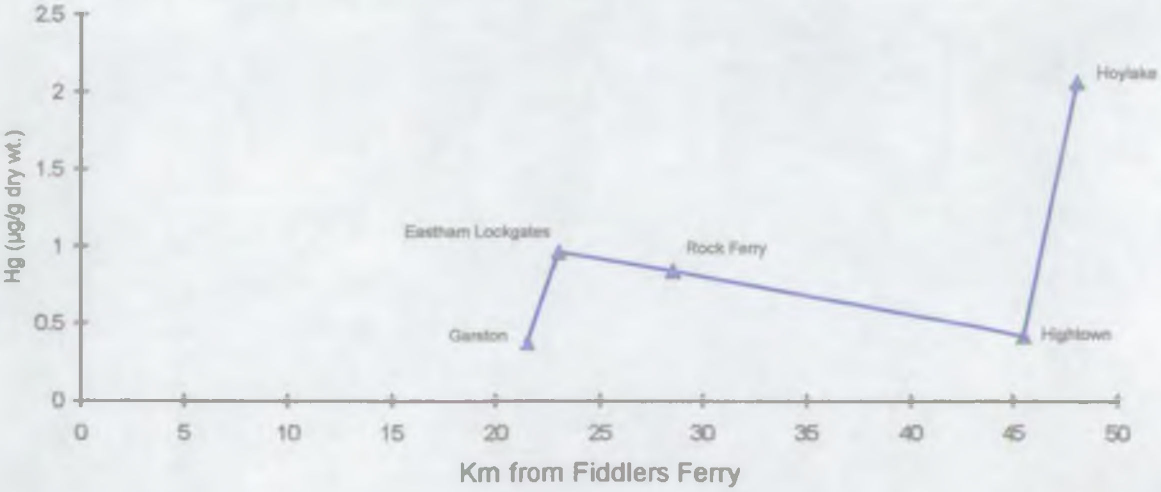
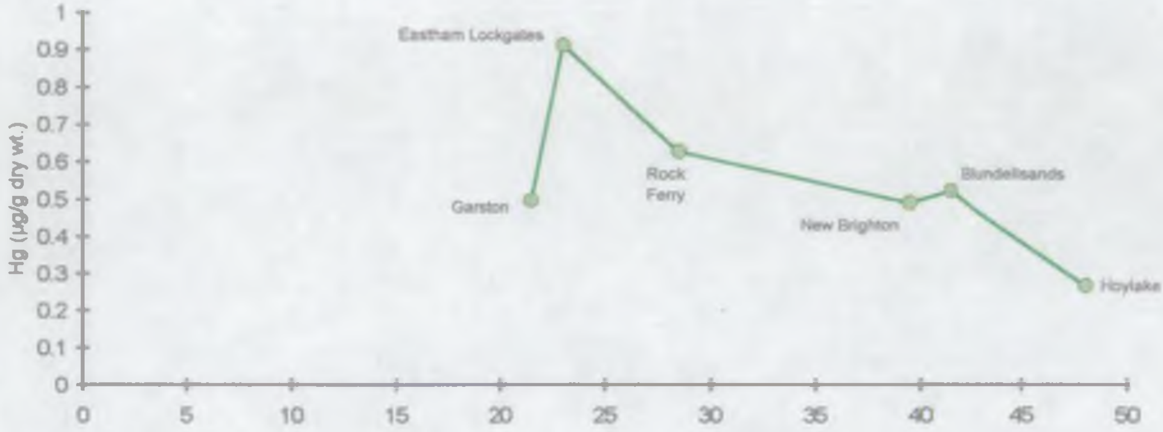
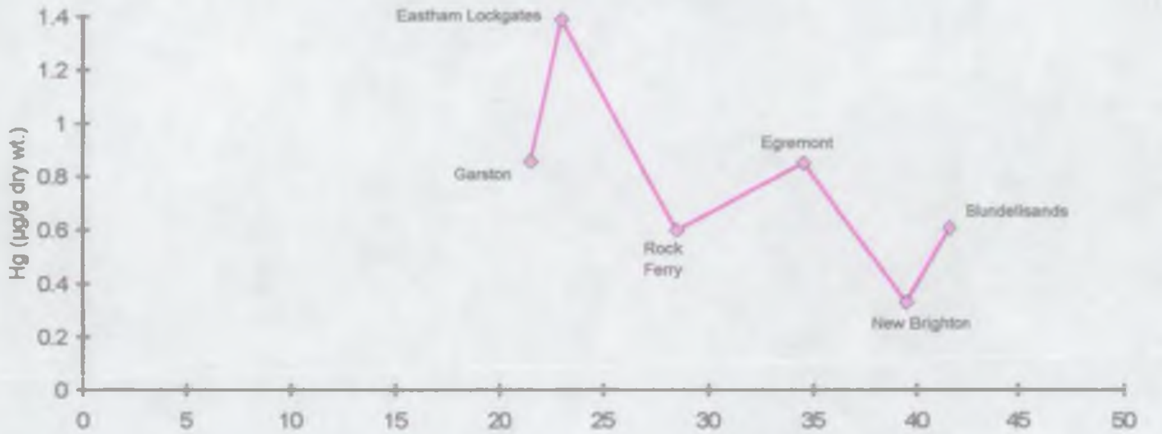


Figure 26. Spatial trends for Mercury, 1993.

A. Mercury in Macoma balthica, 1993.



B. Mercury in Mytilus edulis, 1993.



C. Mercury in Mya arenaria, 1993.

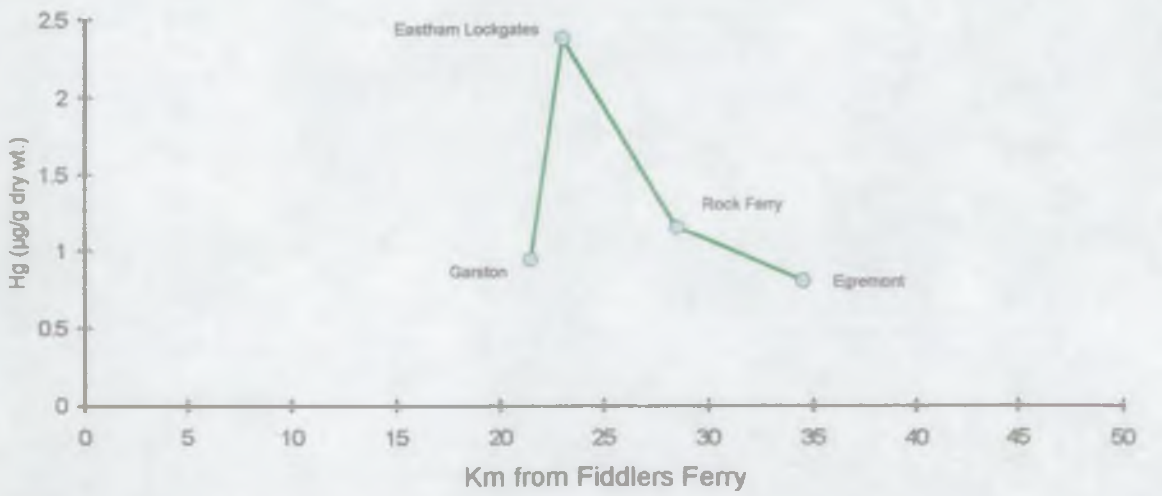
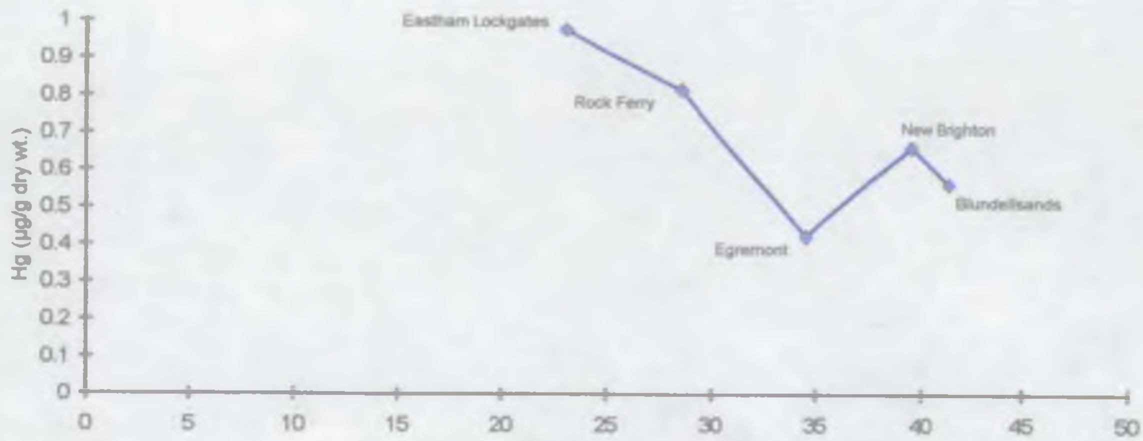
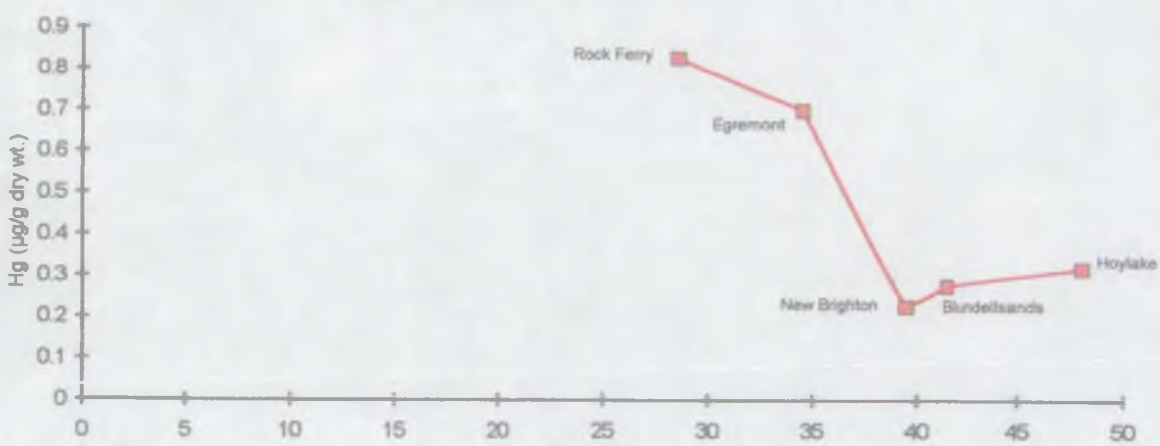


Figure 27. Spatial trends for Mercury, 1993.

A. Mercury in Littorina littorea, 1993.



B. Mercury in Cerastoderma edule, 1993.



C. Mercury in Fucus vesiculosus, 1993.

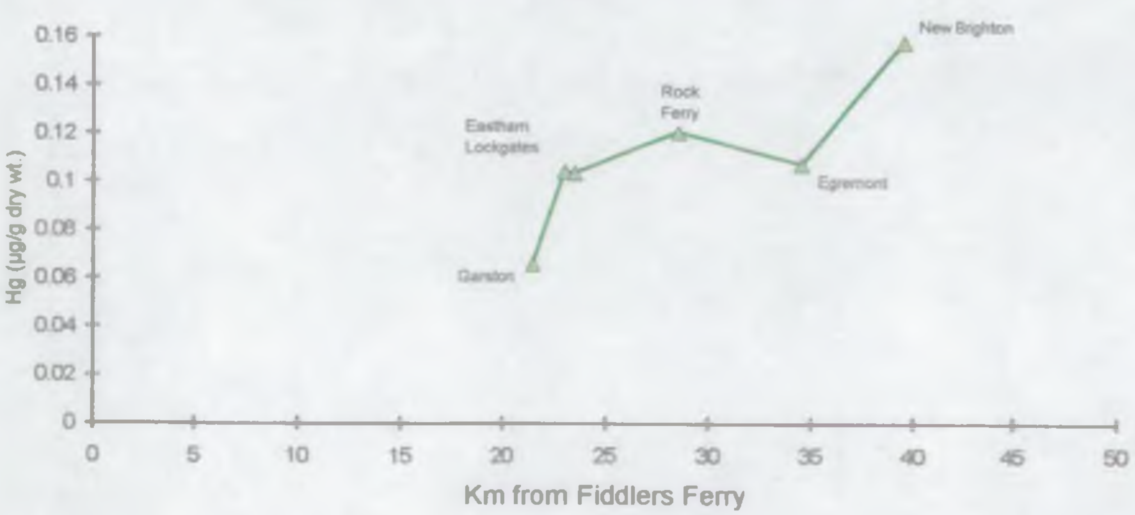
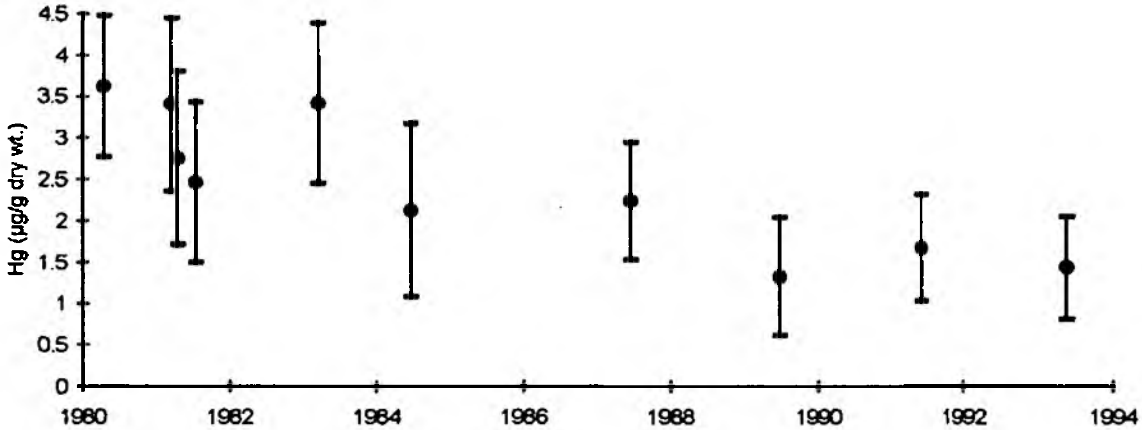
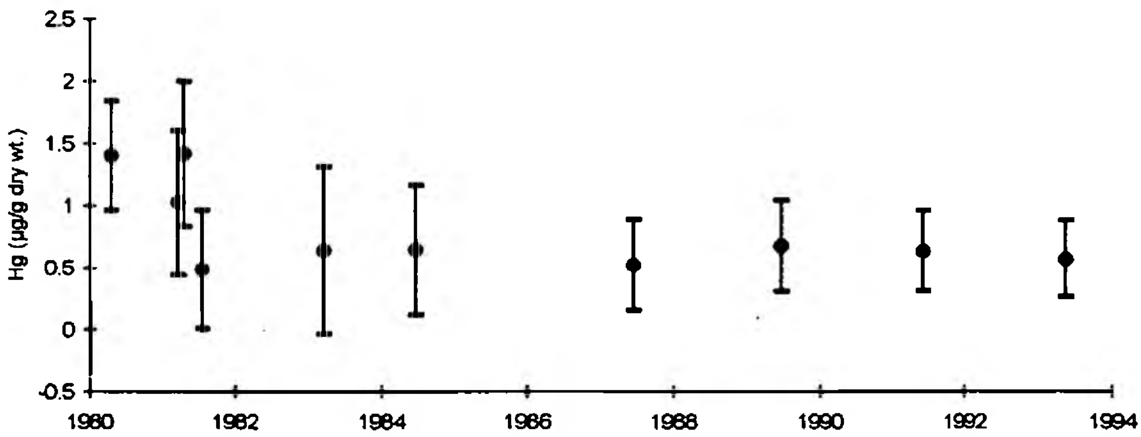


Figure 28. Temporal trends for Mercury, 1980 - 1993.

A. Mercury in Sediments, 1980 - 1993.



B. Mercury in Nereis diversicolor, 1980 - 1993.



C. Mercury in Macoma balthica, 1980 - 1993.

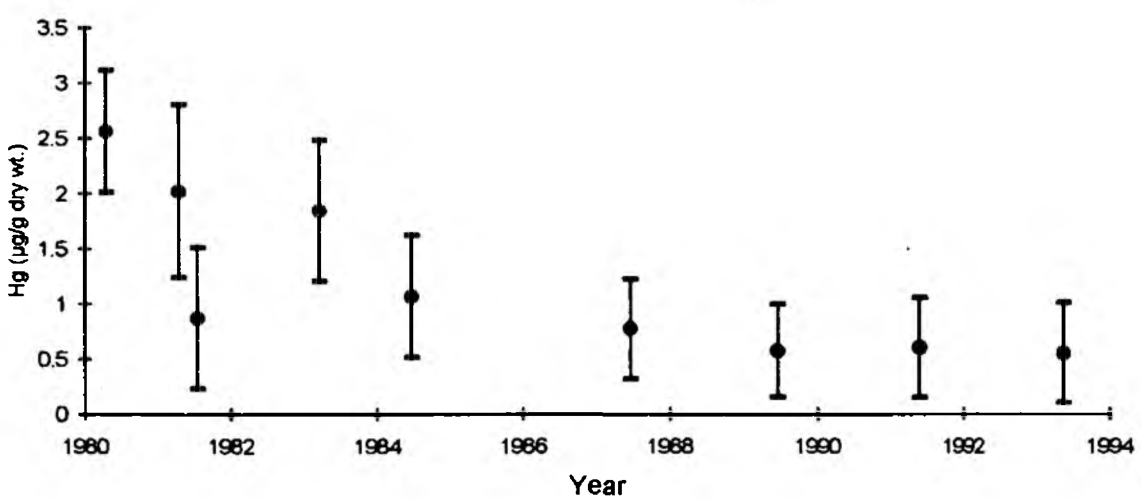
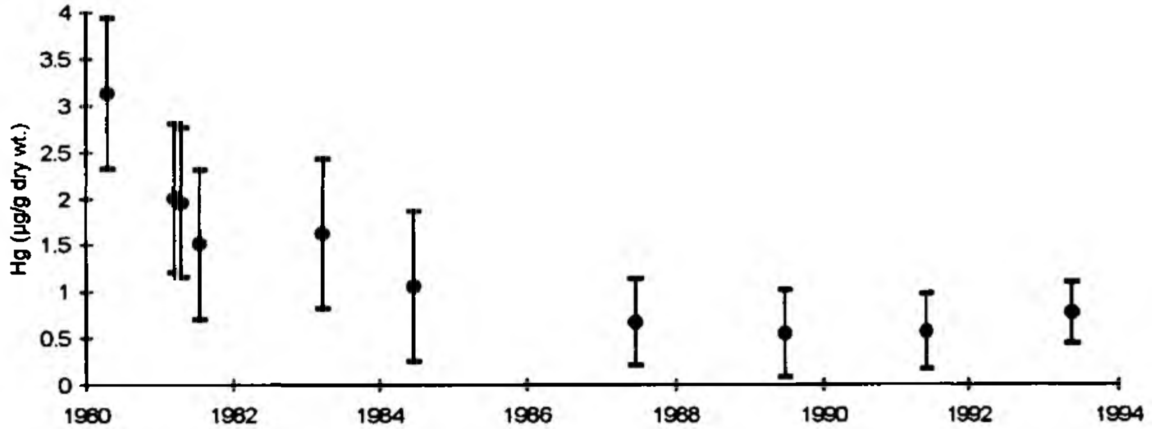
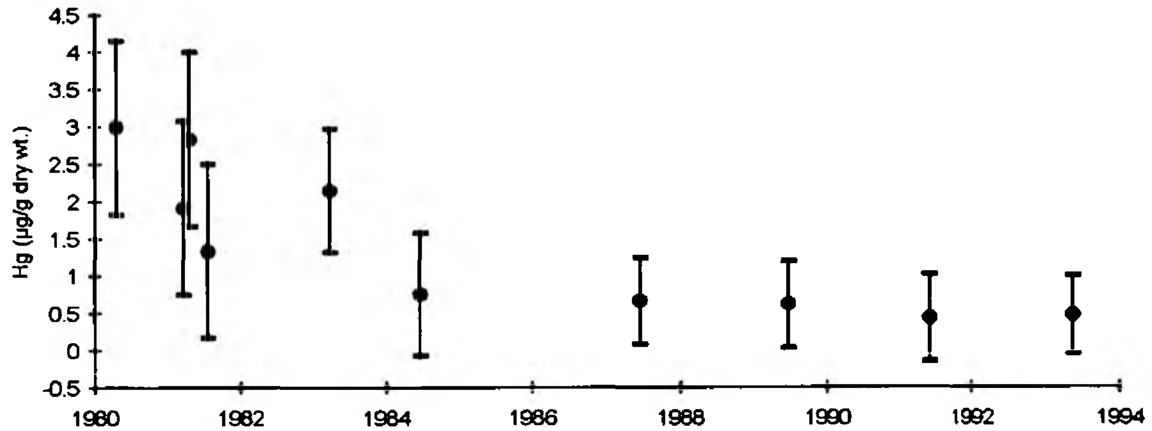


Figure 29. Temporal trends for Mercury, 1980 - 1993.

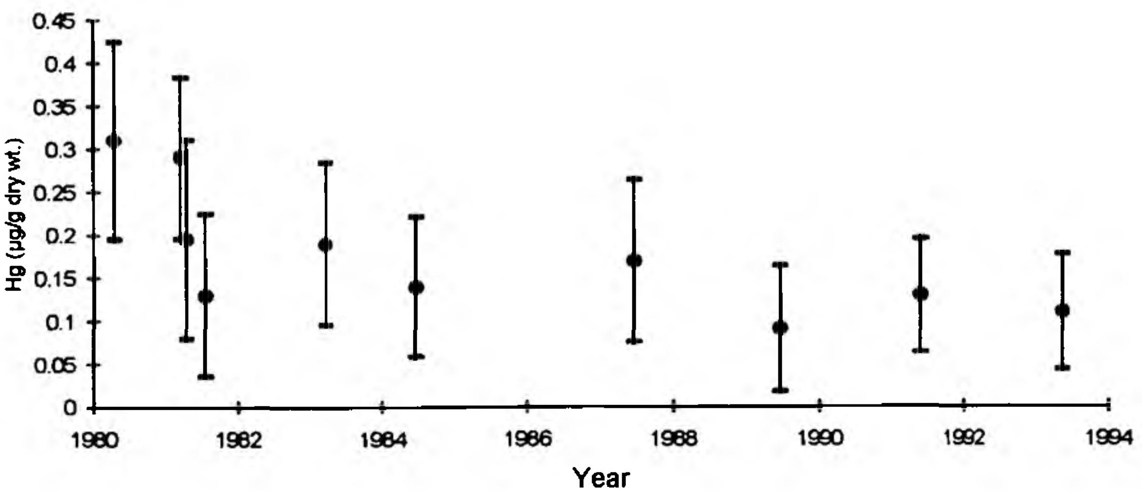
A. Mercury in Mytilus edulis, 1980 - 1993.



B. Mercury in Cerastoderma edule, 1980 - 1993.



C. Mercury in Fucus vesiculosus, 1980 - 1993.



Data for specific sites however, do indicate temporal changes in recent years. Figure 30A shows the results for mercury in *Scrobicularia plana* from Hoylake, where it can be seen that the trend for declining concentrations since 1980 have dramatically reversed in 1993. Possible reasons for this are as yet unknown and may represent an anomalous result. However, the same figure also indicates increases at Egremont in 1991. The disappearance of this population, in 1993, coincides with increased metal burdens (including mercury) as described earlier, and may be related to changes in local sediment conditions, rather than increased inputs.

Table 10 Significance levels for reductions of mercury levels in Mersey samples over the period 1980 - 1993 (ANOVA).

Species	Significance level
Sediment	< 0.0001
Nereis diversicolor	0 0056
Macoma balthica	< 0.0001
Mytilus edulis	0.0001
Cerastoderma edule	0.0002
Fucus vesiculosus	0.0047

Comparisons with other estuaries

Enrichment factors for mean mercury concentrations in Mersey biota relative to new UK baseline data are shown below:

Table 11 Enrichment factors for mercury in Mersey 1993 species relative to UK baseline data.

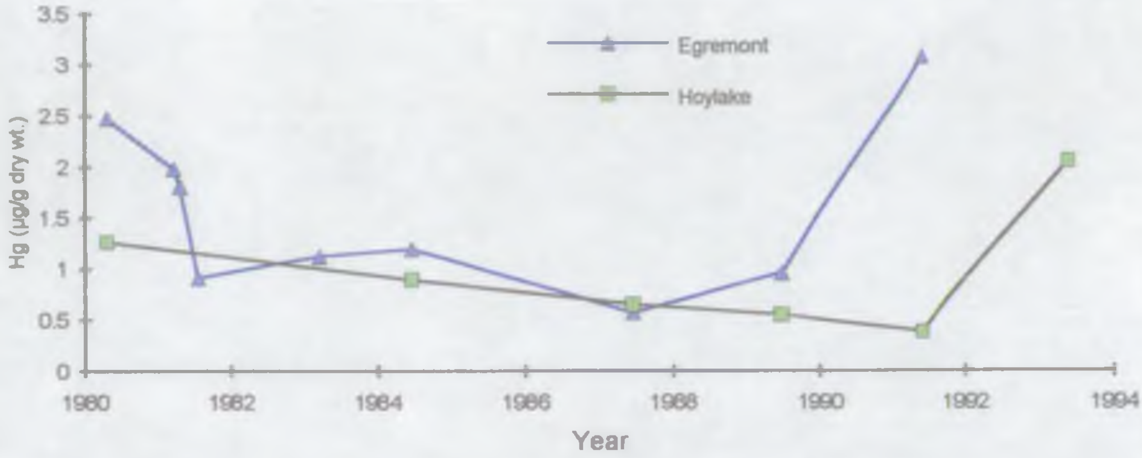
Species	Enrichment Factor*
Fucus vesiculosus	6.11
Cerastoderma edule	2.83
Mytilus edulis	6.50
Littorina littorea	5.51
Macoma balthica	3.36
Scrobicularia plana	9.31
Nereis diversicolor	15.92

* - Mean value for all sites.

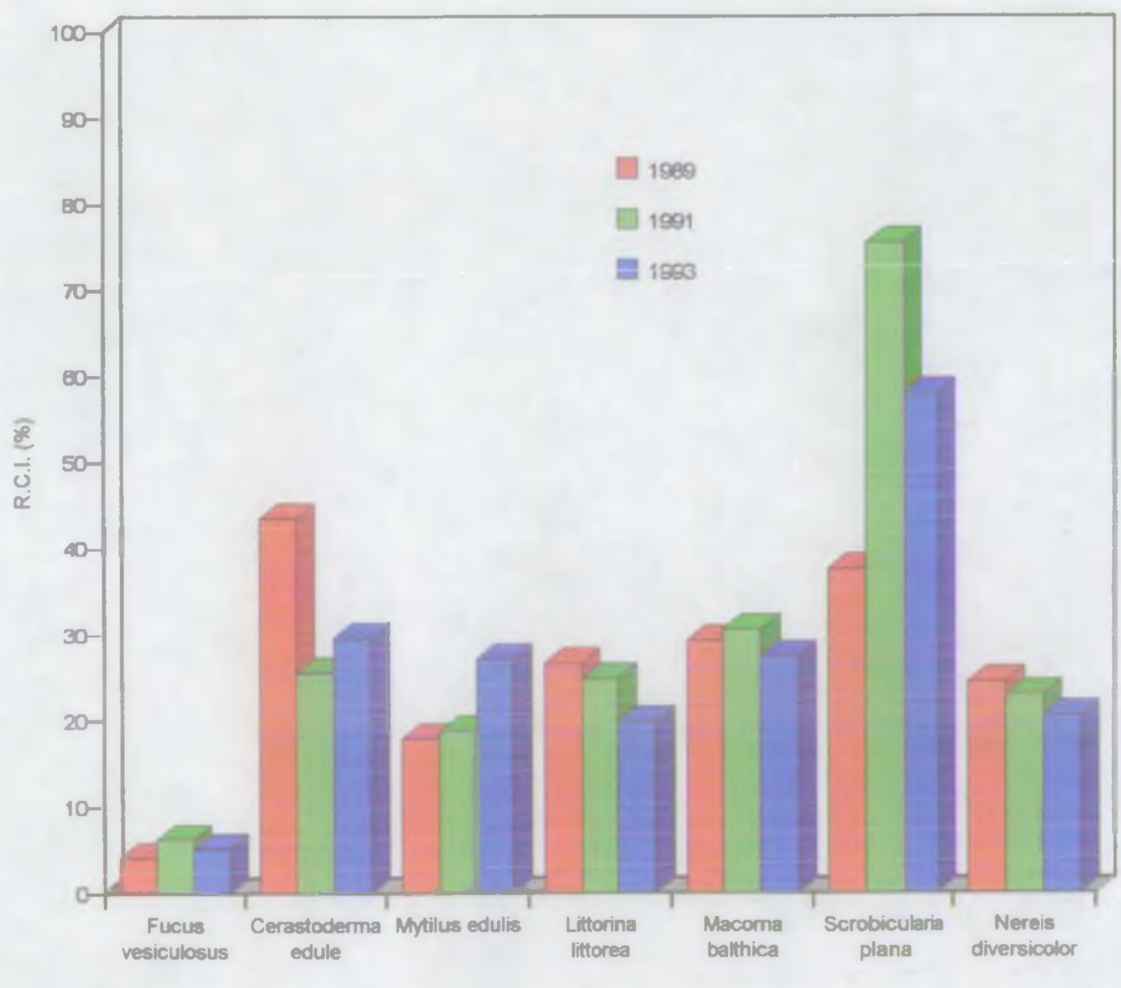
The Mersey has previously been identified as one of the most severely mercury-contaminated estuaries in the UK (Langston, 1986). However, as discussed above, improvements have occurred since the early 1980's so that current mercury burdens are generally lower than previous. As a result, the 1993 Mersey data show that for most species mercury levels are within the lower 30% of recorded values (see R.C.I.'s, Figure 30B). It must however be noted that much of the data on which this comparison has been made refers to earlier Mersey data

Figure 30

A. Mercury in Scrobicularia plana at Egremont & Hoylake, 1980 - 1993.



B. Relative Contamination Indices for Mercury in Mersey Biota



when levels were higher. Average mercury levels in *Scrobicularia plana* are still rated within the top 50% of recorded values, while the 1993 sample from Hoylake exceeds the UK maximum as defined earlier in this report, and in fact represents the second highest tissue concentration for this species ever recorded on our database for the UK. Similarly, mercury concentrations in other species at the most contaminated Mersey sites are still representative of the most highly impacted conditions currently existing in UK estuaries.

Manganese

Data for manganese in 1993 samples are presented in Appendix 8.

Spatial Trends

The distributions of total and HCl-extractable manganese in sediments follow almost identical patterns which are each significantly correlated with the sediment organic content (Total: $r = 0.74, P = 0.0007$; HCl: $r = 0.70$, $P = 0.0018$) as shown in Figure 31A. Manganese like iron, is one of the major elements involved in the redox cycle of estuarine sediments. Reducing conditions favour the dissolution of particulate manganese by formation of soluble Mn (II), while oxidation of this form in aerobic, surface sediments results in the precipitation of manganese oxides as surface coatings. Thus, manganese may be remobilised within the sediments as the result of changing environmental conditions, so that factors other than total sediment concentration may have a direct effect on bioavailability.

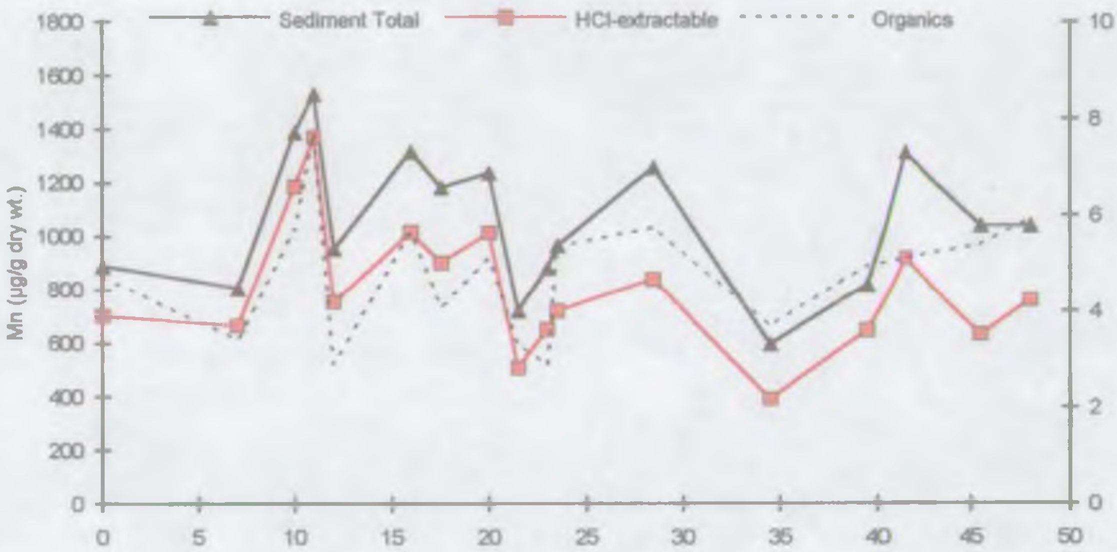
The profile for manganese in *Nereis diversicolor* (Figure 31B) is very similar to that for iron and chromium, with prominent peaks at Hale and Rock Ferry, suggesting once more that availability may be significantly greater at these locations. Profiles for other species show few consistent patterns. *Fucus vesiculosus* exhibits a general decline seawards in line with expected patterns for dissolved manganese, and is repeated in *Littorina littorea*, (again, though, with an upturn in concentrations at Blundellsands - Figure 32A). High manganese burdens are also found at this site for *Cerastoderma edule* and *Macoma balthica* (Figure 32B) in a pattern identical to their iron profiles, suggesting once again that enhanced uptake may occur at this site perhaps modified by the presence of sewage. Finally, *Scrobicularia plana* contains high concentrations of manganese at Garston on the northern shore, falling sharply to lower levels on the south shore and to seaward (Figure 32C). This suggests much greater availability of manganese at this site which may be related to the redox conditions present in the deeper sediment layers where *Scrobicularia plana* is often found.

Temporal Trends

Analysis of data for manganese in sediments shows that there have been some slight variations since surveys began, but that there have been no significant ($P = 0.033$) changes since 1989 (Figure 33A). Data for *Nereis diversicolor* shows that there have been no significant changes except in early 1981, but the trend for mean levels of manganese in this species in the Mersey has been a gradual rise since 1989 (Figure 33B). No other long term changes for manganese in biota are apparent when mean data for each species over the whole estuary are analysed. However, if specific sites are investigated, for some species, strong temporal trends become apparent, particularly at Blundellsands. Figures 34A and 34B show changes over time at this site for *Cerastoderma edule* and *Macoma balthica*, where increases have occurred since samples were first collected there in 1987.

Figure 31. Spatial trends for Manganese, 1993.

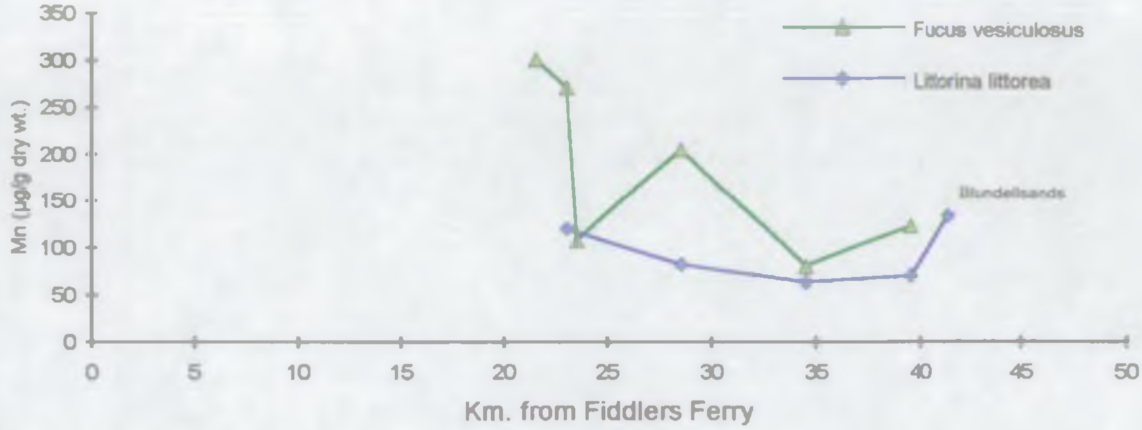
A. Manganese in Sediments,1993.



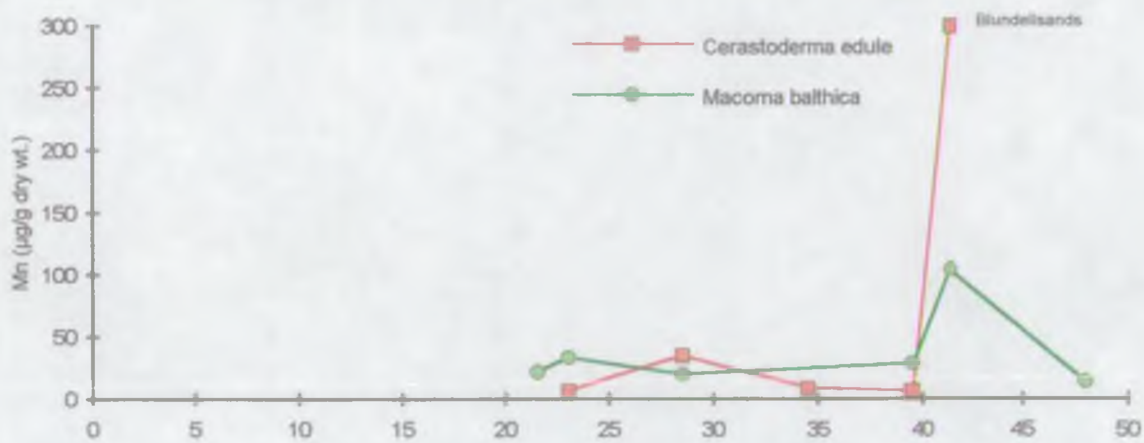
B. Manganese in Nereis diversicolor, 1993.

Figure 32. Spatial trends for Manganese, 1993.

A. Manganese in Fucus vesiculosus and Littorina littorea, 1993.



B. Manganese in Cerastoderma edule and Macoma balthica, 1993.



C. Manganese in Scrobicularia plana, 1993.

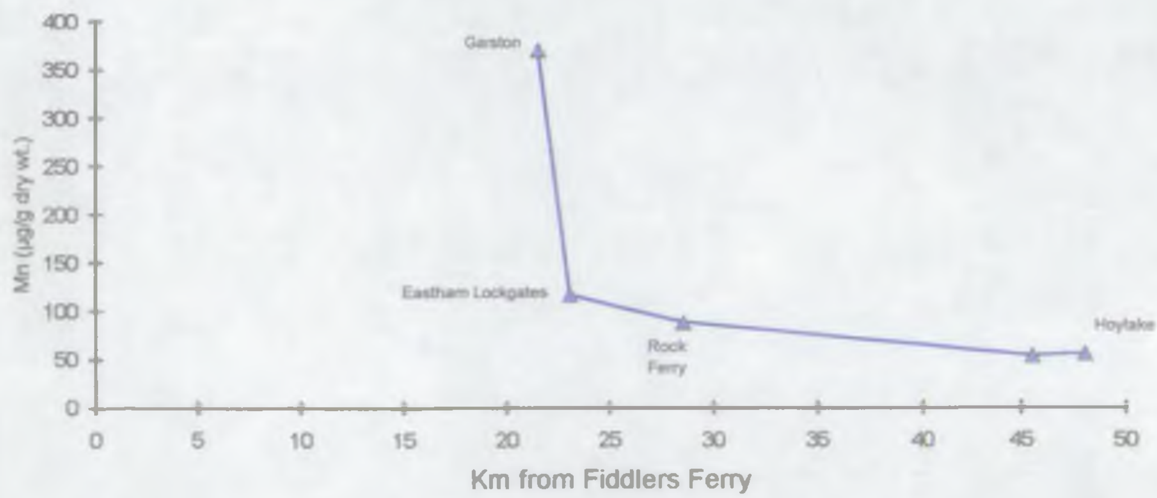
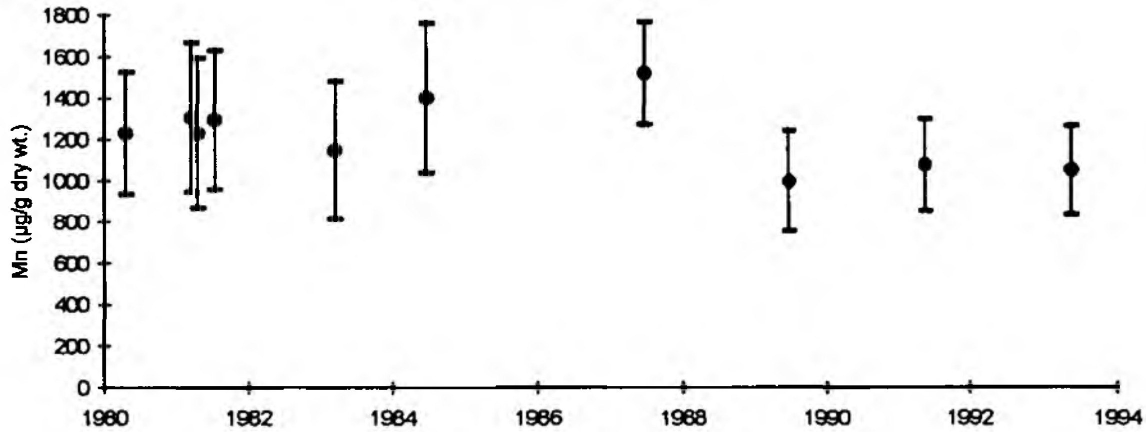


Figure 33. Temporal trends for Manganese, 1980 - 1993.

A. Manganese in Sediments, 1980 - 1993.



B. Manganese in Nereis diversicolor, 1980 - 1993.

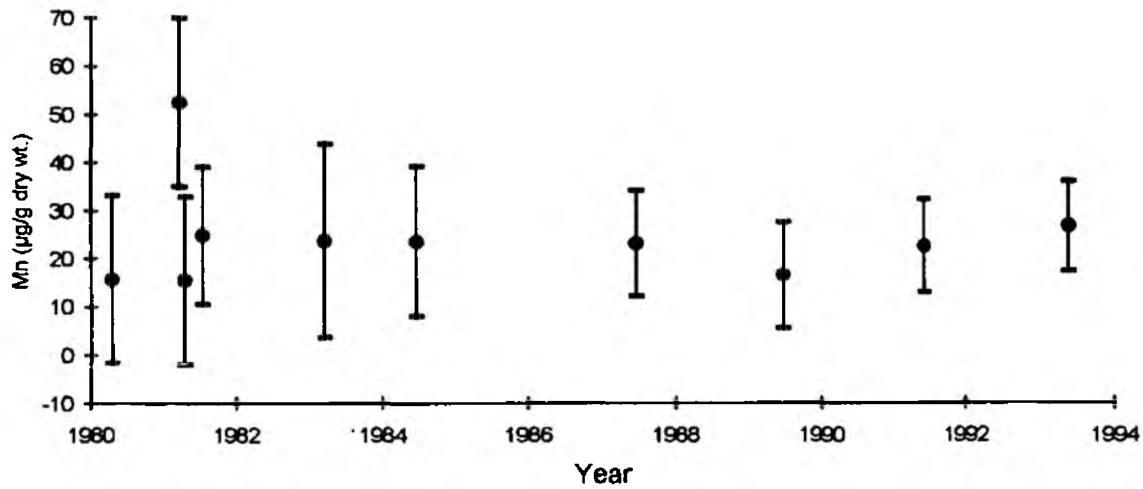
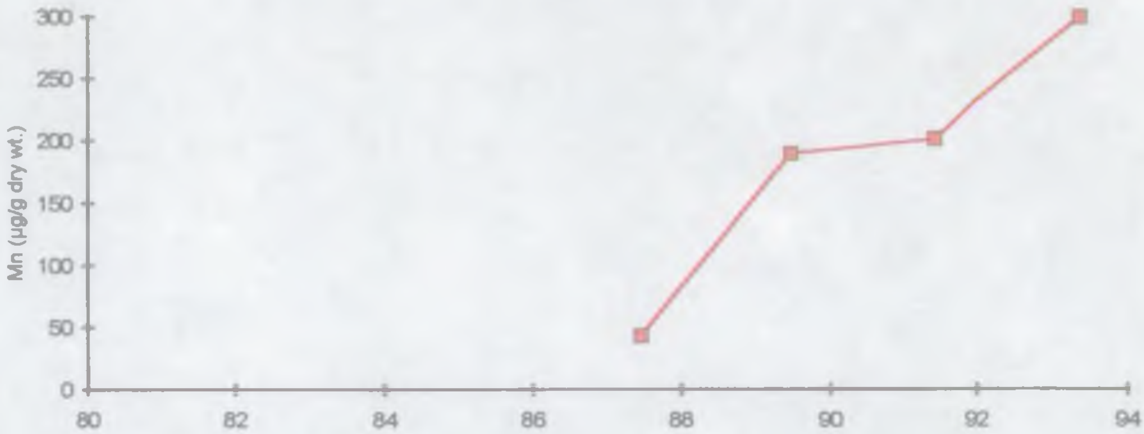
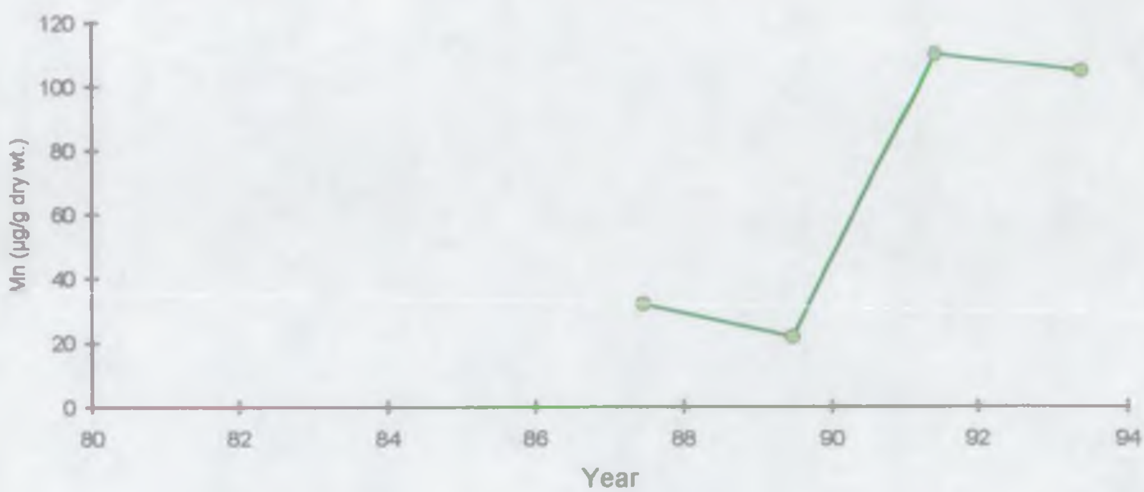


Figure 34. Temporal trends for Manganese, 1980 - 1993.

A. Manganese in Cerastoderma edule at Blundellsands, 1980 - 1993.



B. Manganese in Macoma balthica at Blundellsands, 1980 - 1993.



Comparisons with other estuaries

Manganese is present in relatively high concentrations in Mersey sediments (596 - 1533 µg/g dry weight) compared with most UK estuaries. At a number of sites sampled in the current survey concentrations are higher than those found in metalliferrous regions of the Southwest (e.g. 1160 µg/g, Gannel Estuary). However, in contrast to sediments, manganese concentrations in Mersey biota vary widely between species and between sites, and therefore the relationship between environmental contamination and body burdens is not straightforward. This is partly because manganese can be significantly remobilised from sediments and pore waters as a result of redox changes, even in relatively uncontaminated conditions. This makes comparisons between estuaries more difficult than for some other metals. However, with this limitation in mind, enrichment factors for average manganese burdens of Mersey biota relative to UK baseline data are presented in Table 12.

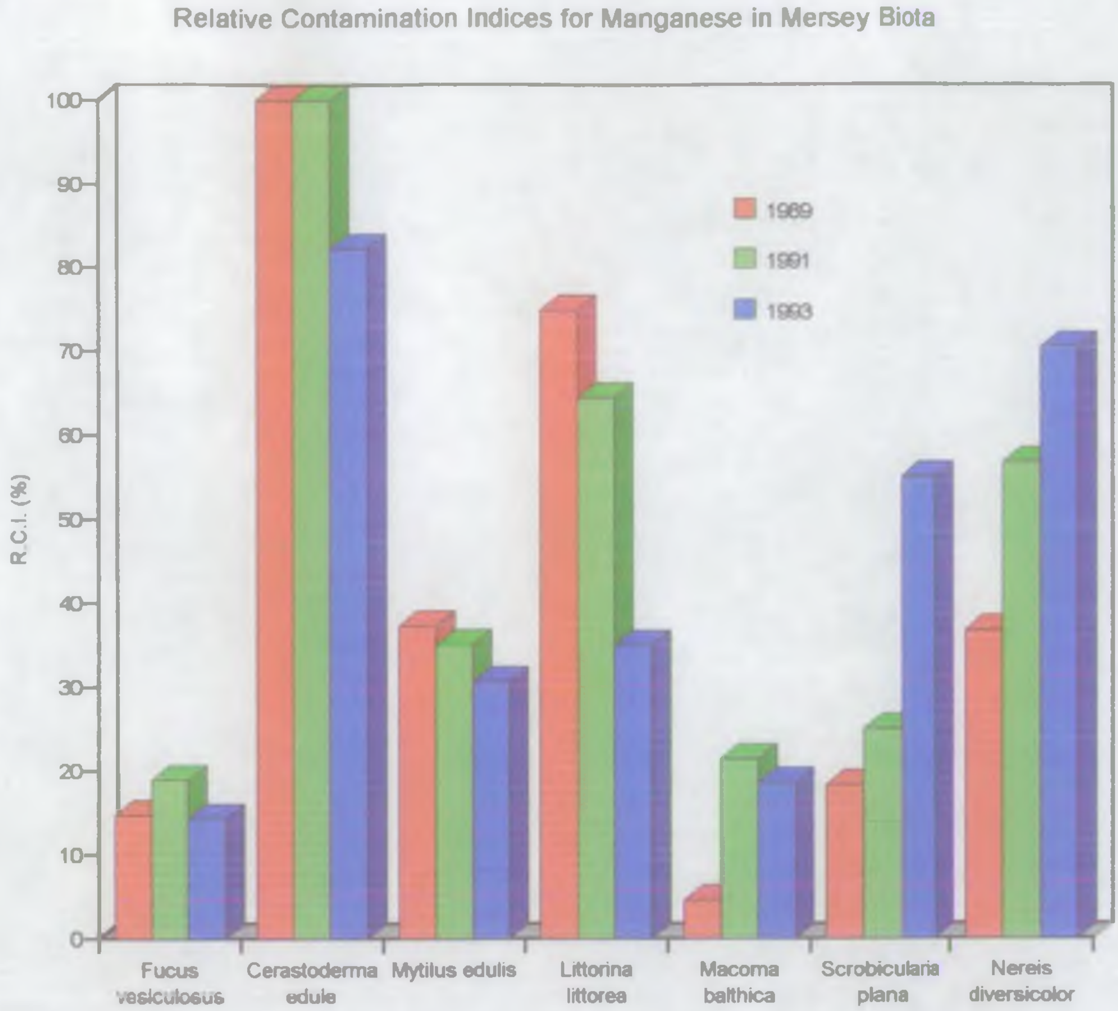
Table 12 Enrichment factors for manganese in Mersey 1993 species relative to UK baseline data.

Species	Enrichment Factor*
Fucus vesiculosus	5.73
Cerastoderma edule	19.26
Mytilus edulis	3.83
Littorina littorea	5.33
Macoma balthica	3.16
Scrobicularia plana	12.11
Nereis diversicolor	4.88

* - Mean value for all sites.

It can be seen that several species contain mean levels of manganese significantly above minimum UK values. Relative Contamination Indices, shown in Figure 35, provide a simplified impression of the status of Mersey biota relative to other UK estuaries, and it is obvious that the mean levels recorded in 1993 for several species places the Mersey within a factor of 2 of the uppermost levels recorded. In addition, *Cerastoderma edule* at Blundellsands, *Scrobicularia plana* at Garston, and *Nereis diversicolor* at Hale and Rock Ferry exhibit the highest manganese levels recorded in the UK on our database. In view of the high sediment loadings, and the potential for release, manganese contamination is a significant feature of the Mersey estuary.

Figure 35



Relative Contamination Indices for Manganese in Mersey Biota
R.C.I. (%)
100
90
80
70
60
50
40
30
20
10
0
1989
1991
1993
Fucus vesiculosus
Cerastoderma edule
Mytilus edulis
Littorina littorea
Macoma balthica
Scrobicularia plana
Nereis diversicolor

Nickel

Data for nickel in 1993 samples are presented in Appendix 9.

Spatial Trends

The profiles for total and HCl-extractable nickel in Mersey sediments are shown in Figure 36A together with that for the sediment organic content. It can be seen that the total nickel and organic profiles are correlated ($r = 0.82$, $P = 0.0001$), as has been demonstrated for a number of other metals. However, only a relatively small fraction of the total is extractable with 1N HCl and therefore assumed to be bioavailable. An exception can be seen at Egremont where levels in HCl extracts are particularly high. This may be related to environmental conditions at this site where sediments were noticeably anaerobic and likely to influence the extractability of nickel.

Levels of nickel in *Nereis diversicolor* show an erratic pattern (Figure 36B) which may be divided into two halves. The first is in the region upstream from Eastham Lockgates where levels are generally higher, while the second, downstream half exhibits lower levels which gradually rise seawards.

Several species show a more significant, and consistent decline in nickel burdens downstream through the estuary. Profiles for *Mytilus edulis* ($r = -0.86$, $P = 0.029$) and *Littorina littorea* ($r = -0.95$, $P = 0.015$) are shown in Figure 36C, while that for *Cerastoderma edule* ($r = -0.91$, $P = 0.012$) is shown in Figure 37A. The latter species is an exceptionally good accumulator of nickel as indicated by concentrations of up to 120 µg/g. It is unfortunate that the deposit feeding bivalves *Scrobicularia plana* and *Macoma balthica* could not be found, despite extensive searches, at Egremont. The profiles for these species are shown in Figures 37B and 37C and exhibit a decline downstream from Eastham Lockgates. *Macoma balthica* however does show a sharp increase from Garston to the lockgates indicating a difference between the north and south banks, possibly relating to inputs of nickel via the Manchester Ship Canal. Additionally, *Macoma balthica* shows a slight increase in nickel levels at Blundellsands in a trend common to many other metals already discussed. The profile for nickel in *Fucus vesiculosus* is shown in Figure 38A and exhibits a slight but significant increase seawards ($r = 0.83$, $P = 0.041$) which presumably reflects recent trends in dissolved nickel in the lower estuary.

Temporal Trends

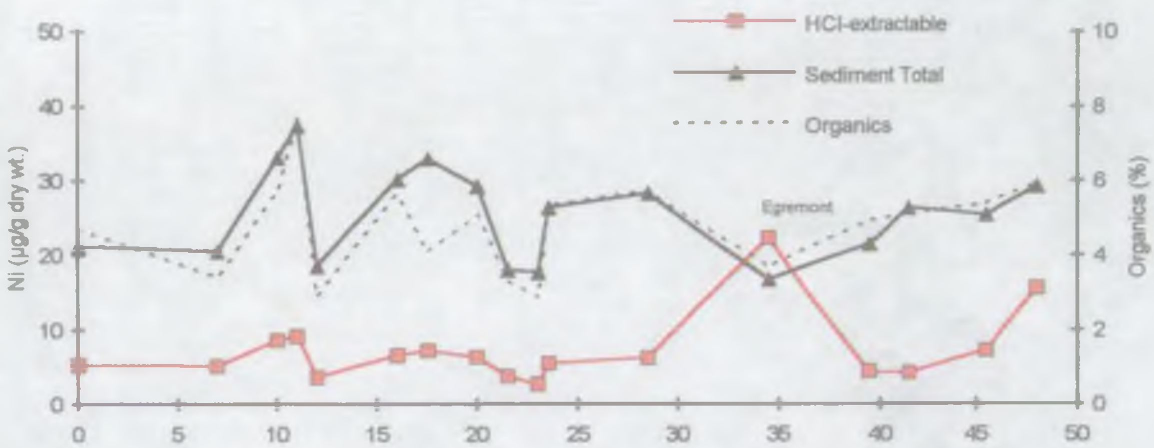
Analysis of data for mean nickel levels in sediments and biota show that there have been no significant changes in nickel levels in the Mersey estuary since the last survey, or overall, since surveys began in 1980 ($P > 0.05$, ANOVA).

Comparisons with other estuaries

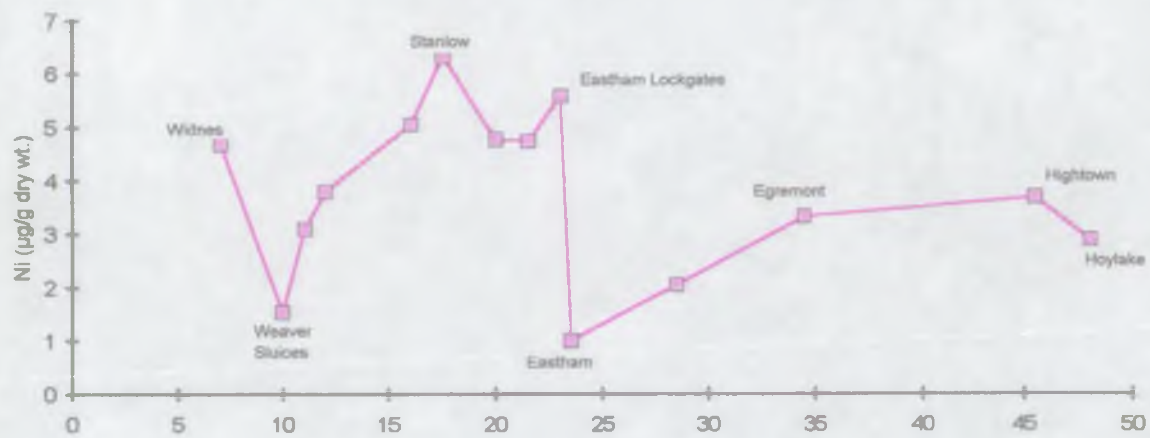
Enrichment factors for mean nickel concentrations in Mersey biota relative to new UK baseline data are shown in Table 13. It can be seen that at most (in *Mytilus edulis*), mean Mersey levels are higher than baseline by a factor of 5.1, whilst in *Macoma balthica* nickel concentrations are just less than twice the baseline level. However, nickel levels in UK estuarine biota as a whole

Figure 36. Spatial trends for Nickel, 1993.

A. Nickel in Sediments, 1993.



B. Nickel in Nereis diversicolor, 1993.



C. Nickel in Littorina littorea and Mytilus edulis, 1993.

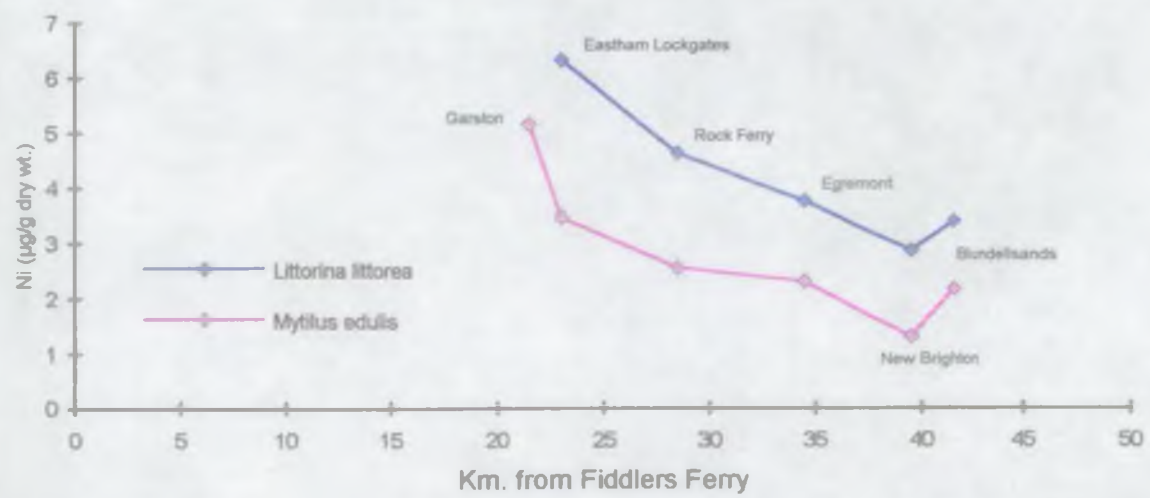
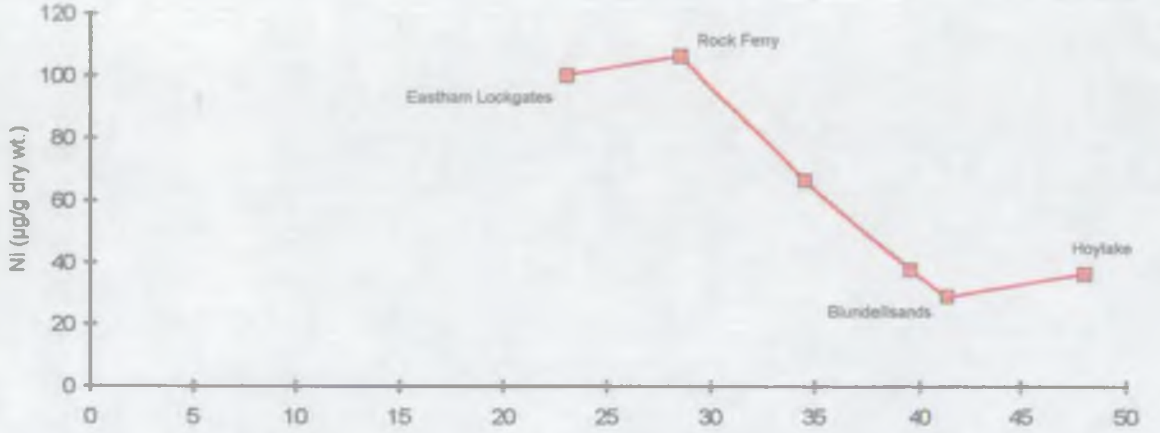
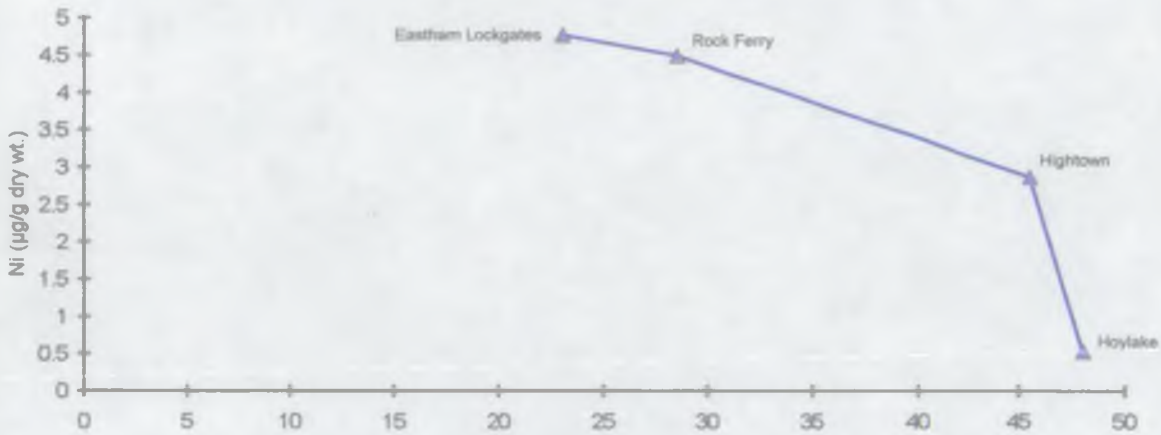


Figure 37. Spatial trends for Nickel, 1993.

A. Nickel in Cerastoderma edule, 1993



B. Nickel in Scrobicularia plana, 1993.



C. Nickel in Macoma balthica, 1993.

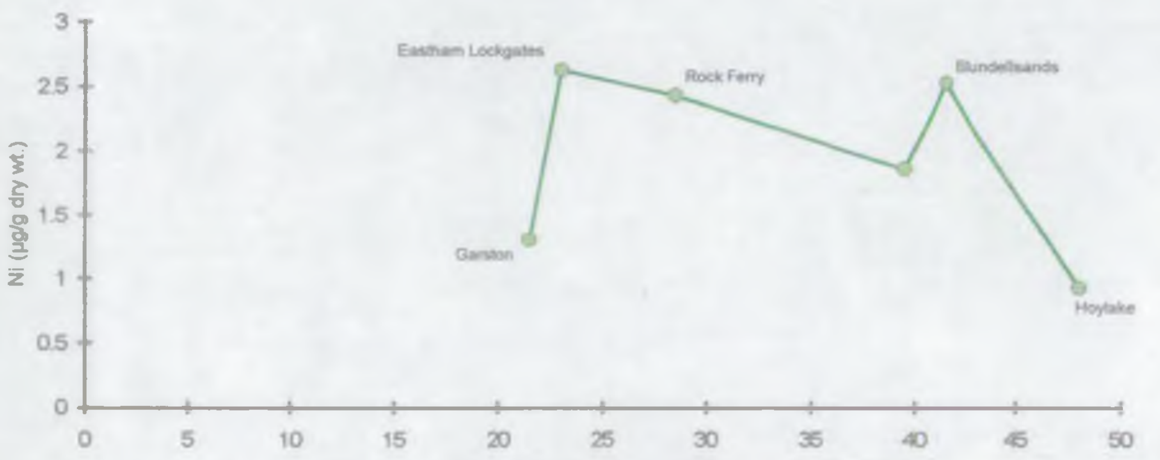
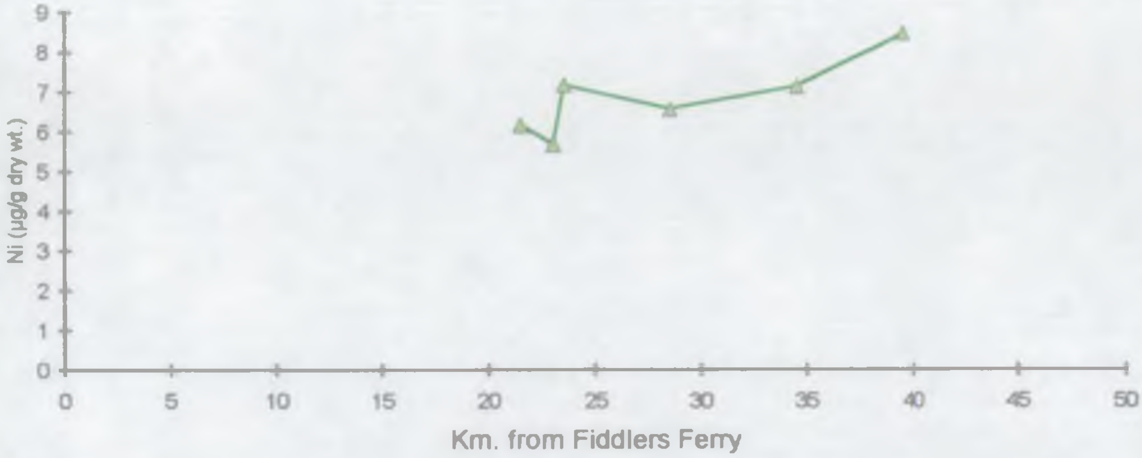
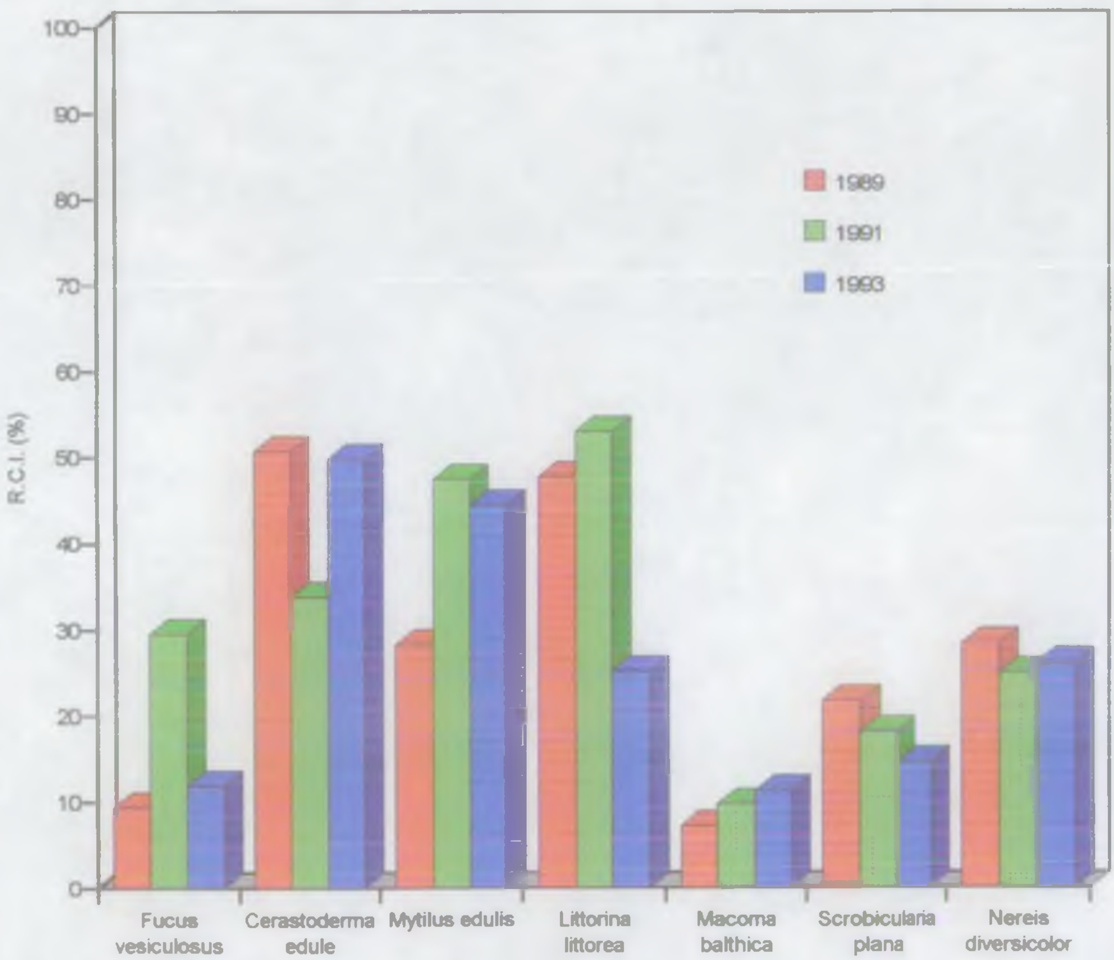


Figure 38

A. Nickel in Fucus vesiculosus, 1993.



B. Relative Contamination Indices for Nickel in Mersey Biota



rarely exceed baseline levels by more than an order of magnitude, which suggests that the overall level of nickel contamination in the Mersey is best described as moderate (see R.C.I.'s, Figure 38B). If individual sites are considered rather than mean values, once again however, at the upper limits of distribution some species such as *Cerastoderma edule* and *Mytilus edulis* exhibit nickel concentrations which approach or even exceed UK maximum levels as defined previously.

Table 13 Enrichment factors for nickel in Mersey 1993 species relative to UK baseline data.

Species	Enrichment Factor*
Fucus vesiculosus	3.45
Cerastoderma edule	2.57
Mytilus edulis	5.14
Littorina littorea	3.57
Macoma balthica	1.94
Scrobicularia plana	2.38
Nereis diversicolor	4.10

* - Mean value for all sites.

Lead

Data for lead in 1993 samples are presented in Appendix 10.

Spatial Trends

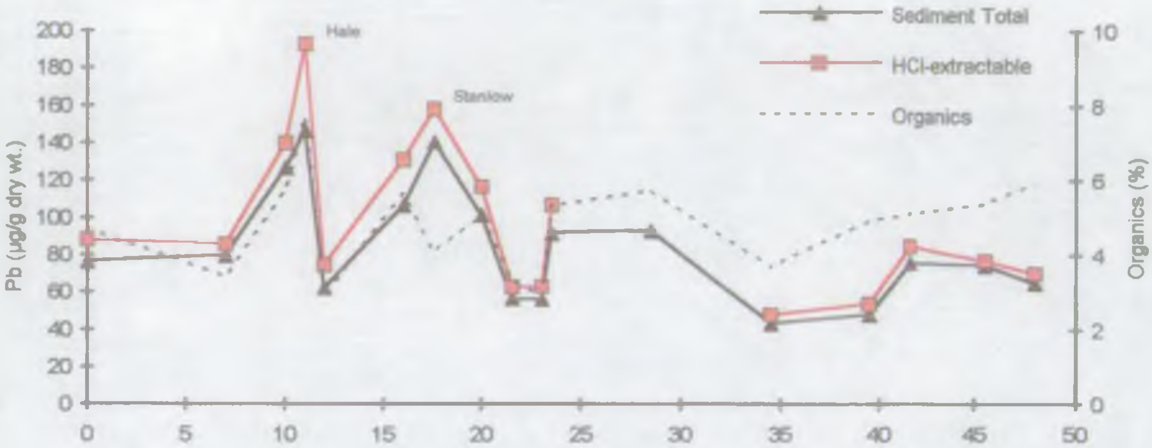
The profiles for total and HCl-extractable lead in sediments are shown in Figure 39A together with that for the sediment organic content. It can readily be seen that most of the lead in Mersey sediments is extractable with 1N HCl and therefore presumably, bioavailable. Again, sediment metal levels correlate significantly with organic content and show an overall decline seawards through the estuary but with peaks superimposed at certain sites. This pattern is also exhibited to some extent by *Nereis diversicolor*, which, although not a particularly good accumulator of lead, does show high levels at Hale (Figure 39B) corresponding with high lead levels in both sediment extracts at this site. High lead content in sediments at other sites are less apparent from the *Nereis diversicolor* profile, while some sites with lower sediment burdens such as at Eastham Lockgates correspond with unexpected high levels in *Nereis diversicolor*. This may be as a result of a difference in speciation of lead between these locations and hence a difference in bioavailability, since compounds such as tetraethyl lead (from likely sources in the Manchester Ship Canal) are known to be more easily taken up by organisms than inorganic lead compounds.

Fucus vesiculosus shows a sharp downstream drop in lead levels from Garston to Eastham, followed by a continuing slight decline seawards along the southern shore (Figure 39C) consistent with expected gradients of dissolved lead concentrations (presumably hydrophilic alkyl-leads) emanating from the mid-upper estuary. However, many benthic invertebrate species such as *Mya arenaria, Mytilus edulis* and *Macoma balthica* (and *Nereis diversicolor*) exhibit an increase from Garston towards Eastham Lockgates (which suggests that these species may be better at integrating inputs from the Manchester Ship Canal) followed by a more gradual decline downstream (Figure 40A). *Littorina littorea* and *Cerastoderma edule* whose upstream limits are at Eastham Lockgates, both show significant decreases in lead concentrations downstream (Figure 40B), and again, whenever a species occurs at Blundellsands, increases in their metal burdens are seen at that site.

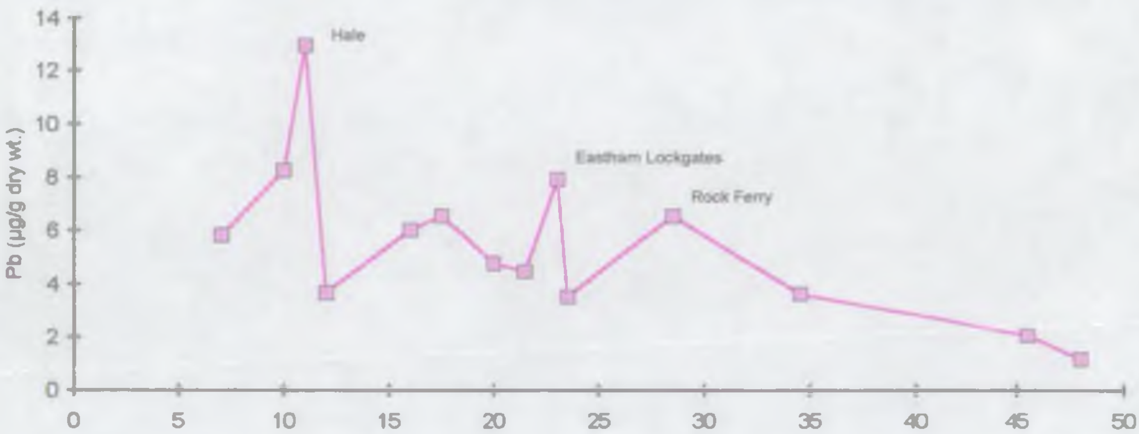
[NOTE: In the previous survey - 1991 - lead levels in *Fucus vesiculosus* also exhibited a clear peak at the mouth of the Manchester Ship Canal, although prior to that highest levels were at Garston. Compared with benthic invertebrates *Fucus vesiculosus* probably responds more quickly to transient changes in dissolved contaminants such as may occur in the upper estuary during 'levelling' operations in the canal. Therefore the precise location of maximum lead levels for *Fucus vesiculosus* may well not coincide entirely with that for benthic invertebrates, depending on recent hydrographic conditions].

Figure 39. Spatial trends for Lead, 1993.

A. Lead in Sediments, 1993.



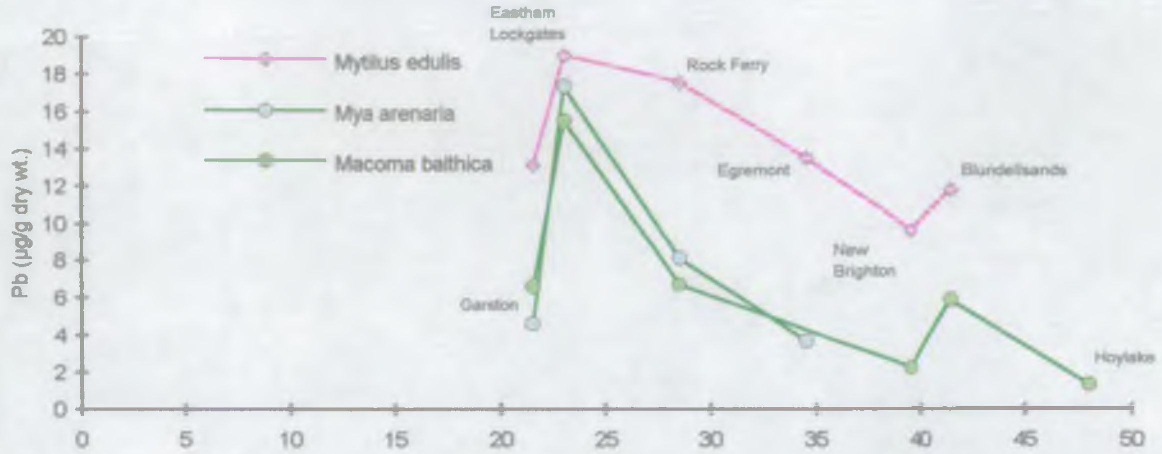
B. Lead in Nereis diversicolor, 1993.



C. Lead in Fucus vesiculosus, 1993.

Figure 40. Spatial trends for Lead, 1993.

A. Lead in Mytilus edulis, Mya arenaria and Macoma balthica, 1993.



B. Lead in Cerastoderma edule and Littorina littorea, 1993.

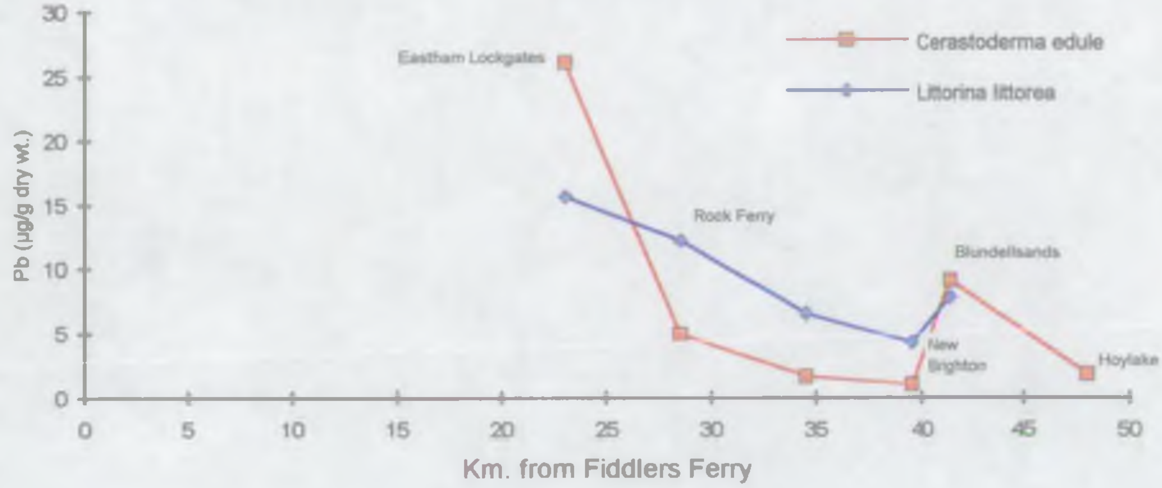
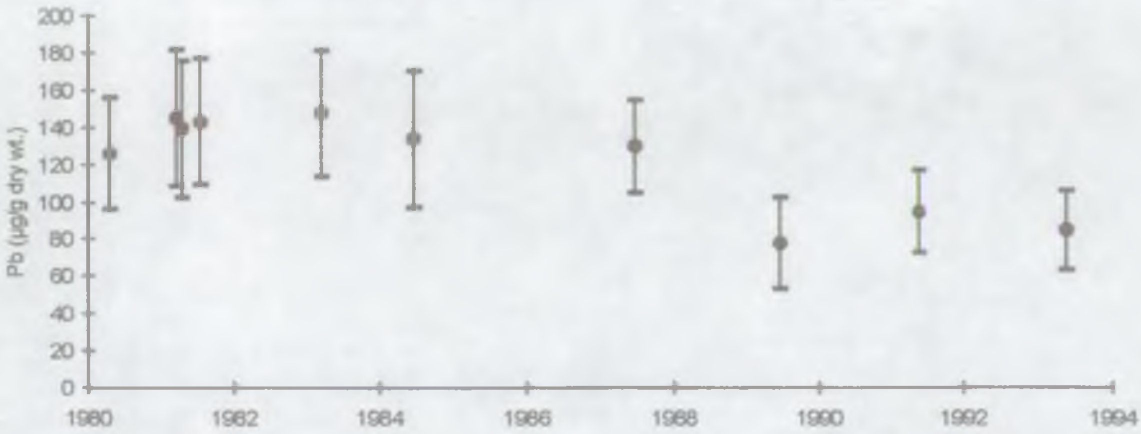
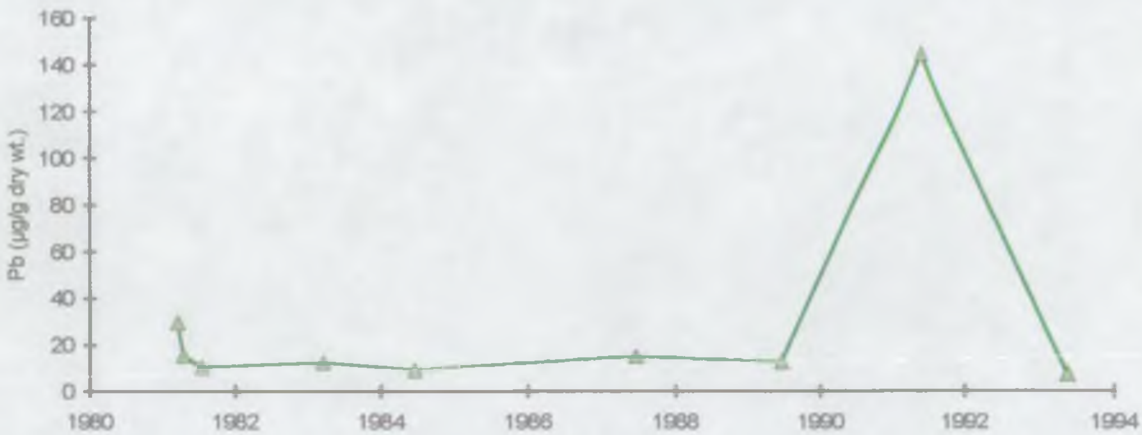


Figure 41. Temporal trends for Lead, 1980 - 1993.

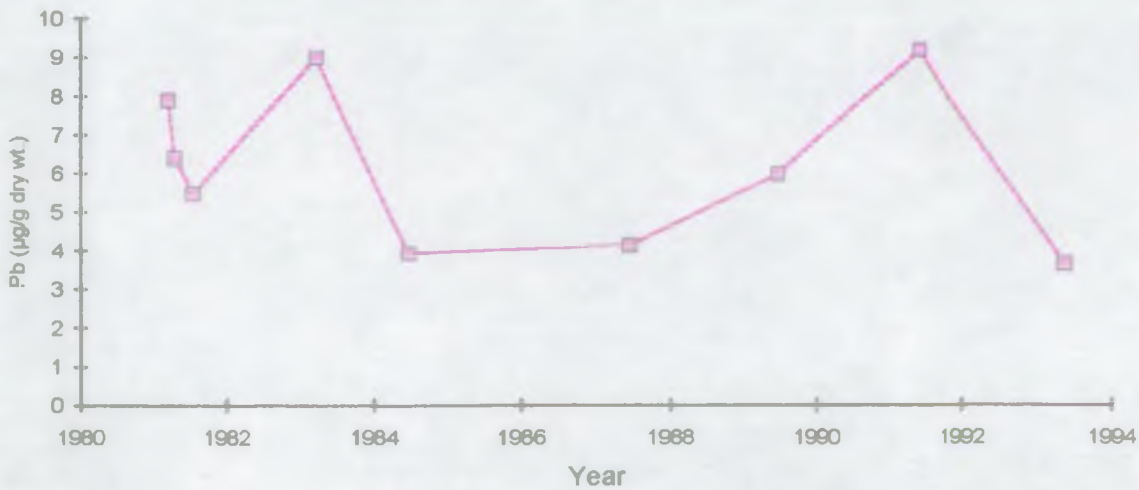
A. Total Lead in Sediments, 1980 - 1993.



B. Lead in Fucus vesiculosus at Eastham, 1980 - 1993.



C. Lead in Nereis diversicolor at Egremont, 1980 - 1993.



Temporal Trends

Although there have been small significant ($P < 0.0001$) decreases in average sediment lead levels since surveys began in 1980, there has been no change in recent years (Figure 41A). In contrast, reduction of lead levels in biota have been a more obvious feature, particularly in earlier surveys (1980 - 1984), although these reductions are site and species dependent. The average percentage decrease in lead concentrations between 1980 and 1987 were:

Fucus vesiculosus	75%
Nereis diversicolor	56%
Littorina littorea	51%
Scrobicularia plana	28%
Macoma balthica	21%
Mytilus edulis	14%

Data for *Fucus vesiculosus* (probably the best indicator of alkyl-lead species), and *Nereis diversicolor* (the most widespread species) show that reductions have, not surprisingly, been most noticeable at upstream sites and took place between 1980 and 1984. Current results indicate that there has been no significant change in lead levels since the last survey for any of the species collected. This may however hide changes at particular sites. For example, high lead levels in *Fucus vesiculosus* at Eastham reported in the last survey, appear to have now declined to previous levels, and perhaps record the effect of a pulse input in 1991 (Figure 41B). A similar but less extreme event can be seen for *Nereis diversicolor* at Egremont where the trend for gradually increasing levels between 1987 and 1991 appears to have reversed by 1993 (Figure 41C).

Comparisons with other estuaries

Lead concentrations in biota from UK estuaries cover a range spanning 2 - 3 orders of magnitude. Thus, although enrichment factors for mean Mersey data, relative to UK minimum values (Table 14), are in some instances quite high (notably in *Fucus vesiculosus*, indicating the relative importance of hydrophilic alkyl-lead) the actual mean levels are considerably lower than the highest UK levels, most common in metalliferous mining regions (inorganic lead). This is reflected in the Relative Contamination Indices for lead in Mersey species (Figure 42). However, there are considerable variations in lead levels between sites for each species, with highest levels often occurring towards the upper limits of distribution as already described, while in the lower estuary, levels are considerably reduced. Thus, for the majority of species, values span more than an order of magnitude, and in the case of *Cerastoderma edule* collected from the entrance to the Manchester Ship Canal values are in excess of previous UK maxima. Such variability must be considered when attempting to classify or rank the estuary as a whole.

Figure 42

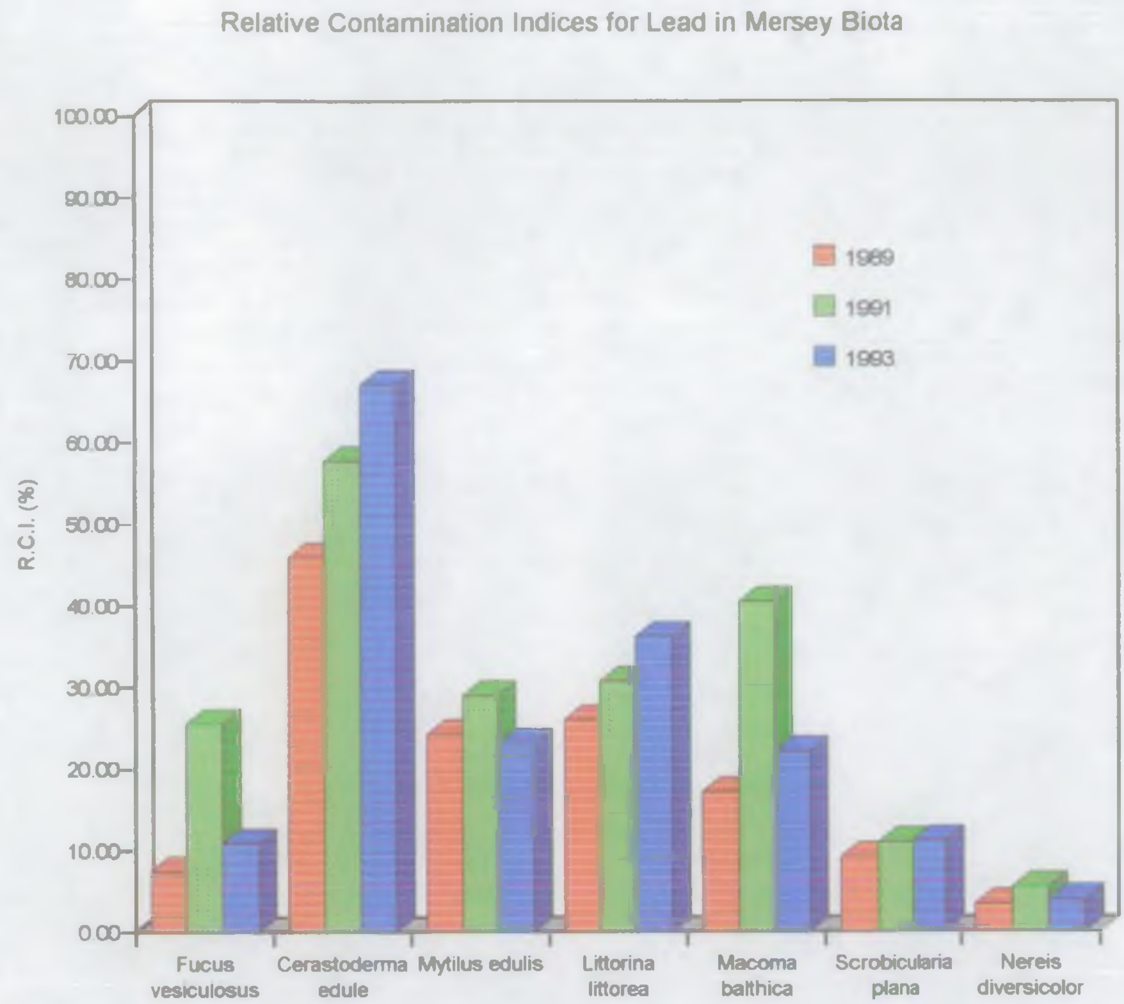

Relative Contamination Indices for Lead in Mersey Biota
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
R.C.I. (%)
1989
1991
1993
Fucus vesiculosus
Cerastoderma edule
Mytilus edulis
Littorina littorea
Macoma balthica
Scrobicularia plana
Nereis diversicolor

Table 14 Enrichment factors for lead in Mersey 1993 species relative to UK baseline data.

Species	Enrichment Factor*
Fucus vesiculosus	17.66
Cerastoderma edule	4.97
Mytilus edulis	4.45
Littorina littorea	10.09
Macoma balthica	2.27
Scrobicularia plana	5.95
Nereis diversicolor	13.06

* - Mean value for all sites.

Selenium

Data for selenium in 1993 samples are presented in Appendix 11.

Spatial Trends

The concentrations of selenium in Mersey sediments range from 0.2 - 1.2 µg/g dry weight. Peak values occur at Hale and Stanlow, and overall, concentrations are significantly correlated to the organic content of the sediments ($r = 0.73$, $P = 0.0008$), as shown in Figure 43A.

Since selenium is an essential element and perhaps regulated in some species, the range of concentrations along the length of the estuary is not extensive, though there is some evidence of contamination. The profile for selenium accumulation in *Nereis diversicolor* is somewhat different to that seen for most metals in that the peak at Hale is not evident. Instead, the highest levels of selenium in *Nereis diversicolor* occur at Oglet, with elevated levels also at Stanlow, Garston and Eastham Lockgates together with Hightown in the outer estuary (Figure 43B). Overall there is no significant correlation between selenium levels in sediments and *Nereis diversicolor.*

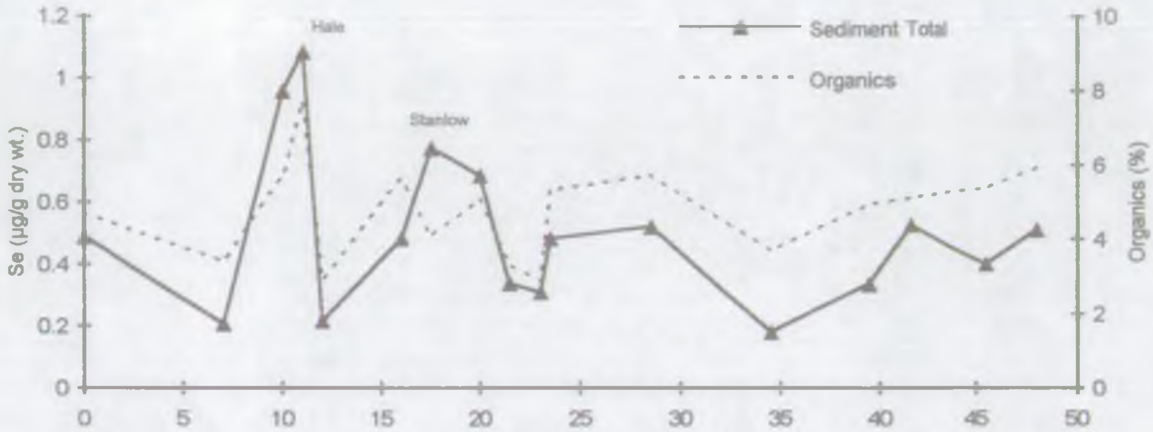
Of the remaining invertebrate species (Figures 43C - 44B), all show a trend towards a reduction in concentration seawards from Eastham Lockgates (generally in line with observations for sediments and *Nereis diversicolor*), although the magnitude of this decrease varies. Additionally, species which also occur at Garston tend to show lower levels at this location on the northern shore of the estuary than at Eastham Lockgates almost directly opposite on the south bank, possibly indicating that the Manchester Ship Canal may provide a source of selenium. This is also apparent in *Fucus vesiculosus*, although in the lower half of the estuary the profile for *Fucus vesiculosus* increases seawards suggesting increasing concentrations of dissolved selenium in that direction (Figure 44C). However, the oxidation state is of major significance for selenium accumulation (Se^{4+} is much more readily available than Se^{6+}) and may well influence profiles within the estuary, especially in *Fucus vesiculosus.* Increased levels of selenium in species at Blundellsands are less apparent than for some other metals.

Temporal Trends

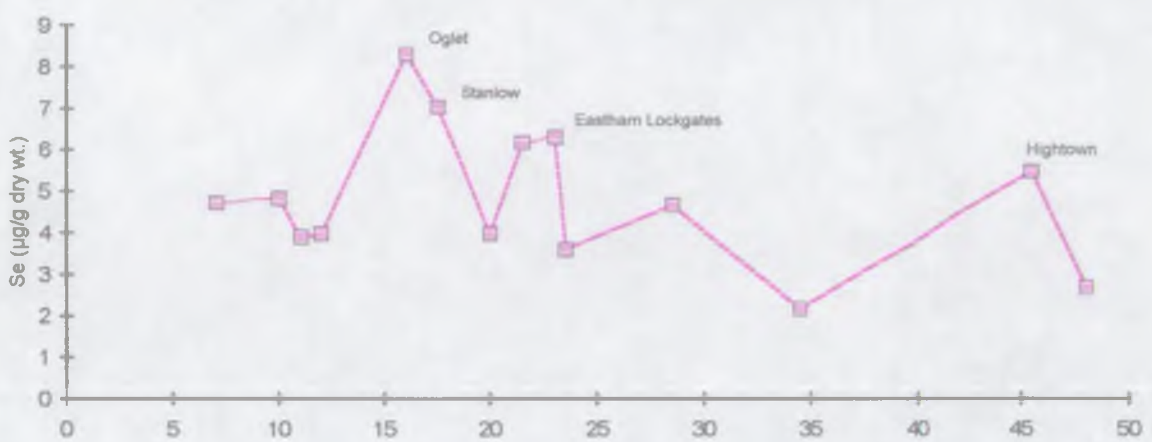
Data for selenium is limited to that from the 1983 survey onwards. As a consequence, temporal trends can be established with less certainty than for other metals. Sediment selenium levels have shown significant changes since 1983, both increasing and decreasing, but over a very small concentration range (< 1 µg/g) as shown in Figure 45A. It can be seen that while the 1991 survey showed a significant increase compared to 1989, data for 1993 indicates a return to levels similar to those of 1989. Data for biota show that over the estuary as a whole there have been no significant changes in selenium levels since 1991 except in the case of *Macoma balthica* which has seen a slight increase from 2.17 µg/g to 3.82 µg/g

Figure 43. Spatial trends for Selenium, 1993.

A. Selenium in Sediments, 1993.



B. Selenium in Nereis diversicolor, 1993.



C. Selenium in Scrobicularia plana, 1993.

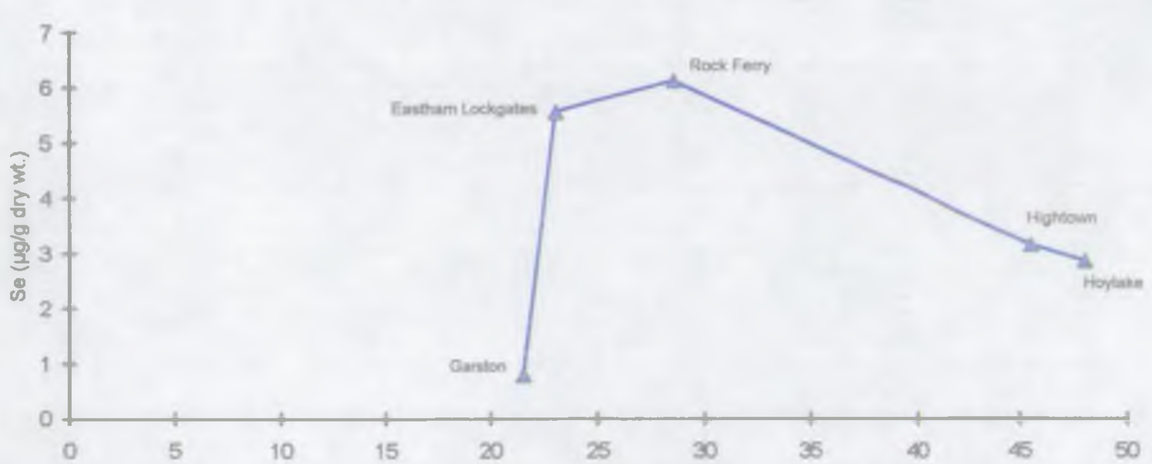
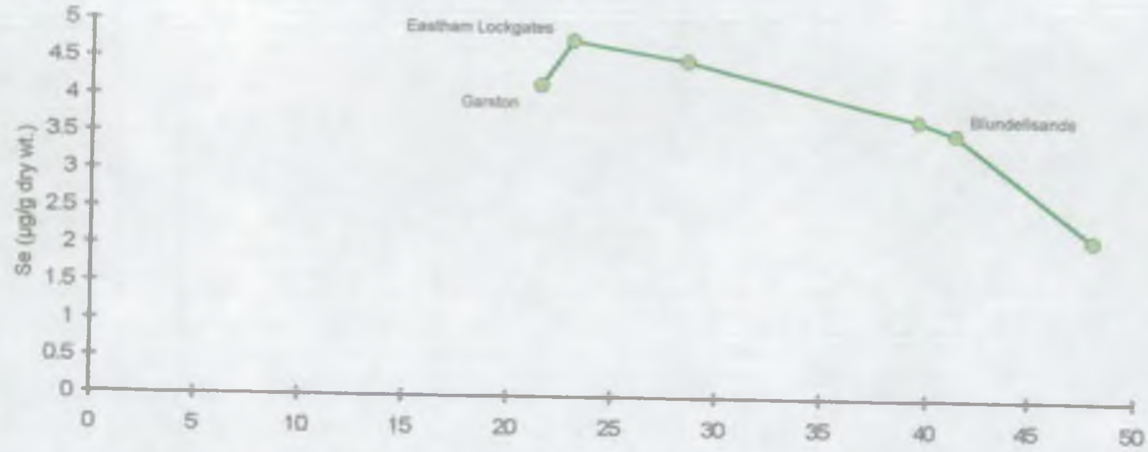
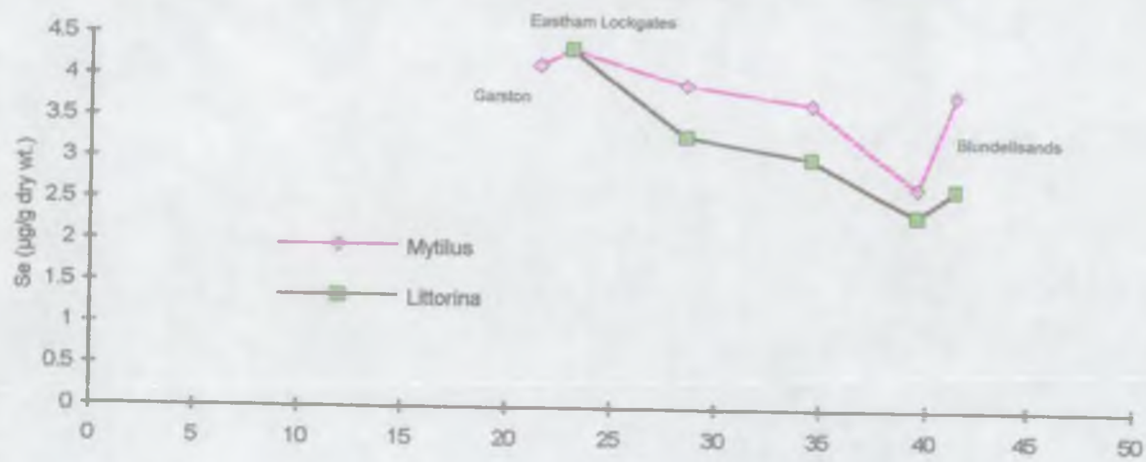


Figure 44. Spatial trends for Selenium, 1993.

A. Selenium in Macoma balthica, 1993.



B. Selenium in Mytilus edulis & Littorina littorea, 1993.



C. Selenium in Fucus vesiculosus, 1993.

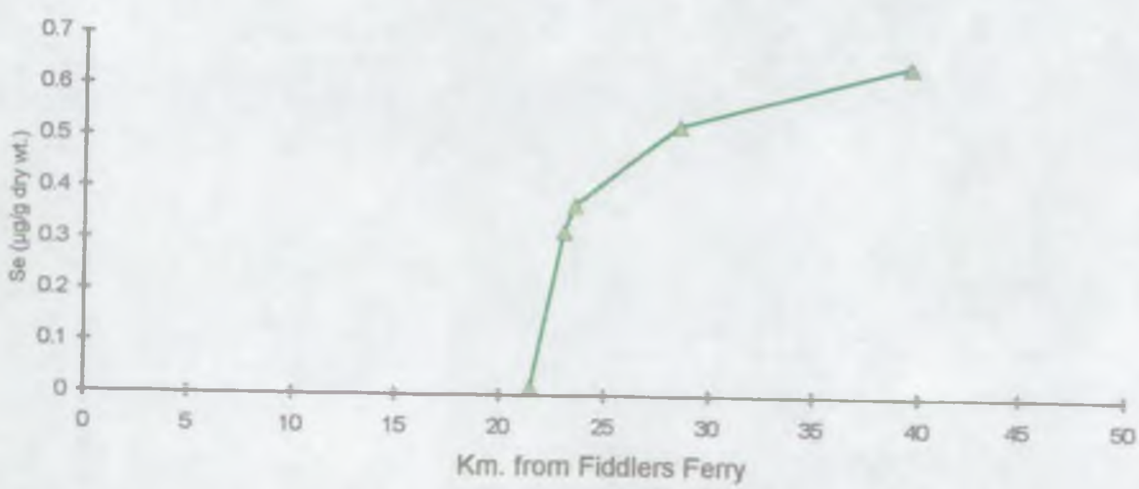
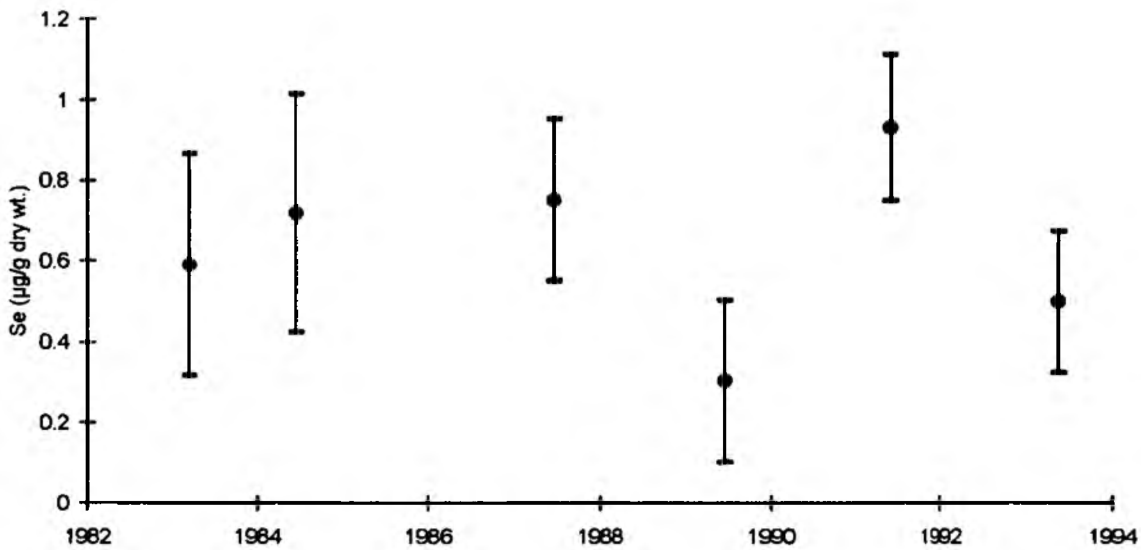
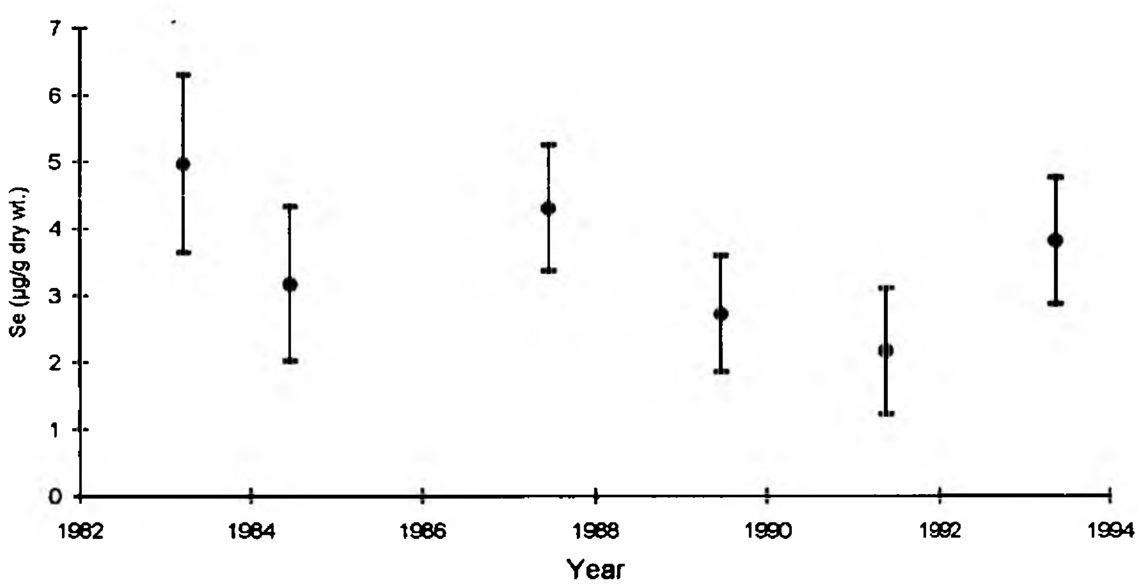


Figure 45. Temporal trends for Selenium, 1983 - 1993.

A. Total Selenium in Sediments, 1983 - 1993.



B. Selenium in Macoma balthica, 1983 - 1993.



(Figure 45B). Likewise, long term comparisons indicate no significant time dependent changes since 1983 ($P > 0.05$, ANOVA).

Comparisons with other estuaries

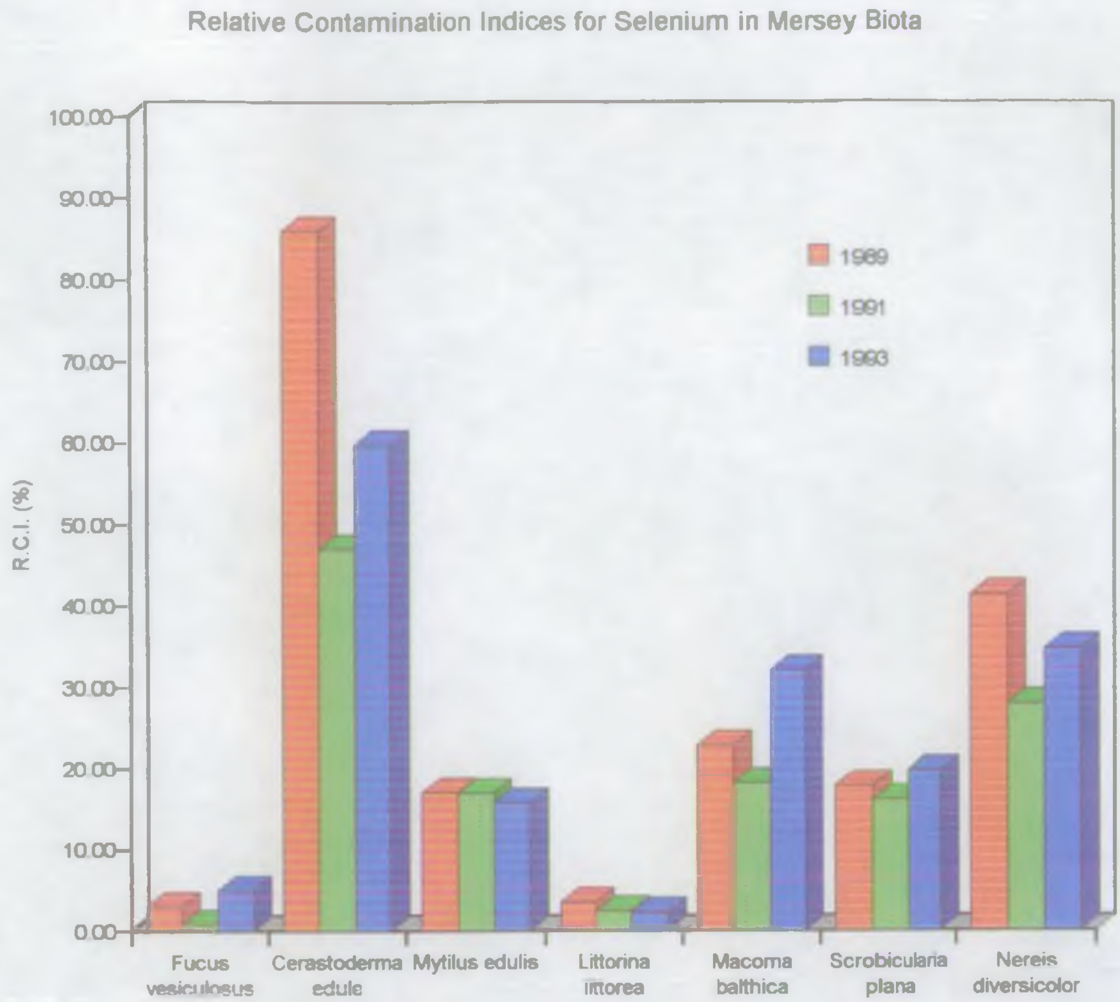
Data for selenium in UK estuarine biota are not so extensive compared to that for many other metals so that comparisons are perhaps somewhat less valid for this element than others. Also, since selenium is regarded as an essential element, regulation of tissue burdens in many organisms is likely to obscure small differences in environmental contamination. (Interestingly the distinction between essential and toxic levels for selenium are considered to be relatively small). Enrichment factors relative to UK baseline data are shown in Table 15 where it can be seen that values for most species exceed baseline levels by a factor of 3 or less. The exception is *Fucus vesiculosus* which has an enrichment factor of almost 18. However, the range of concentrations encountered in this species in the UK spans two orders of magnitude, and the baseline level is also very low. Thus, for all species monitored in 1993 mean selenium levels lie within the lowest 20% of values recorded on our database (Figure 46), and the level of contamination in the Mersey is best described as low - moderate, and only at the more contaminated upstream sites is accumulation significant.

Table 15 Enrichment factors for selenium in Mersey 1993 species relative to UK baseline data.

Species	Enrichment Factor*
Fucus vesiculosus	17.86
Cerastoderma edule	1.26
Mytilus edulis	1.71
Littorina littorea	3.09
Macoma balthica	1.57
Scrobicularia plana	1.99
Nereis diversicolor	2.47

* - Mean value for all sites.

Figure 46


Relative Contamination Indices for Selenium in Mersey Biota
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
R.C.I. (%)
1989
1991
1993
Fucus vesiculosus
Cerastoderma edule
Mytilus edulis
Littorina littorea
Macoma balthica
Scrobicularia plana
Nereis diversicolor

Tin

Data for tin in 1993 samples are presented in Appendix 12.

Spatial Trends

The profiles for total, and HCl-extractable tin in Mersey sediments (Figure 47A) are of a similar pattern to those of many other metals, and correlate significantly with the sediment organic content (HCl: r = 0.53, P = 0.028; Total: r = 0.74, P = 0.0007).

The distribution of tin concentrations in *Nereis diversicolor* along the estuary are significantly correlated with the HCl-extractable fraction (r = 0.58, P = 0.036), and to a lesser extent, total tin (r = 0.57, P = 0.041). It is clear from this profile (Figure 47B) that tin appears to be particularly bioavailable to *Nereis diversicolor* at Hale compared with other sites.

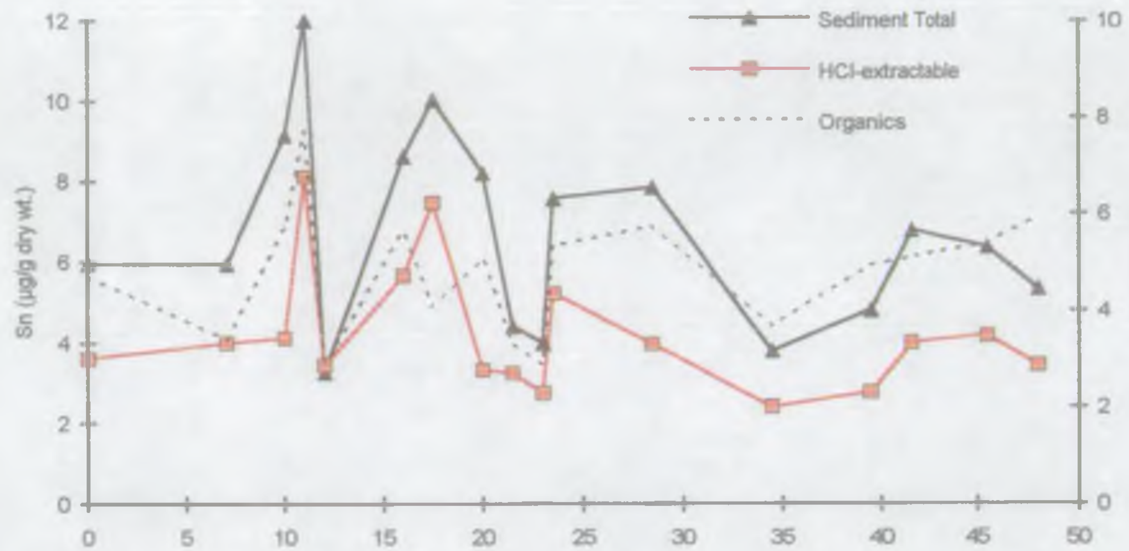
In most other species tin concentrations decrease in a seaward direction. The profiles for *Mya arenaria* and *Scrobicularia plana* are shown in Figures 48A - 48B. Profiles for *Fucus vesiculosus* and *Littorina littorea* are very significantly correlated (r = 0.98, P = 0.017) as shown in Figure 48C which may reflect the fact that *Fucus vesiculosus* is often a primary food source for this herbivorous gastropod. *Mytilus edulis* again shows an upturn in tissue levels at Blundellsands, while *Cerastoderma edule* also has its maximum tin concentrations at this location (Figure 49A & 49B), in common with many other metals. The profile for *Macoma balthica* is very different and shows elevated levels at New Brighton (Figure 49C).

Temporal Trends

Analysis of the data for total tin concentrations in Mersey sediments since 1980 indicate that levels have been lower since 1989, compared to earlier in the decade. Additionally, there has been no significant reduction in total tin levels since the last survey in 1991. Trends for HCl-extractable tin however (Figure 50A), indicate a gradual reduction in levels in this fraction since 1984 (P < 0.0001, ANOVA). This pattern is to a certain extent reflected in the mean tin concentrations in *Nereis diversicolor*, where there has been an overall trend (P = 0.0035, ANOVA) for reduction in mean levels the early 1980's (Figure 50B). There has not however, been any significant change in tin levels in any species since the last survey in 1991. It seems likely that the longer-term reductions in tin observed in the majority of species may be related to a decline in use of highly bioavailable organotins, especially tributyltin (TBT) following legislation restricting their use on small vessels, introduced in the 1980's, coupled with the decline in commercial shipping activity during that decade. Although reductions of other forms of tin cannot be discounted, it is interesting to note the high concentrations of tin in *Mya arenaria* at upstream sites in the Mersey (up to 14 µg/g): *Mya arenaria* is unique in its ability to accumulate TBT (Langston *et al* 1987), suggesting that organotins are indeed the most likely form of bioavailable tin in the estuary.

Figure 47. Spatial trends for Tin, 1993.

A. Tin in Sediments, 1993.



B. Tin in Nereis diversicolor, 1993.

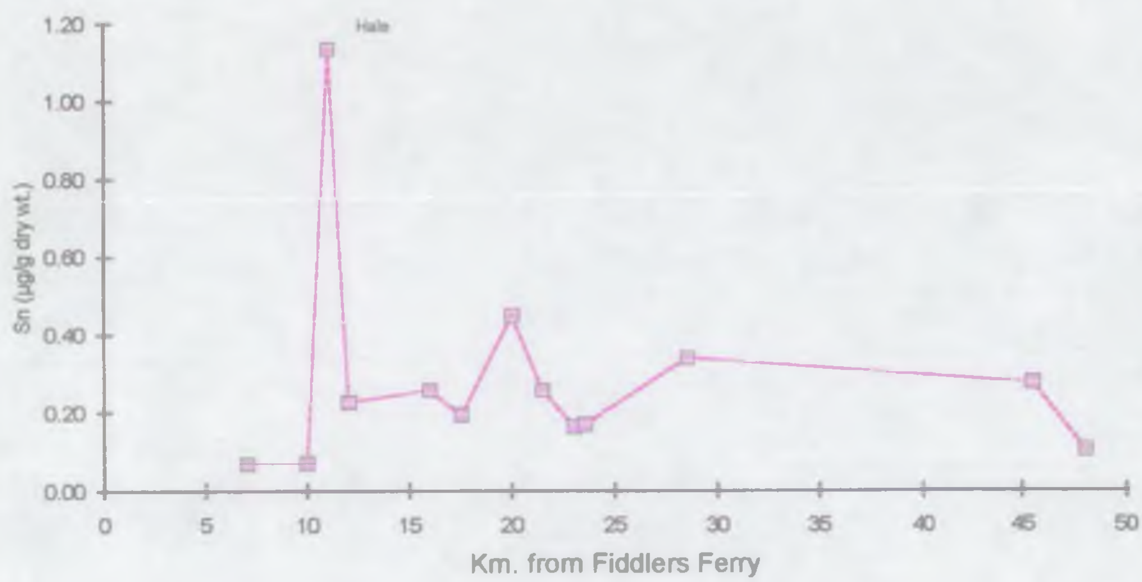
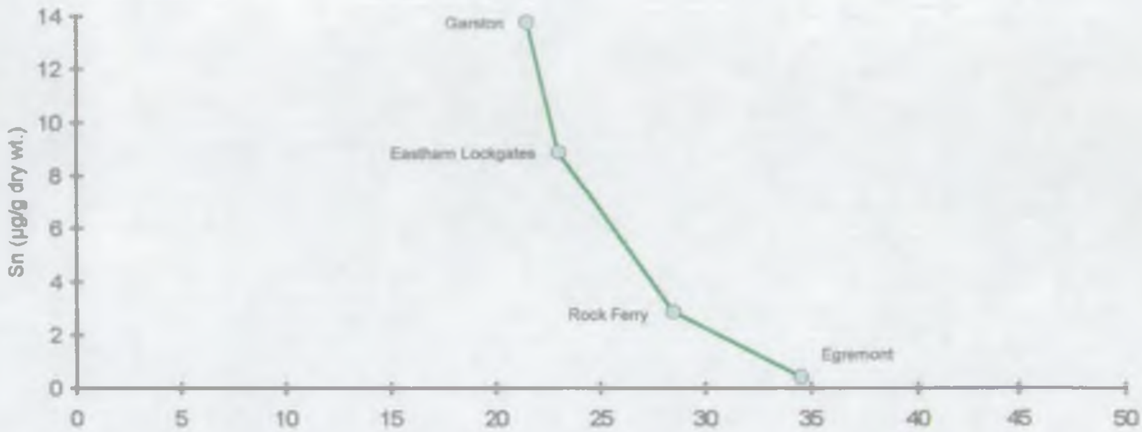
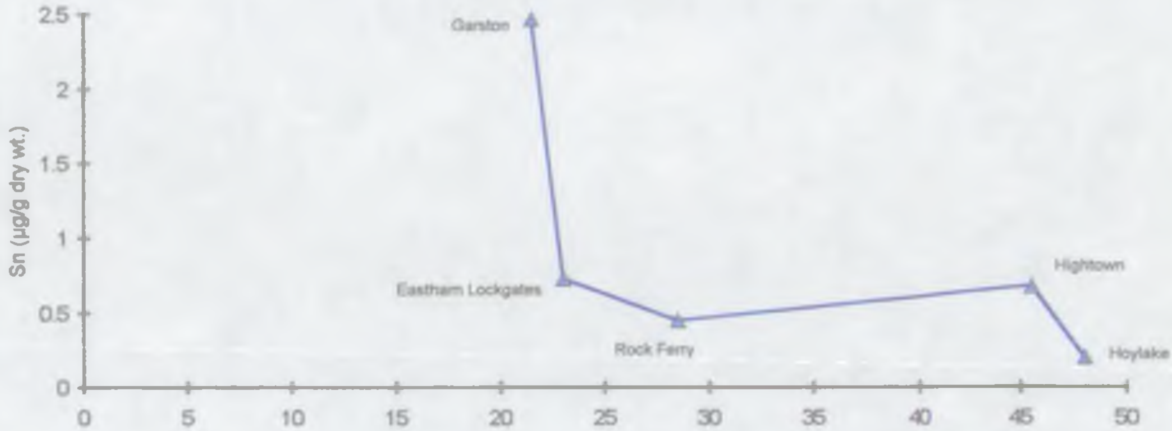


Figure 48. Spatial trends for Tin, 1993.

A. Tin in Mya arenaria, 1993.



B. Tin in Scrobicularia plana, 1993.



C. Tin in Fucus vesiculosus and Littorina littorea, 1993.

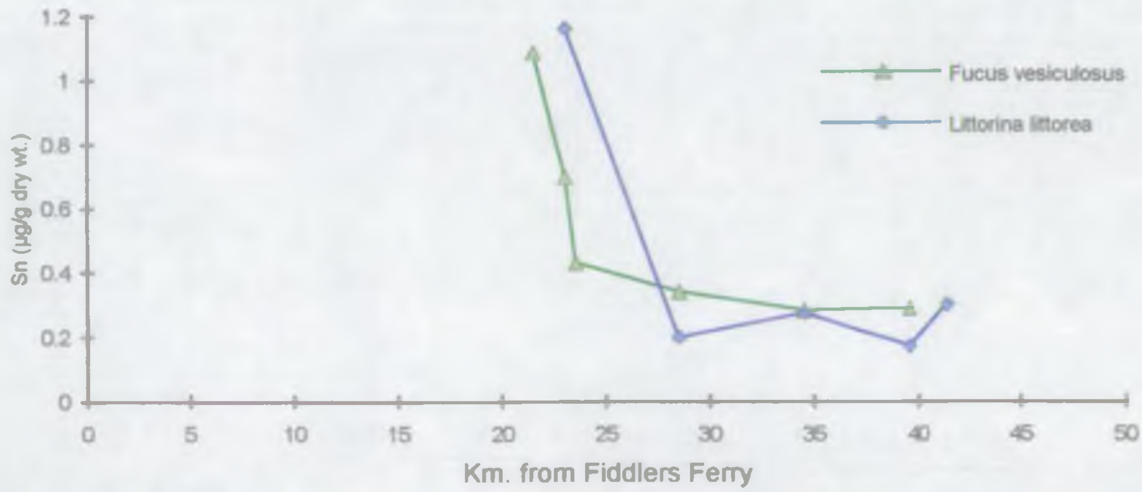


Figure 49. Spatial trends for Tin, 1993.

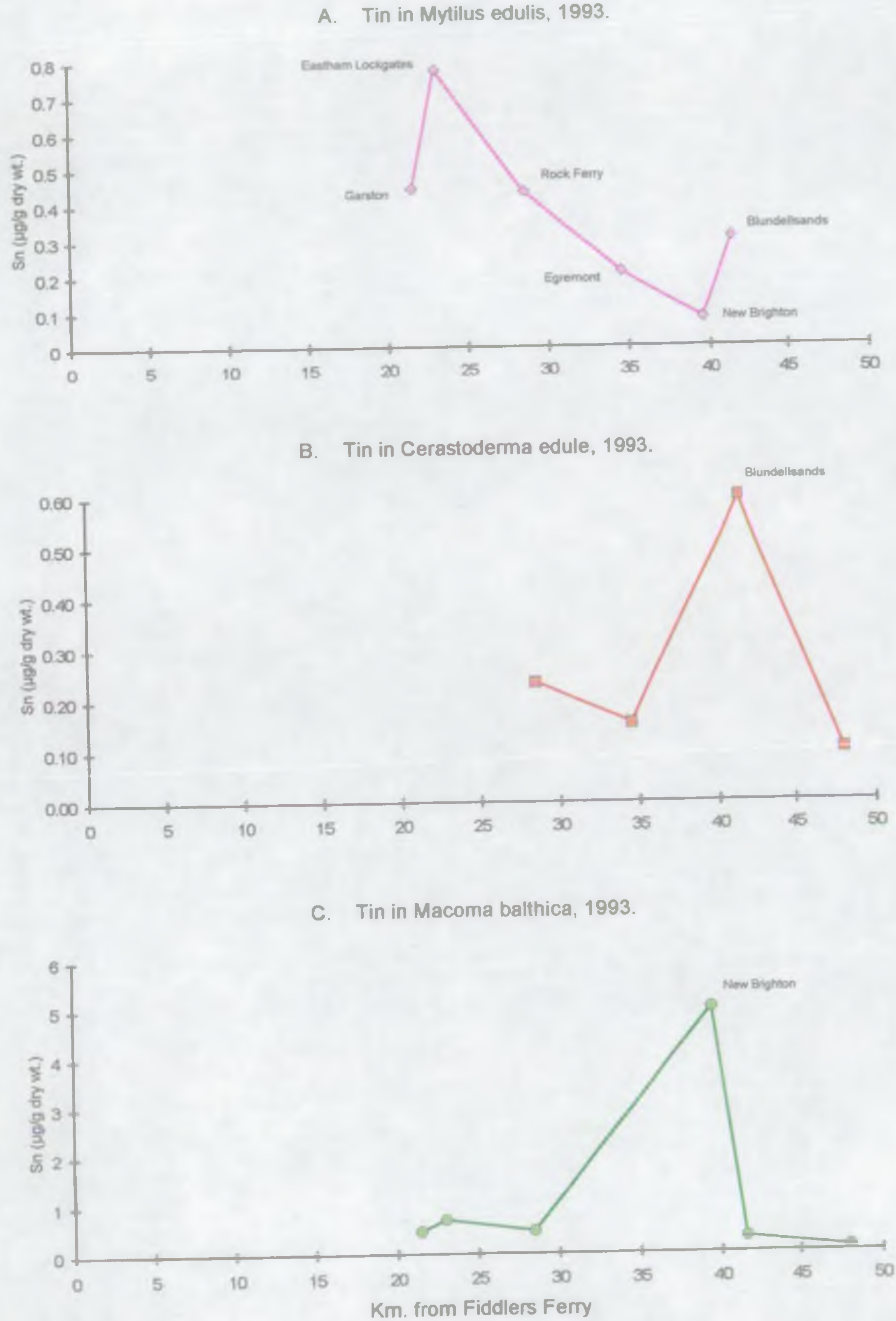
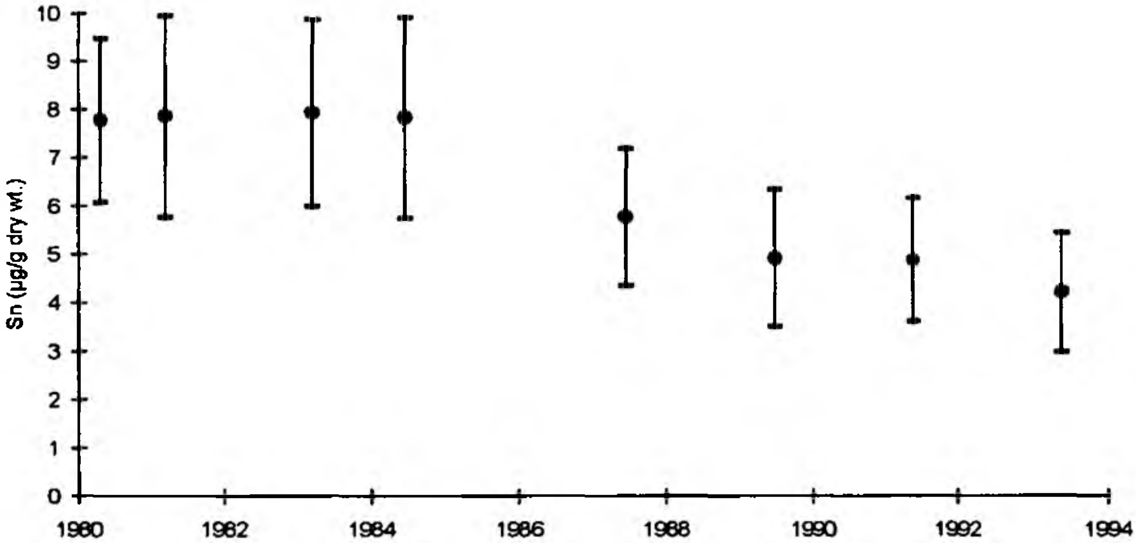


Figure 50. Temporal trends for Tin, 1980 - 1993.

A. Tin in Sediment HCl Extracts, 1980 - 1993.



B. Tin in Nereis diversicolor, 1980 - 1993.

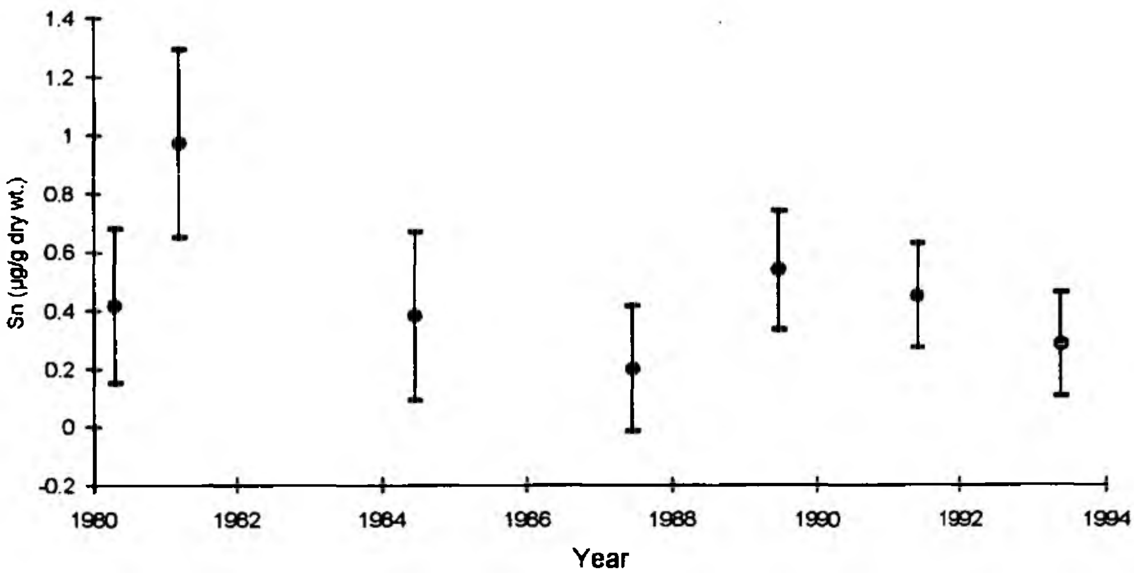
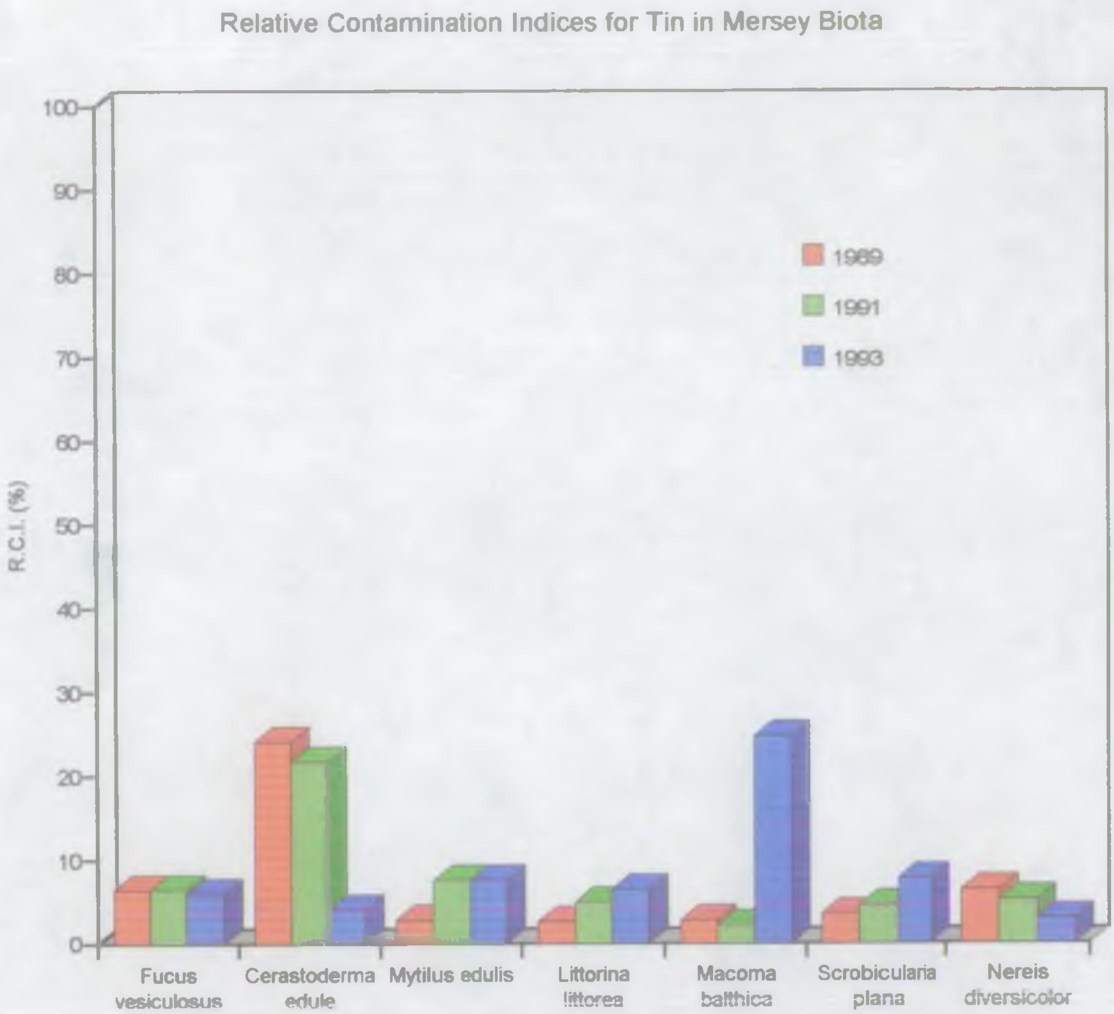


Figure 51


Relative Contamination Indices for Tin in Mersey Biota
R.C.I. (%)
100
90
80
70
60
50
40
30
20
10
0
1989
1991
1993
Fucus vesiculosus
Cerastoderma edule
Mytilus edulis
Littorina littorea
Macoma balthica
Scrobicularia plana
Nereis diversicolor

Comparisons with other estuaries

Enrichment factors for mean tin concentrations in Mersey biota relative to UK baseline data range from 1.39 (*Cerastoderma edule*) to 22.26 (*Littorina littorea*) as shown in Table 16. These mean levels may be considered as relatively unremarkable however, compared to concentrations recorded in species from estuaries heavily impacted with organotins. An exception is the case of *Macoma balthica* from Hoylake which in 1993 contained the third highest concentration of tin recorded for that species, although as mentioned earlier, the source of this contamination remains unknown. Similarly, the elevated concentrations in *Mya arenaria* at upstream sites are indicative of inputs (as TBT). Relative Contamination Indices for mean tin concentrations in Mersey species (Figure 51) provide a simplified view and suggest that overall contamination is best described as moderate.

Table 16 Enrichment factors for tin in Mersey 1993 species relative to UK baseline data.

Species	Enrichment Factor*
Fucus vesiculosus	16.90
Cerastoderma edule	1.39
Mytilus edulis	9.38
Littorina littorea	22.26
Macoma balthica	4.25
Scrobicularia plana	7.04
Nereis diversicolor	4.47

* - Mean value for all sites.

Zinc

Data for zinc in 1993 samples are presented in Appendix 13.

Spatial Trends

Profiles for total and HCl-extractable zinc in Mersey sediments are shown in Figure 52A, where a significant overall gradient declining seawards can be seen for both extracts. In the case of total zinc there is a significant correlation with the sediment organic content ($r = 0.50$, $P = 0.043$).

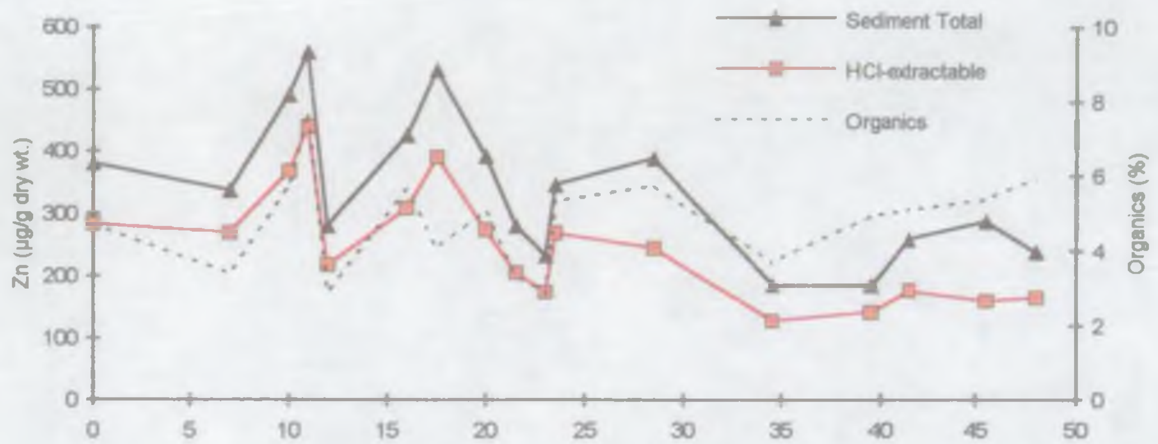
Zinc is an essential element in many invertebrates, where it is a component of enzyme systems. Zinc uptake is therefore often regulated, as for example by *Nereis diversicolor* where, as shown in Figure 52B, zinc levels generally lie in the range 100 - 200 µg/g. An exception is at Hale where higher levels are found, which may indicate that regulatory mechanisms are unable to cope with the high concentrations of zinc found in the sediments at this site. The deposit feeding bivalves *Scrobicularia plana* and *Macoma balthica* show decreasing tissue zinc burdens downstream from Eastham Lockgates (Figure 52C), but as has been seen for many other metals there is a steep rise prior to this from Garston, on the opposite bank of the estuary (*S. plana*). This steep Garston / Eastham Lockgates rise is also apparent for *Mya arenaria* and *Mytilus edulis* (Figure 53A), and since sediment levels are not dramatically different at these sites, it suggests that zinc is more available at Eastham Lockgates, probably in solution. Zinc like cadmium has a tendency to remain in solution in estuaries, so the uptake of dissolved zinc may therefore be significant for many organisms. Zinc accumulation by *Fucus vesiculosus* tends to be relatively high compared with many other species, and it is therefore considered to be a good indicator of dissolved zinc. The results of the current survey for *Fucus vesiculosus* (Figure 53B) show that levels generally increase upstream, particularly at Eastham Lockgates, perhaps indicating an input of dissolved zinc via the Manchester Ship Canal. Although *Littorina littorea* feeds on *Fucus vesiculosus*, it is also fairly efficient at regulating zinc and shows very little variation in concentrations throughout the estuary (Figure 53C).

Temporal Trends

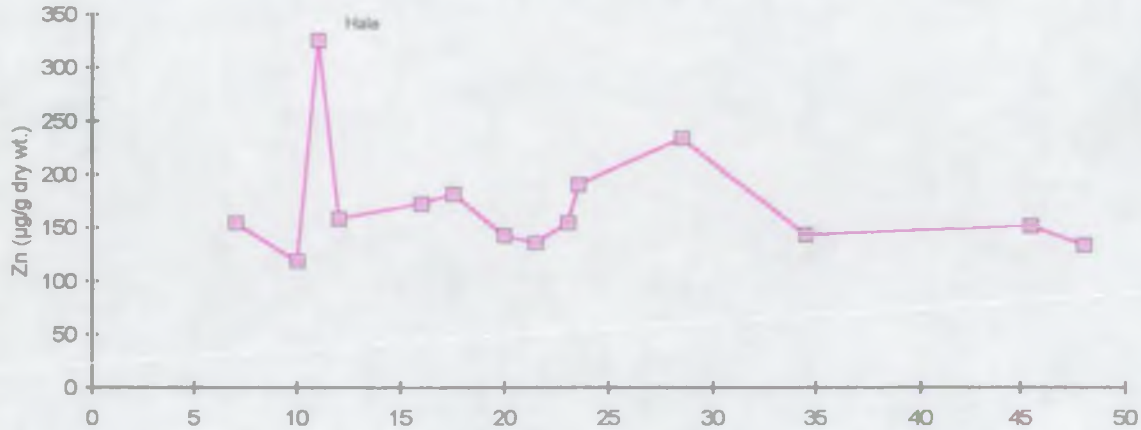
Analysis of data for total and HCl-extractable zinc in sediments since 1980 shows that small but significant decreases have occurred from the higher levels prevalent in the early 1980's, to the lower levels of the late 1980's. There have not however been any significant changes in mean zinc concentrations in Mersey sediments between 1989 and 1993 (Figure 54A). Dissolved zinc concentrations, as indicated by *Fucus vesiculosus* have shown a similar, highly significant change with time from very high levels in 1980 - 1981, down to lower levels recently. However, once again, there has been no significant change between the last 3 or 4 surveys (Figure 54B). *Macoma balthica* and *Scrobicularia plana* both showed significant changes in zinc burdens in the early surveys, although further changes have not occurred since 1984 (Figures 54C - 55A). *Nereis diversicolor*, *Littorina littorea*, *Mytilus edulis* and *Cerastoderma edule* do not

Figure 52. Spatial trends for Zinc, 1993.

A. Zinc in Sediments, 1993.



B. Zinc in Nereis diversicolor, 1993.



C. Zinc in Scrobicularia plana and Macoma balthica, 1993.

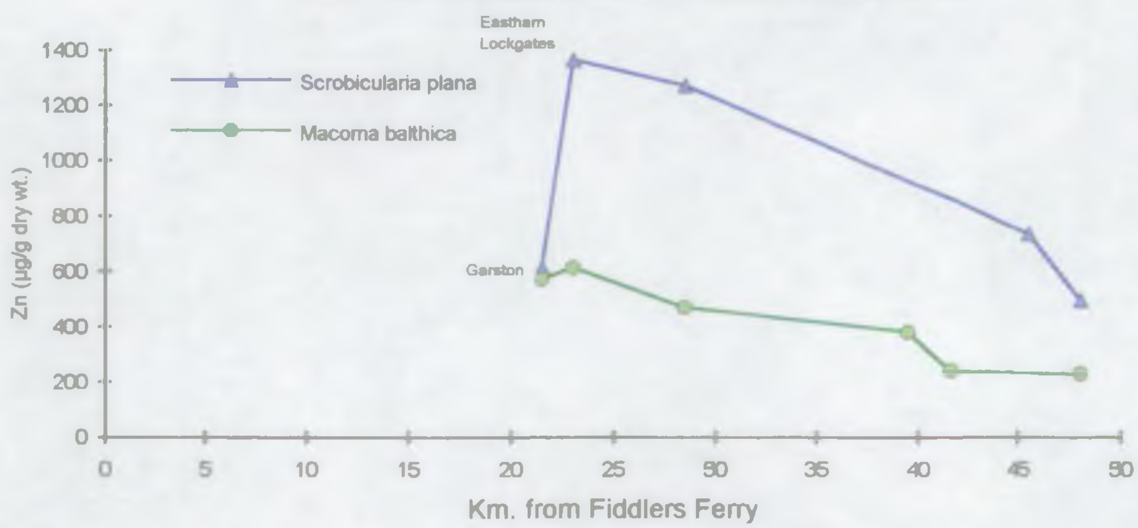
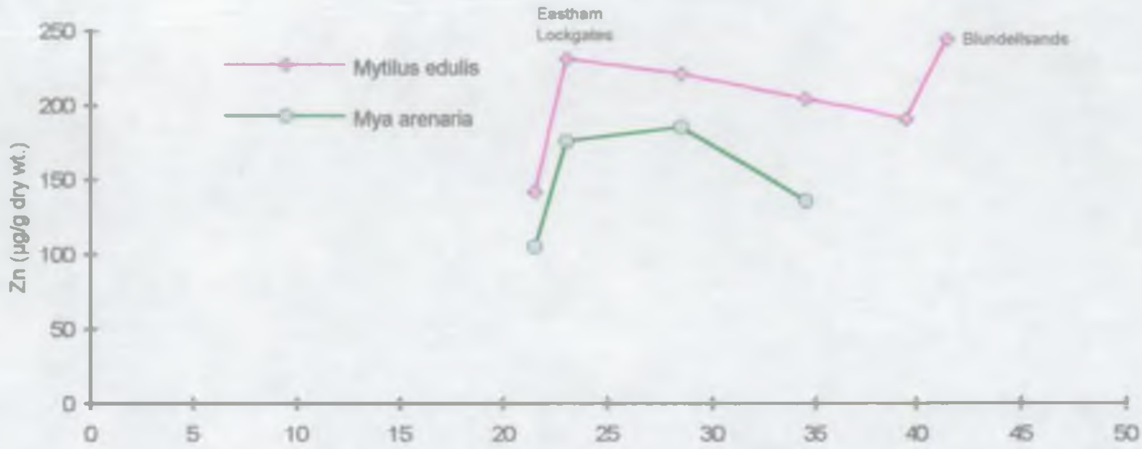
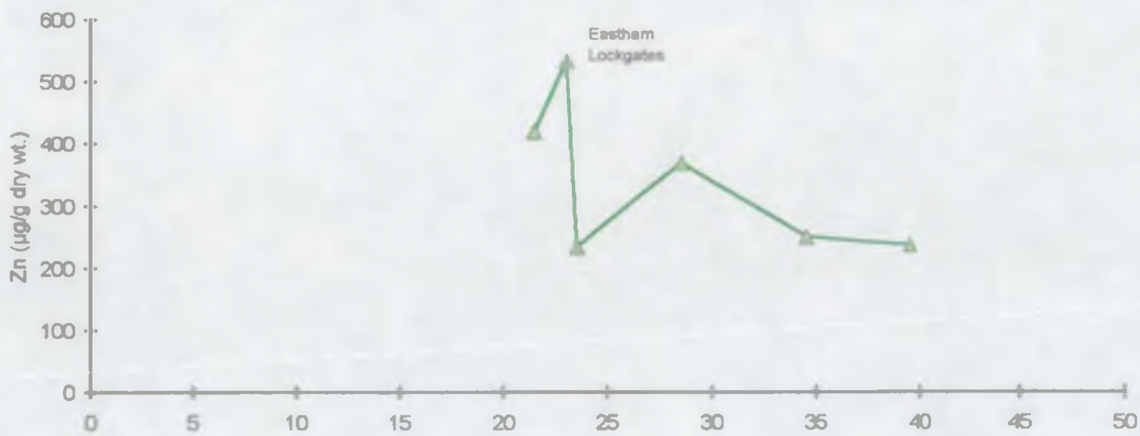


Figure 53. Spatial trends for Zinc, 1993.

A. Zinc in Mytilus edulis and Mya arenaria, 1993.



B. Zinc in Fucus vesiculosus, 1993.



C. Zinc in Littorina littorea, 1993.

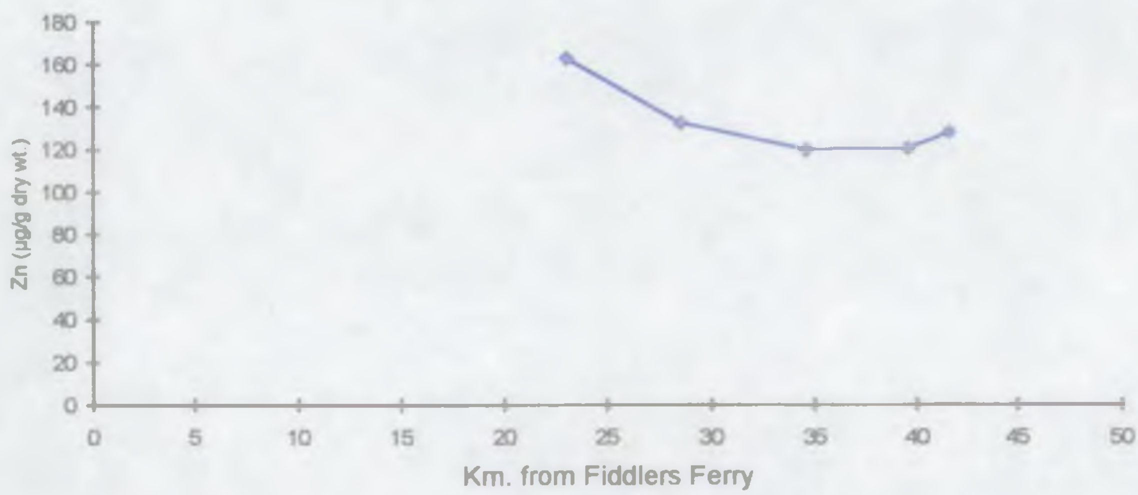
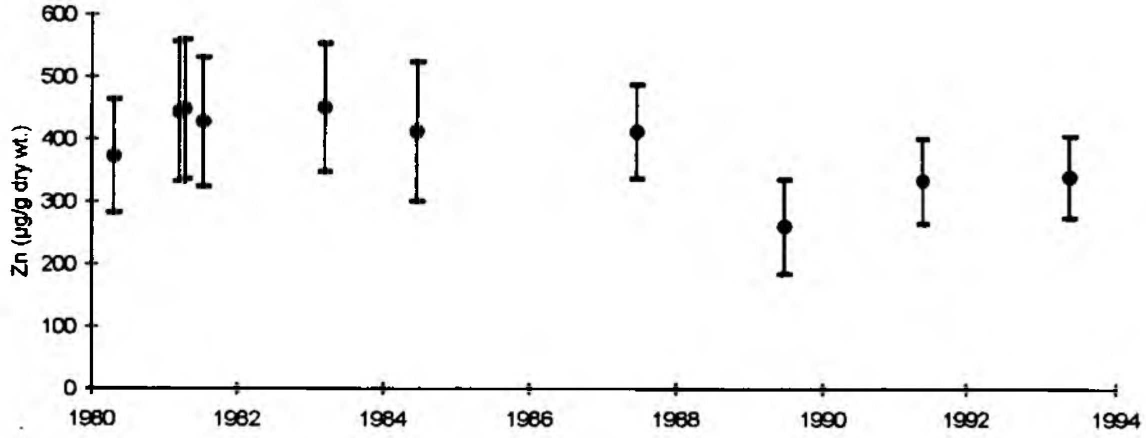
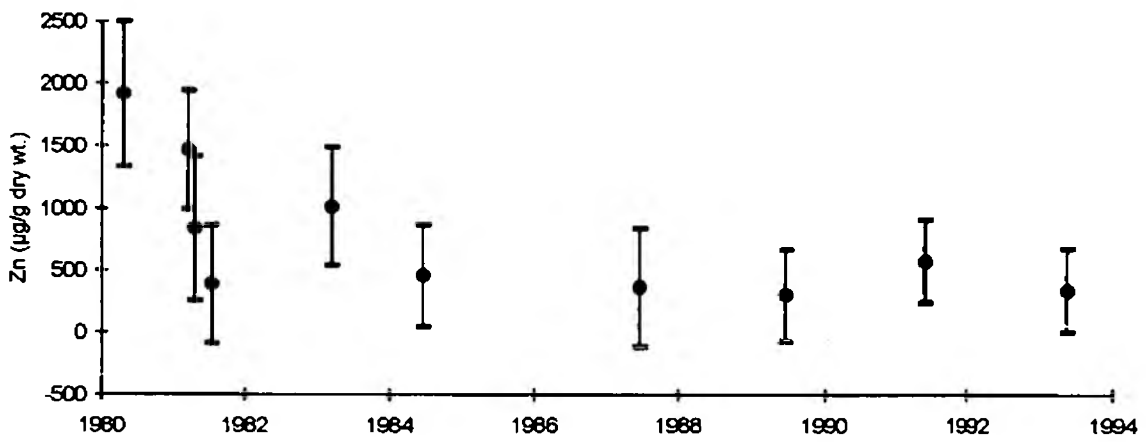


Figure 54. Temporal trends for Zinc, 1980 - 1993.

A. Total Zinc in Sediments, 1980 - 1993.



B. Zinc in Fucus vesiculosus, 1980 - 1993.



C. Zinc in Macoma balthica, 1980 - 1993.

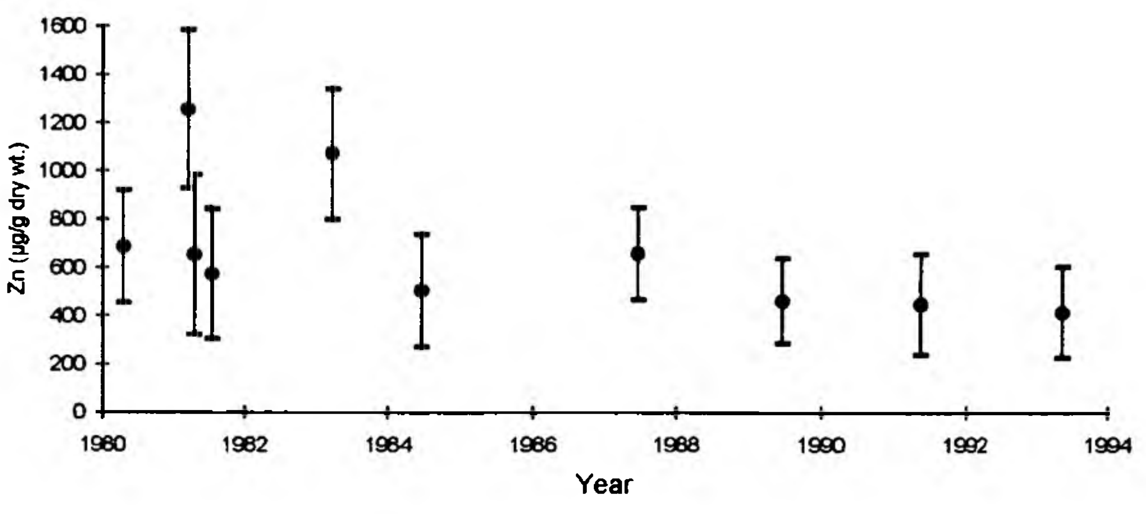
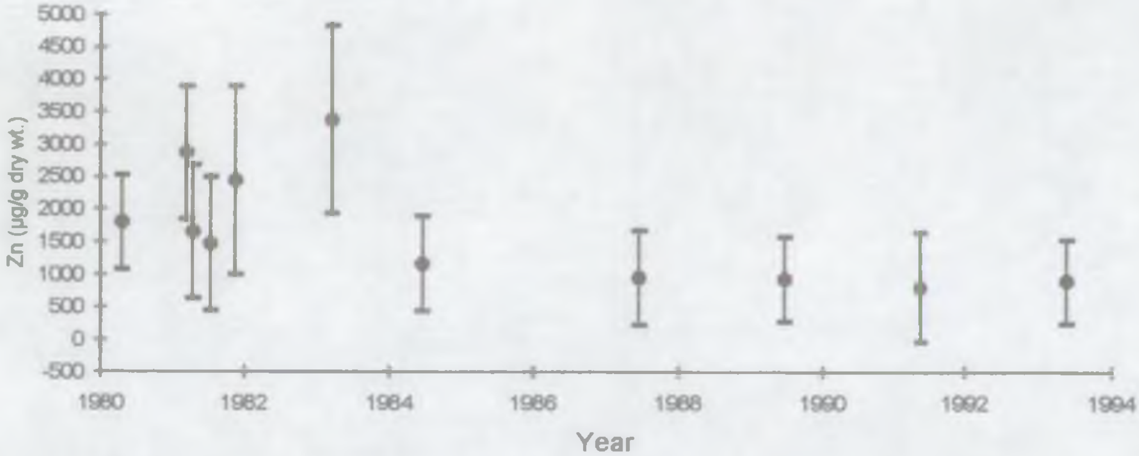
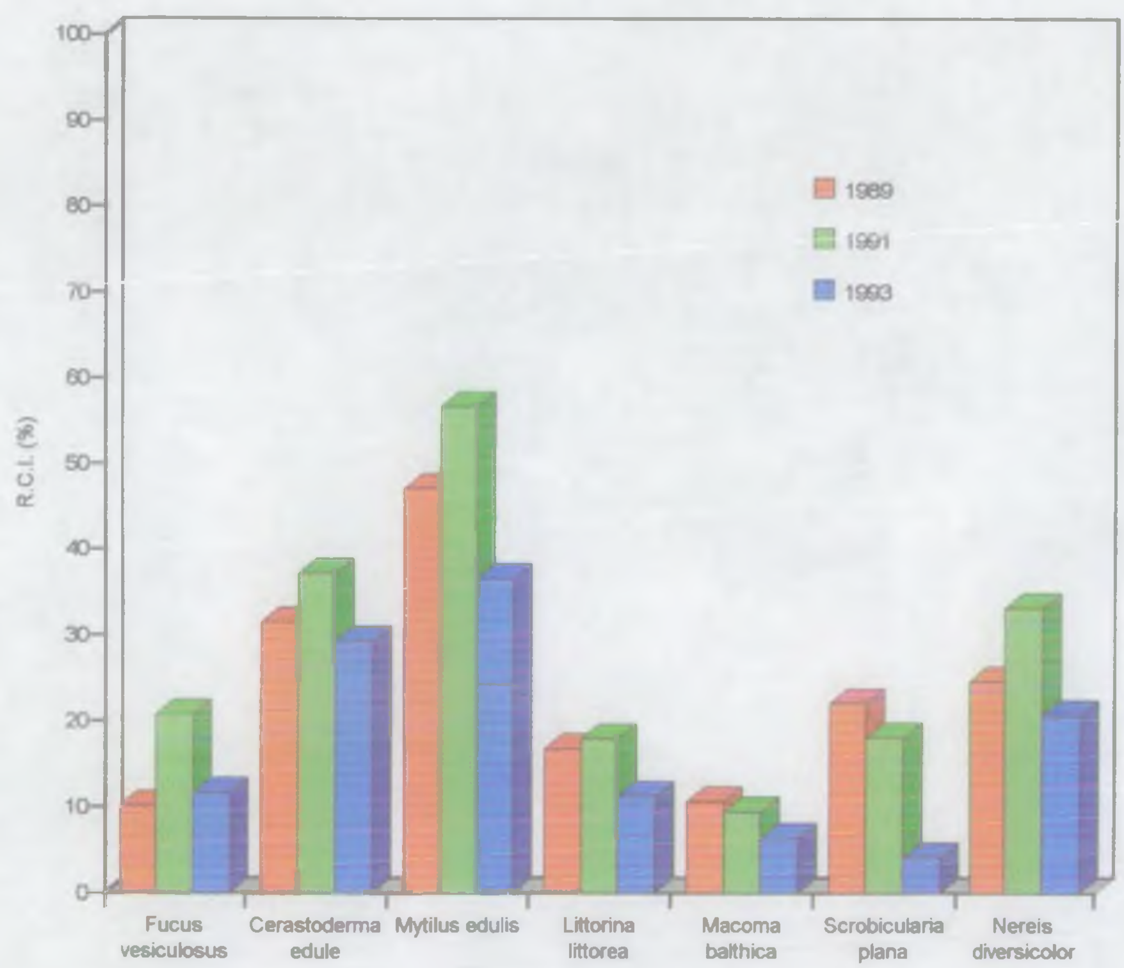


Figure 55

A. Zinc in Scrobicularia plana, 1980 - 1993.



B. Relative Contamination Indices for Zinc in Mersey Biota



reflect these changes in sediment-bound and dissolved zinc contamination, probably due to regulation of uptake.

Comparisons with other estuaries

Because zinc is an essential trace element, and its uptake is regulated in a number of the invertebrate species used in these studies, the degree of environmental contamination may be underestimated. Thus, as with all but the most exceptionally polluted estuaries, enrichment factors for zinc in Mersey biota compared to UK baseline data (Table 17) are generally low, although a factor of 8.43 for *Fucus vesiculosus* suggests that dissolved zinc is an important route for uptake in the Mersey. Overall however, Relative Contamination Indices, as shown in Figure 55B, indicate that mean zinc contamination in the Mersey is probably best described as low to moderate compared with the most heavily zinc polluted sites in the UK.

Table 17 Enrichment factors for zinc in Mersey 1993 species relative to UK baseline data.

Species	Enrichment Factor*
Fucus vesiculosus	8.43
Cerastoderma edule	2.27
Mytilus edulis	2.97
Littorina littorea	1.74
Macoma balthica	1.21
Scrobicularia plana	3.27
Nereis diversicolor	1.55

* - Mean value for all sites.

Discussion

Evaluating the biological significance of metal contamination in the Mersey estuary is complicated by a number of factors;

1) The Mersey is subjected to contamination by a broad spectrum of metals each with differing chemical and biological characteristics.

2) There are likely to be a large number of sources of metals to the estuary so that contamination will vary both spatially and temporally.

3) Different species have differing affinities for metals and accumulate them from diverse sources (water, sediment, suspended solids, food) or may regulate their body concentrations. Consequently there is no single universal indicator and a variety of organisms is thus required to establish an overall picture of metal bioavailability. Furthermore, in estuaries, the distribution of any organism is usually limited by salinity or by the availability of suitable substrate: As a result no single species is present at all sites along the length of the Mersey.

In order to produce a more comprehensive view of the contamination status of the estuary we have included full measurements of sediment (total and 1N HCl extractable) metal data for the current survey.

In the previous section, 'Results' were presented and discussed separately on a metal-by-metal basis, partly because of arguments outlined above. Surprisingly, however there are a number of consistent observations which emerge for groups of metals when these are compared in the different sample types. The major conclusions are summarised below.

Spatial trends

Sediments

The profiles for total metals in sediments recorded in 1993 are similar to those seen in previous surveys, with highest levels in the upper/middle region of the estuary (Figure 56). The major difference between results from previous surveys and the present one is that the majority of metals analysed (with the exception of silver) show a major peak at Hale/Weaver Sluices in addition to the 'normal' peak, centred at Stanlow. Furthermore, the patterns of sediment metal distribution along the length of the estuary show a considerable degree of similarity (again with the exception of silver). Multivariate correlation analysis was performed using the data for all total metal concentrations in Mersey sediments collected in 1993, and the results, in the form of a correlation matrix are shown in Table 18. For clarity, only the significant correlations ($P < 0.05$) are listed. From these results it is apparent that the total concentrations of most of these metals are significantly correlated, and in addition the levels of most metals (cadmium, copper and mercury are exceptions) are significantly correlated with the sediment organic

Table 18. Correlation Coefficients for Total Metals in Sediments, 1993.

	Organics	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
Organics		0.495	0.521		0.696		0.677		0.738	0.821	0.581	0.733	0.737	0.495
Ag									0.515	0.536			0.490	
As				0.870	0.892	0.958	0.832	0.949	0.761	0.853	0.964	0.865	0.898	0.949
Cd					0.763	0.936	0.560	0.954	0.535	0.580	0.859	0.685	0.742	0.942
Cr						0.897	0.878	0.899	0.917	0.908	0.942	0.913	0.946	0.897
Cu							0.752	0.991	0.727	0.780	0.981	0.834	0.908	0.990
Fe								0.733	0.863	0.916	0.836	0.908	0.840	0.722
Hg									0.732	0.772	0.962	0.836	0.885	0.988
Mn										0.901	0.817	0.838	0.841	0.733
Ni											0.892	0.906	0.931	0.794
Pb												0.882	0.960	0.969
Se													0.893	0.827
Sn														0.903
Zn														

Only significant ($P < 0.05$) correlations are shown.

Figure 56

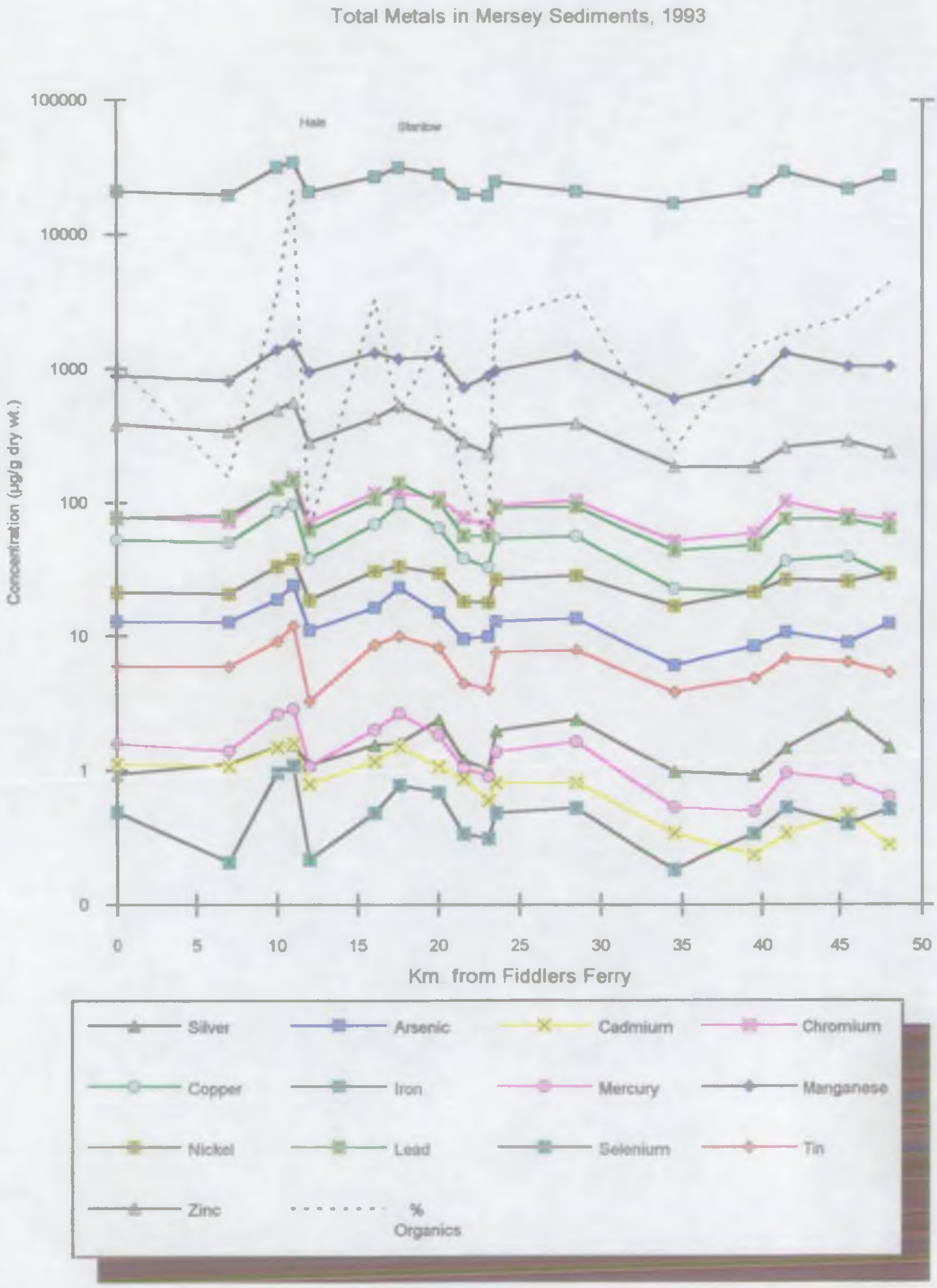
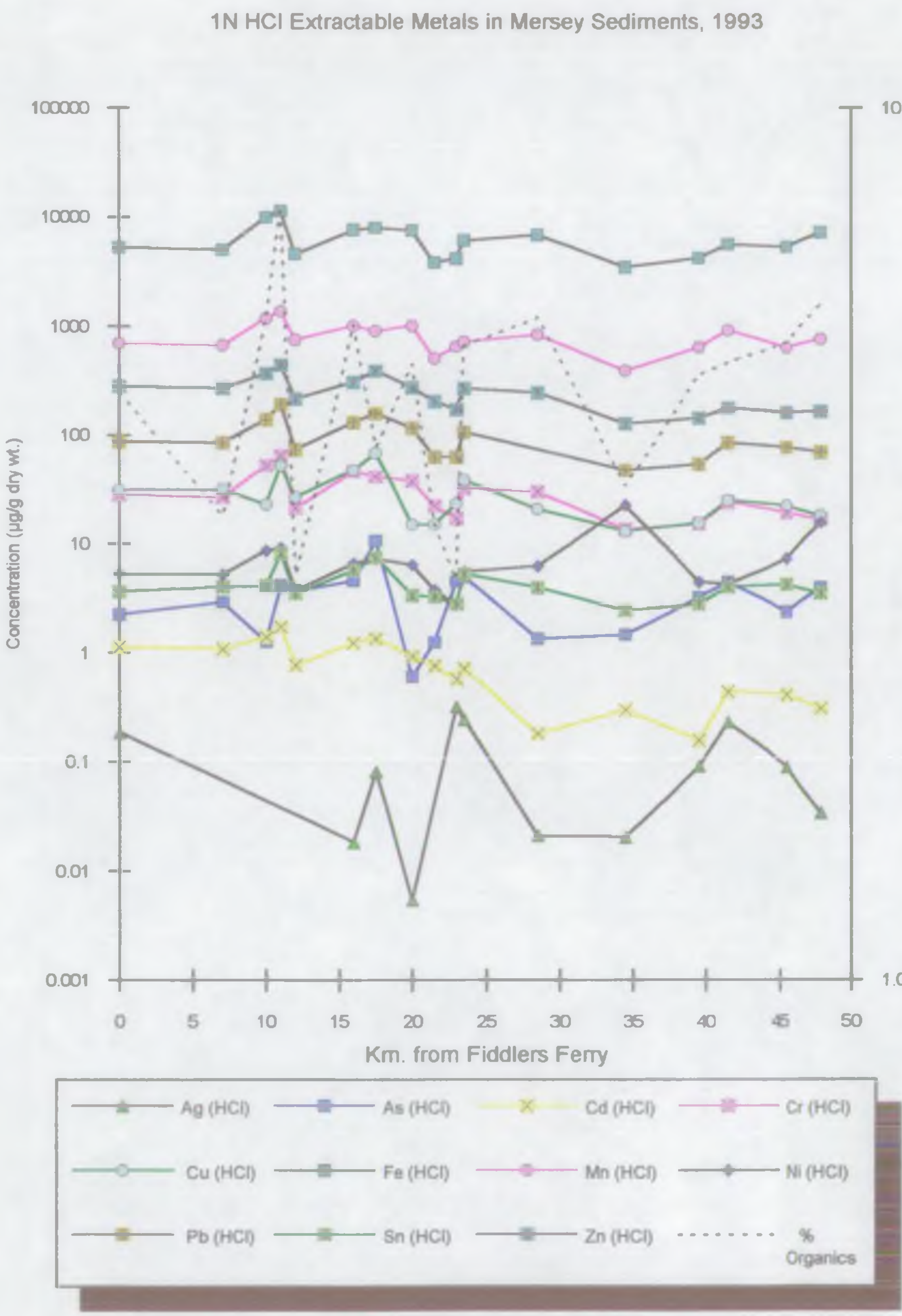

Total Metals in Mersey Sediments, 1993
Hale
Stanlow
100000
10000
1000
100
10
1
0
10
1
Concentration (µg/g dry wt.)
Organics (%)
0
5
10
15
20
25
30
35
40
45
50
Km. from Fiddlers Ferry
Silver
Arsenic
Cadmium
Chromium
Copper
Iron
Mercury
Manganese
Nickel
Lead
Selenium
Tin
Zinc
% Organics

Table 19. Correlation Coefficients for 1N HCL Extractable Metals in Sediments, 1993.

	Organics	Ag	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Sn	Zn
Organics					0.614		0.777	0.700		0.617	0.531	
Ag												
As						0.805					0.632	
Cd					0.855	0.701	0.668	0.674		0.877	0.703	0.914
Cr						0.645	0.905	0.897		0.965	0.793	0.943
Cu							0.527	0.492		0.776	0.914	0.760
Fe								0.934		0.915	0.734	0.827
Mn										0.882	0.671	0.790
Ni												
Pb											0.896	0.950
Sn												0.823
Zn												

Only significant ($P < 0.05$) values shown.

Figure 57



1N HCl Extractable Metals in Mersey Sediments, 1993
100000
10000
1000
100
10
1
0.1
0.01
0.001
Concentration (µg/g dry wt.)
10.00
1.00
Organics (%)
0
5
10
15
20
25
30
35
40
45
50
Km. from Fiddlers Ferry
Ag (HCl)
As (HCl)
Cd (HCl)
Cr (HCl)
Cu (HCl)
Fe (HCl)
Mn (HCl)
Ni (HCl)
Pb (HCl)
Sn (HCl)
Zn (HCl)
% Organics

content. While this may be a contributory factor governing the distribution of metals in estuarine sediments, it is not solely responsible, and other factors such as the proximity to sources of metals, granulometry and grainsize distribution, together with physicochemical factors such as sediment redox potential and pH will all influence total metal concentrations in sediments. Figure 56 shows the profiles for all metals in sediments together with that for the organic content. However, due to the wide range of concentrations encountered between these different metals logarithmic concentration scales have been used in order to compress all data onto one diagram for comparative purposes, the effect of which is to reduce the appearance of peaks and troughs compared to a linear scale. Nevertheless, Figure 56 together with Table 18 serve to exhibit the similarities in distribution of total metals in Mersey sediments.

The data for 1N-HCl extractable metals has been treated identically to that for the total extracts. The results for correlation analysis are presented in Table 19, where it can be seen that there are fewer significant correlations overall, than for the total metal concentrations. However, the same general pattern is apparent for most metals (Figure 57), namely higher levels in the upper/middle reaches of the estuary, with a peak centred at Hale/Weaver Sluices (although this latter site may be of secondary significance for some metals e.g. copper and tin), and at Stanlow, with lower concentrations towards the seaward end of the estuary. Copper and arsenic are somewhat different in that highest levels in HCl extracts occur at Stanlow, which as has been shown earlier in this report for copper, is reflected in greater bioavailability at that site. Some HCl extracts, notably silver and nickel show no significant correlations with any other metals, which is in turn due to the occurrence of significant peaks at Eastham Lockgates and Egremont respectively, features not apparent for other metals.

<u>Biota</u>

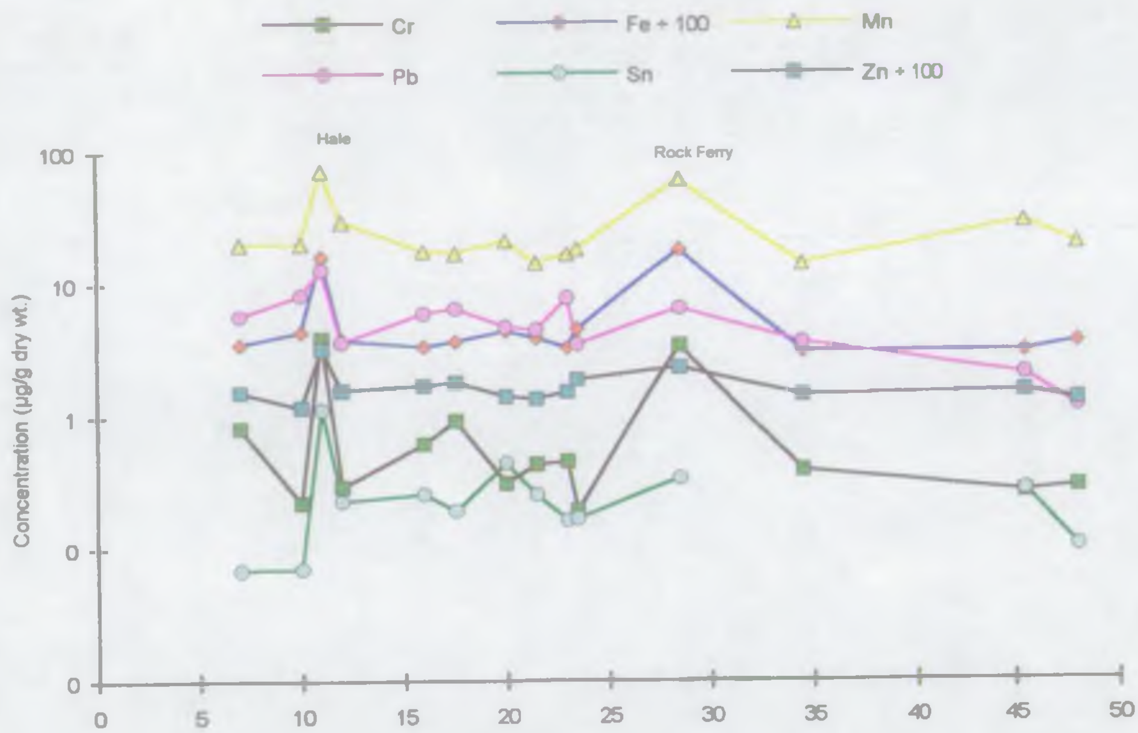
The species with the most extensive range in the Mersey estuary (collected at 14 out of 17 sites visited, upstream as far as Widnes) was the rag worm, *Nereis diversicolor*. The value of this species has been increased in the last two surveys by the addition of samples at Weaver Sluices, Mount Manisty, and upstream of Eastham Locks. This has resulted in a better resolution of contamination data in the mid - upper reaches of the estuary, and enables a better appreciation of differences between north and south banks, which for some metals appears significant.

Metal profiles in *Nereis diversicolor* fall into three main groups:

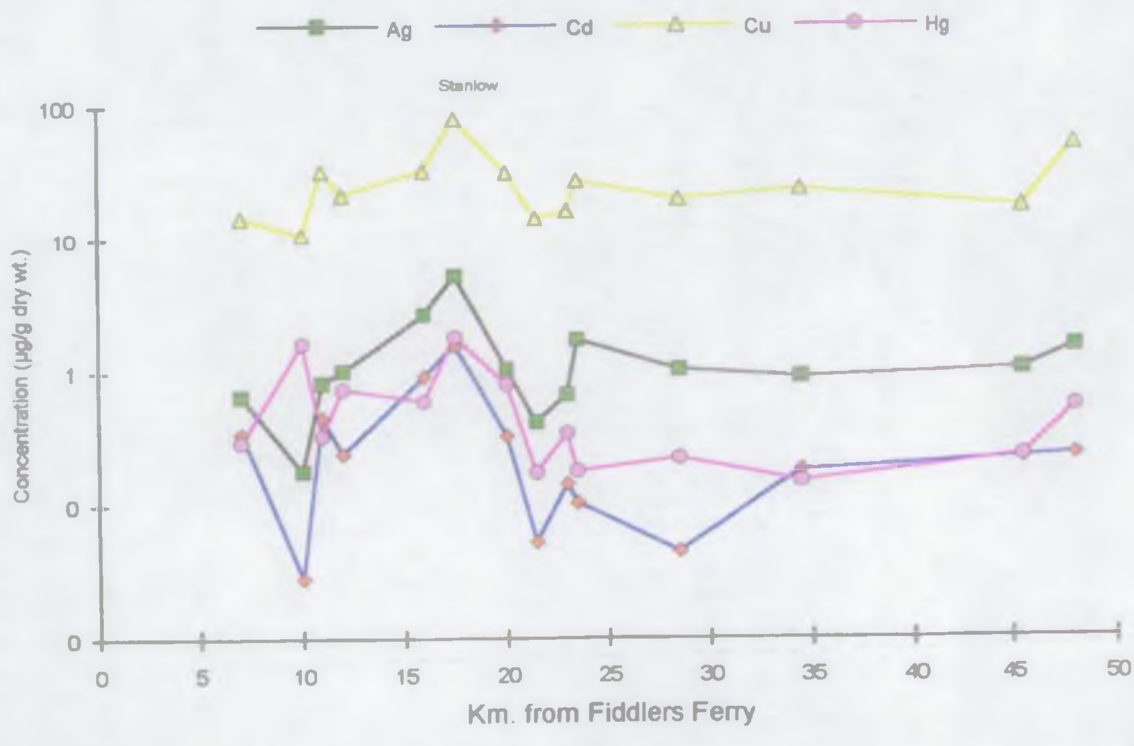
1. Fe, Mn, Cr, Zn, Pb and Sn all exhibit high levels at Hale (Figure 58A), corresponding to high levels in total and HCl sediment extracts.

Figure 58. Spatial trends for Metals in Nereis diversicolor, 1993.

A. Cr, Fe, Mn, Pb, Sn and Zn



B. Cu, Cd, Ag and Hg



2. Of this previous group, Fe, Mn and Cr show an additional distinct peak at Rock Ferry. The reasons for this are not clear, but may be related to recent sediment disturbance resulting from excavation and pipe laying at this site.

3. Cu, Cd and Ag (and to a lesser extent Hg) show major peaks at Stanlow (Figure 58B) reflecting probable inputs in that region. In addition, copper levels in *Nereis diversicolor* are very significantly correlated with 1N HCl sediment extracts as already discussed. In the case of mercury (Figure 25B) a bank effect is apparent with higher Hg levels in *Nereis diversicolor* on the southern shore corresponding to likely sources of input in the Weaver Sluices/Stanlow region.

Although they are often more efficient accumulators of metals compared with *Nereis*, the majority of other species used in these surveys are confined to the lower reaches of the estuary where metal contamination may be lower and gradients masked by inter-site variations in bioavailability.

This is particularly true of the deposit feeding clams *Scrobicularia plana* and *Macoma balthica*. Thus, although sediment concentrations may be the major factor determining metal accumulation in these species (metals in clams generally increase upstream), there are situations where other parameters significantly modify tissue burdens - for example redox conditions in sediments (Cu, Mn, Fe, Zn, Ag); salinity and flushing rates of pore- water (Mn); complexation with organics/surface coatings on sediments (As, Hg).

It was shown in the previous survey (Langston *et al* 1992) that anomalously high concentrations of Ag, Cu, Hg, and to some extent Pb (but not Cd) were present in *Scrobicularia* at Egremont and were undoubtedly related to unusual environmental factors at that site. Unfortunately, neither *Scrobicularia plana* or *Macoma balthica* could be found at this site in 1993 to establish whether metal availability has changed. It will be interesting to see in future surveys whether clams return at this site, and if so, whether unusual metal burdens persist.

In *Scrobicularia plana*, Cr, Ni and Fe all show an increase upstream as far as Eastham Lockgates (Figure 59A) - unfortunately insufficient sample was available from Garston for the determination of these elements. This pattern is repeated for As, Cd, Zn and Se, but in the case of these four metals there is a decrease 'upstream' beyond Eastham Lockgates at Garston (Figure 59B), which is actually on the northern shore suggesting that the likely source for the metals listed above is in the region of the lockgates and emanates from the Manchester Ship Canal.

In contrast, Cu, Mn and Sn all exhibit a sharp increase in concentration in *Scrobicularia plana* at Garston compared with levels at Eastham Lockgates (Figure 59C) implying a source, or greater bioavailability of these metals at Garston on the northern shore of the estuary.

Figure 59. Spatial trends for Metals in Scrobicularia plana, 1993.

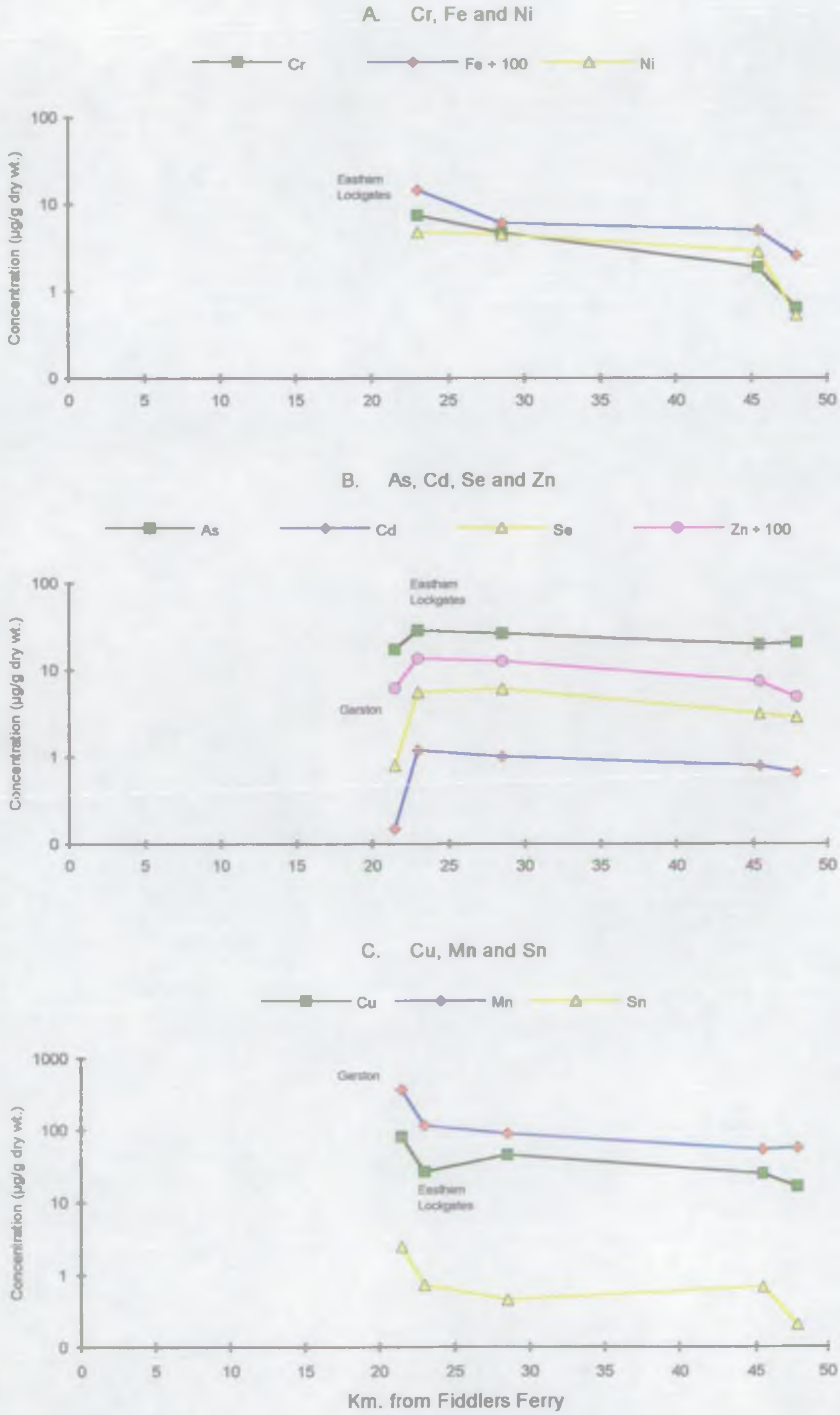
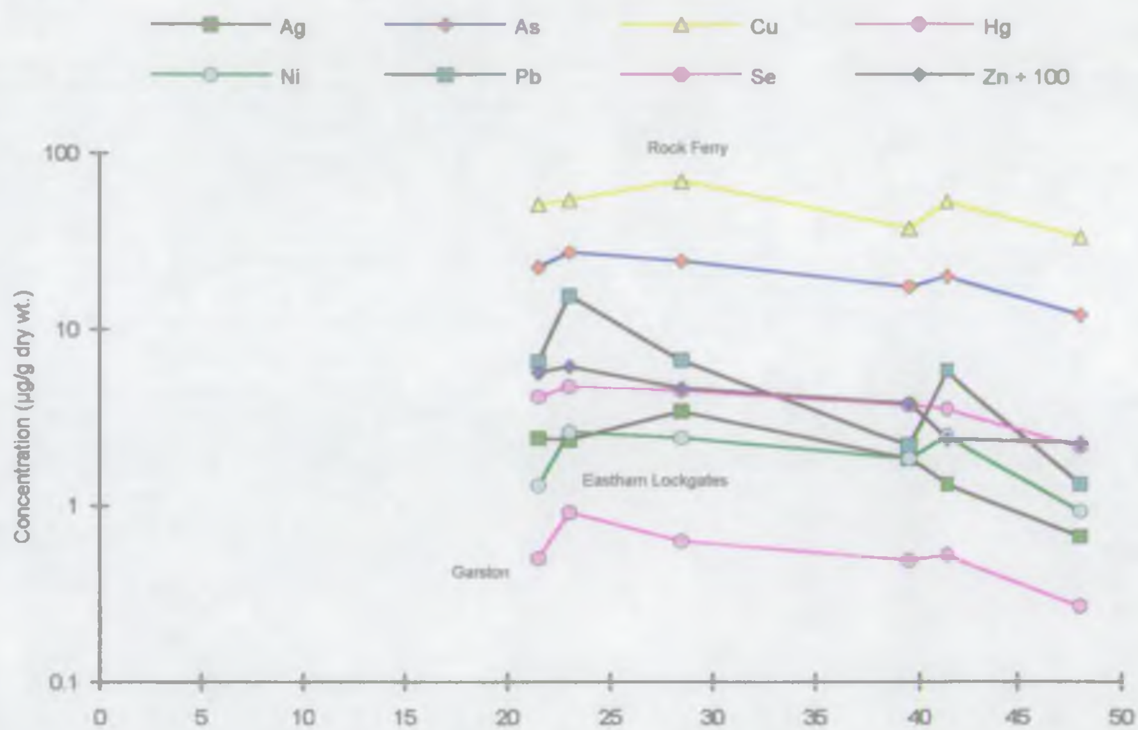


Figure 60. Spatial trends for Metals in Macoma balthica, 1993.

A. Ag, As, Cu, Hg, Ni, Pb, Se and Zn



B. Cr, Cu, Fe, Mn, Ni and Pb

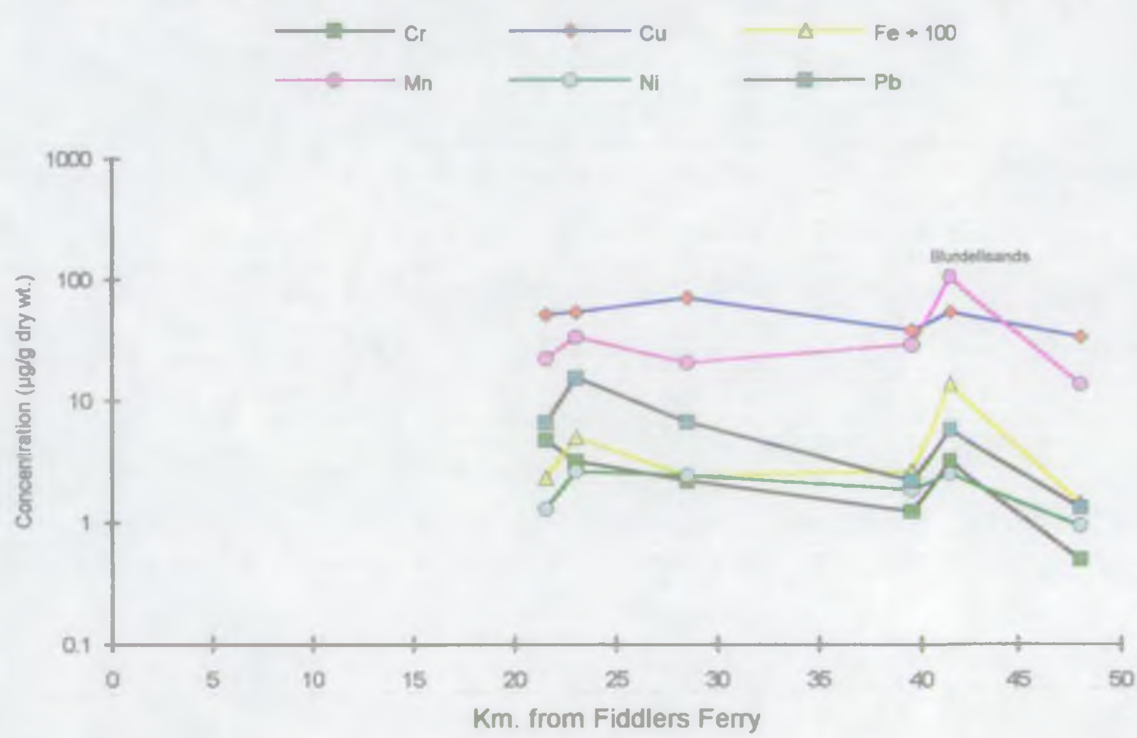
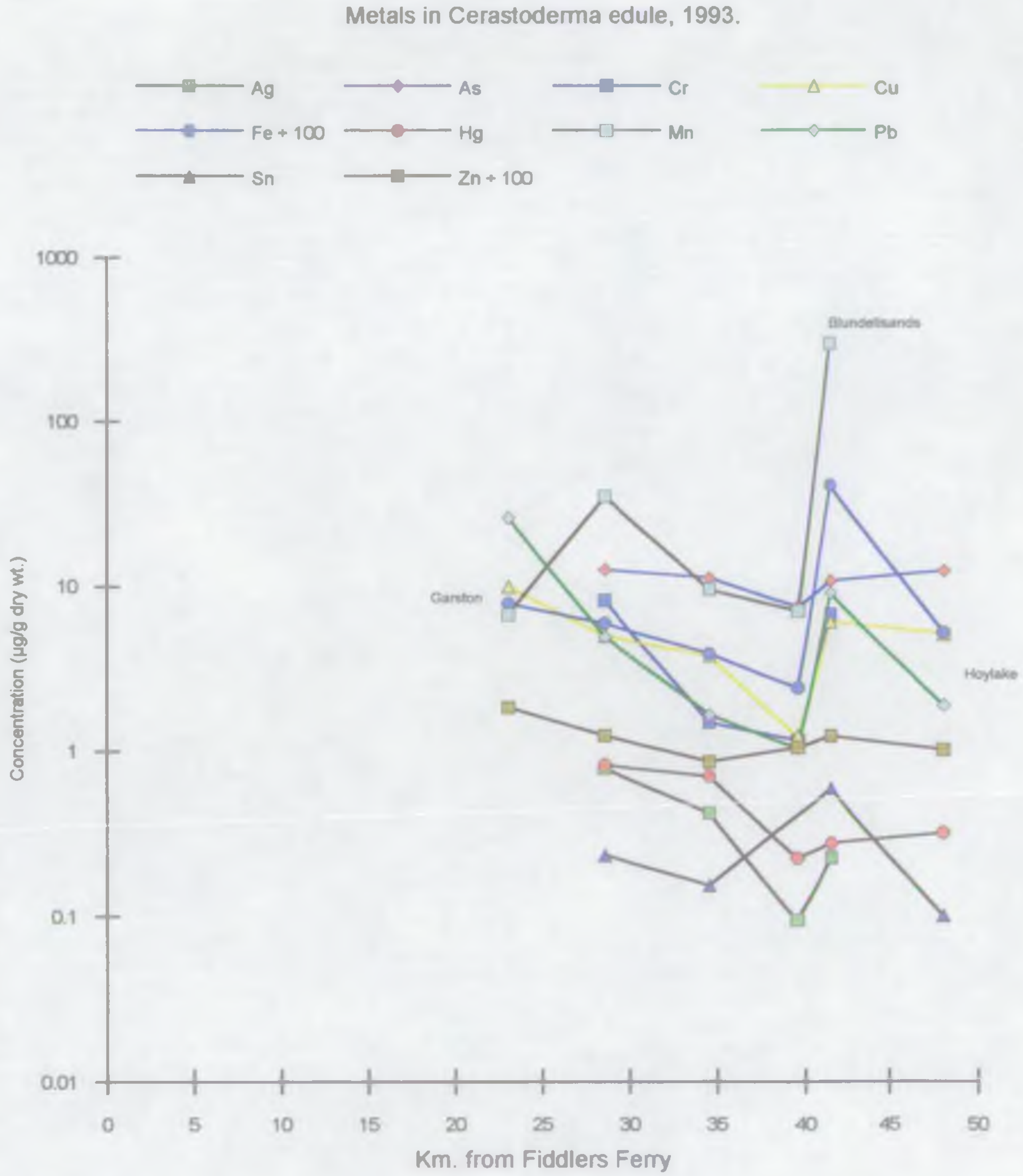


Figure 61


Metals in Cerastoderma edule, 1993.
Ag
As
Cr
Cu
Fe ÷ 100
Hg
Mn
Pb
Sn
Zn ÷ 100
1000
100
10
1
0.1
0.01
Concentration (µg/g dry wt.)
Blundellsands
Garston
Hoylake
0
5
10
15
20
25
30
35
40
45
50
Km. from Fiddlers Ferry

Correlation analysis for metals in *Macoma balthica* shows that there are some significant ($P < 0.05$) correlations between concentrations of different metals in this deposit feeding clam. Cu, Ag, As, Se, Zn, Hg, Pb and to a lesser extent Ni show the broadly similar pattern of an increase in levels moving downstream and across the estuary from Garston to Eastham Lockgates or Rock Ferry followed by a decrease moving seawards through the estuary (Figure 60A). These profiles probably reflect sources of metals in the lockgate region as already mentioned, and also the recent sediment disturbance at Rock Ferry, which may have resulted in increased levels of available metals at that site.

Profiles for Fe and Mn in *Macoma balthica* are characterised by the high concentrations recorded at Blundellsands as discussed in the results section of this report. In addition, less dramatic but nevertheless, significant increases in levels of Cr, Pb, Ni and Cu in *Macoma balthica* can be seen at this site (Figure 60B), probably resulting from sewage enhanced uptake.

The suspension feeding bivalve *Cerastoderma edule* and *Mytilus edulis* were, in 1993, sampled as far upstream as Eastham Lockgates and Garston respectively, and at Hoylake (for *Cerastoderma edule*) towards the seaward end of the estuary, thus extending the limits of collection for these species from previous surveys, and increasing their value as indicators of metal levels in the Mersey.

Metal burdens in *Cerastoderma edule* generally follow a pattern of highest levels occurring at Eastham Lockgates with a fall in concentrations downstream (Ag, As, Cr, Cu, Fe, Hg, Pb, Sn, Zn) as shown in Figure 61. The magnitude of this decrease varies but it is a generally consistent pattern. Additionally, for several metals (Cr, Cu, Fe, Mn, Pb, Sn) there follows an abrupt increase in concentrations at Blundellsands, and, in the case of Fe, Pb and Sn, tissue levels decrease once more at Hoylake. In combination this data suggests sources of metals in the middle region of the estuary, possibly in the region of the Manchester Ship Canal, and enhanced bioavailability for some metals at Blundellsands, probably linked to discharges of sewage in that area.

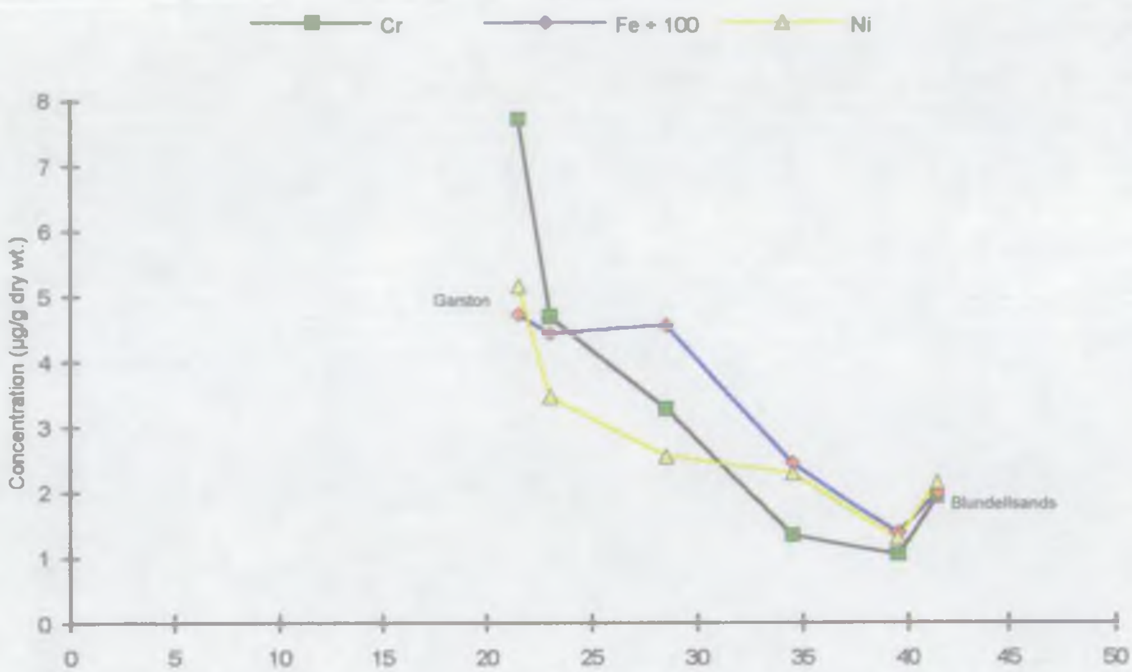
Mytilus edulis was found as far upstream as Garston on the northern shore and at Eastham Lockgates to the south. Correlation analysis of metal levels in *Mytilus edulis* divides the metal profiles into two main groups, although there are similarities between both:

1. Cr, Ni and Fe exhibit highest levels at Garston (although this is less pronounced for Fe compared with Cr and Ni), followed by a reduction in tissue burdens downstream towards New Brighton. An increase in tissue concentrations is again apparent at Blundellsands (Figure 62A).

2. As, Cd, Pb, Sn, (Ag, Hg) all increase in concentration from Garston to reach maximum levels at Eastham Lockgates. This is followed by a decrease in levels downstream towards

Figure 62. Spatial trends for Metals in Mytilus edulis, 1993.

A. Cr, Fe and Ni



B. Ag, As, Cd, Hg, Pb

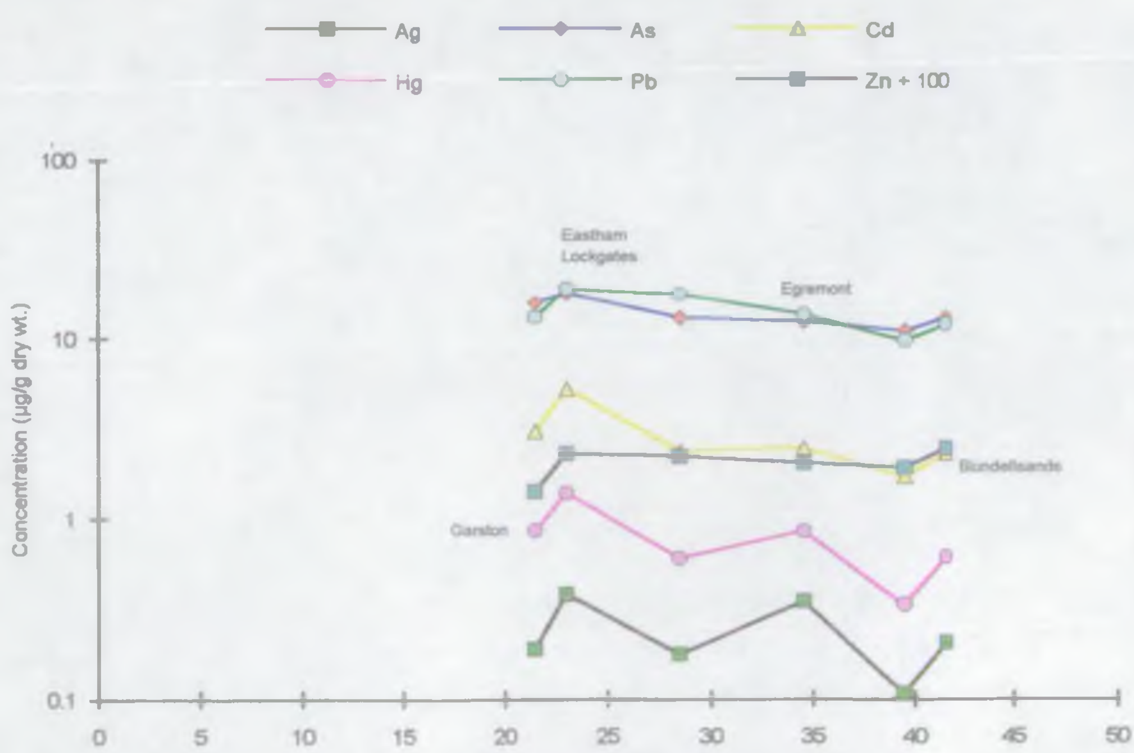
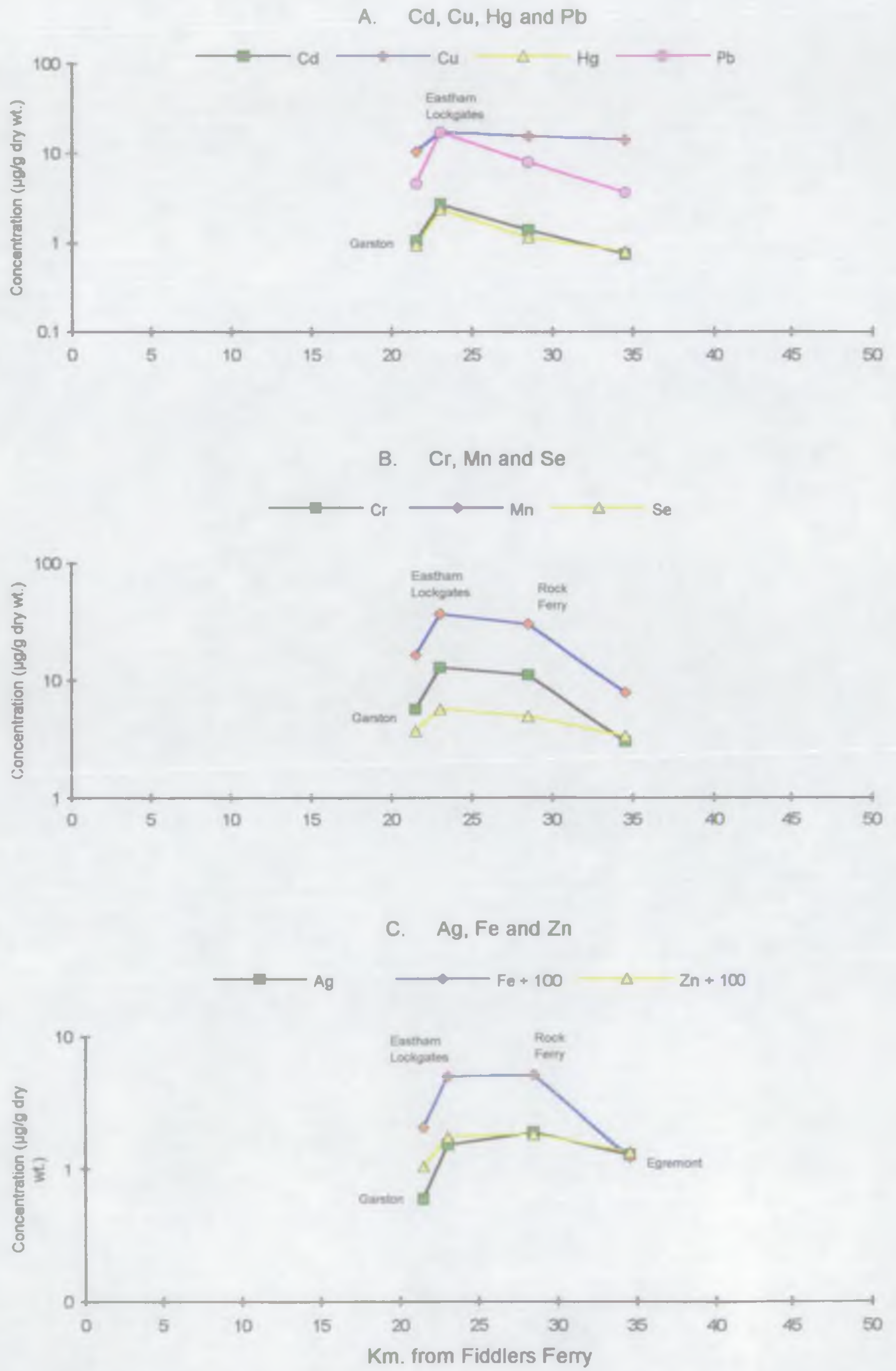


Figure 63. Spatial trends for Metals in Mya arenaria, 1993.



New Brighton. Ag and Hg however, show a secondary peak at Egremont, while all these metals show a further increase in concentration (of variable magnitude) at Blundellsands (Figure 62B).

The Sand Gaper *Mya arenaria* was found at four locations in 1993 compared to only one site in 1991, and has therefore been included in the suite of metal profile indicators used in the current survey. Correlation analysis of the data for *Mya arenaria* shows some similar patterns to other infaunal molluscs:

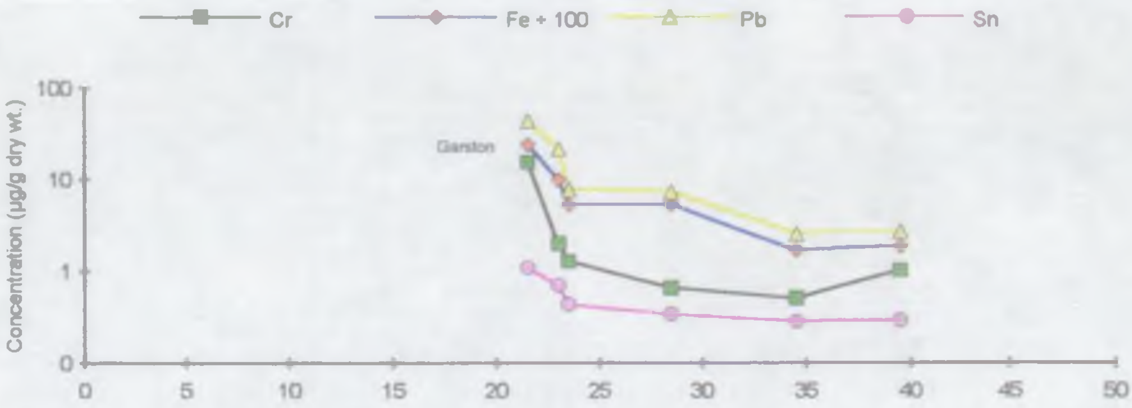
1. Cd, Cu, Hg and Pb show a pronounced increase in tissue levels across the estuary from Garston to Eastham Lockgates followed by a decrease in concentrations downstream (Figure 63A), suggesting that the Manchester Ship Canal may be a source of these anthropogenic metals.
2. Cr, Mn and Se show a similar pattern to that described above, but the decrease downstream is less pronounced with relatively high levels at Rock Ferry (Figure 63B).
3. Ag, Fe and Zn tissue concentrations increase from Garston via Eastham Lockgates to reach maximum levels at Rock Ferry (Figure 63C), followed by a decrease towards Egremont (the seaward limit of recovery for this species).

The alga *Fucus vesiculosus* derives most of its metal burden in dissolved form, and it is therefore taken to be an indicator of metals in solution. Correlation analysis for the 1993 data shows there to be three major distribution groups:

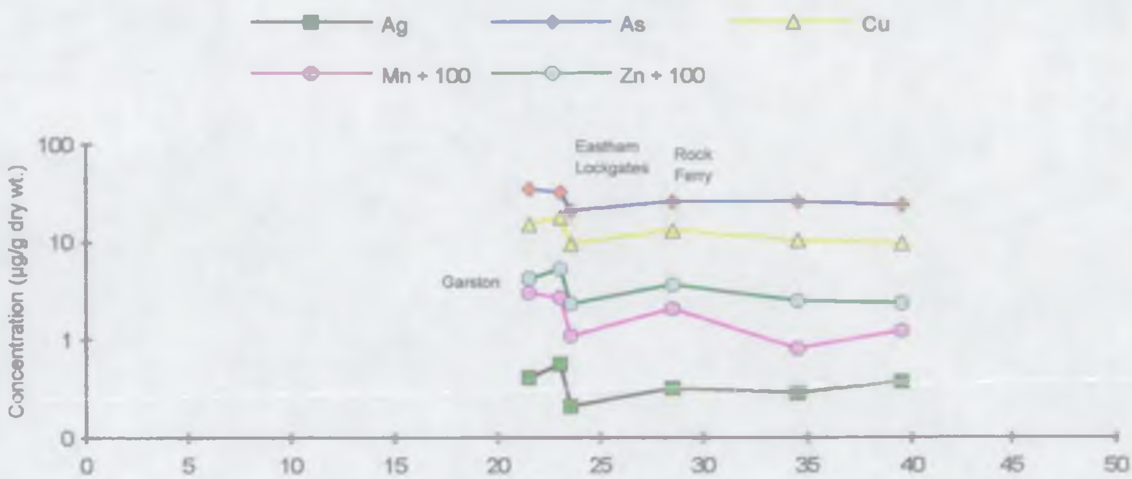
1. Cr, Fe, Pb and Sn all increase in concentration moving upstream, reaching a maximum at Garston (Figure 64A), implying sources of these metals in the middle/upper region of the estuary.
2. Ag, Cu and Zn show a slight increase from Garston to Eastham Lockgates (Figure 64B) followed by a pronounced drop towards Eastham, with a further increase towards Rock Ferry, and generally little change further downstream.
   As and Mn behave very similarly to this group but show a slight decrease from Garston to Eastham Lockgates. The overall implication is that the Manchester Ship Canal is a probable source for some of these metals. *Fucus* responds fairly quickly to changes in dissolved metal concentrations, and a short term exposure to contamination such as might occur during "levelling" operations in the canal could easily result in corresponding bioaccumulation of metals. It would be interesting to confirm whether profiles of metals in *Fucus* along the estuary are indeed influenced by such events.
3. Unusually, Cd, Hg and Se concentrations in *Fucus vesiculosus* all increase seawards through the estuary (Figure 64C), suggesting increased levels of dissolved, available metals in that direction.

Figure 64. Spatial trends for Metals in Fucus vesiculosus, 1993.

A. Cr, Fe, Pb and Sn



B. Ag, As, Cu, Mn and Zn



C. Cd, Hg and Se

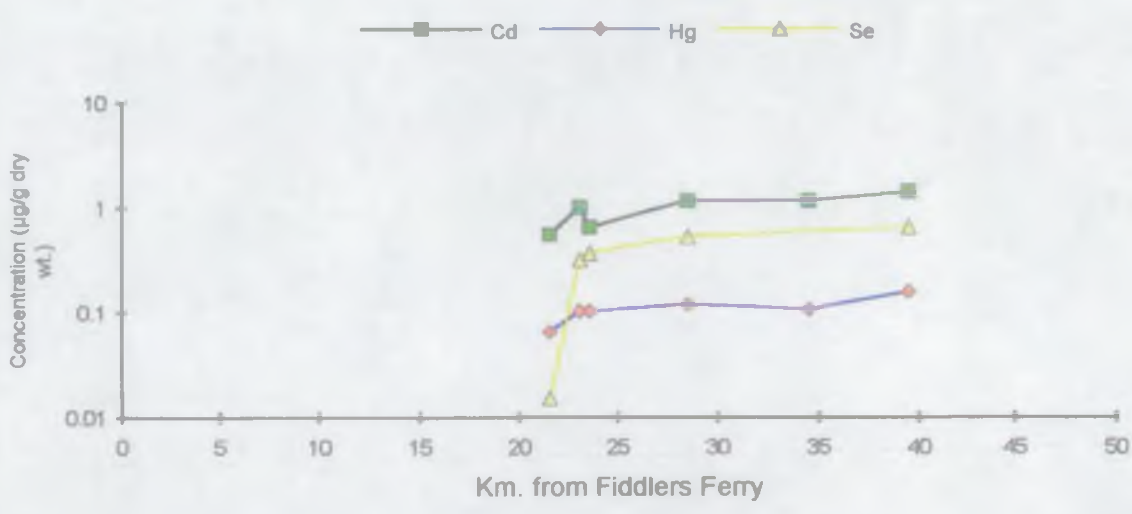
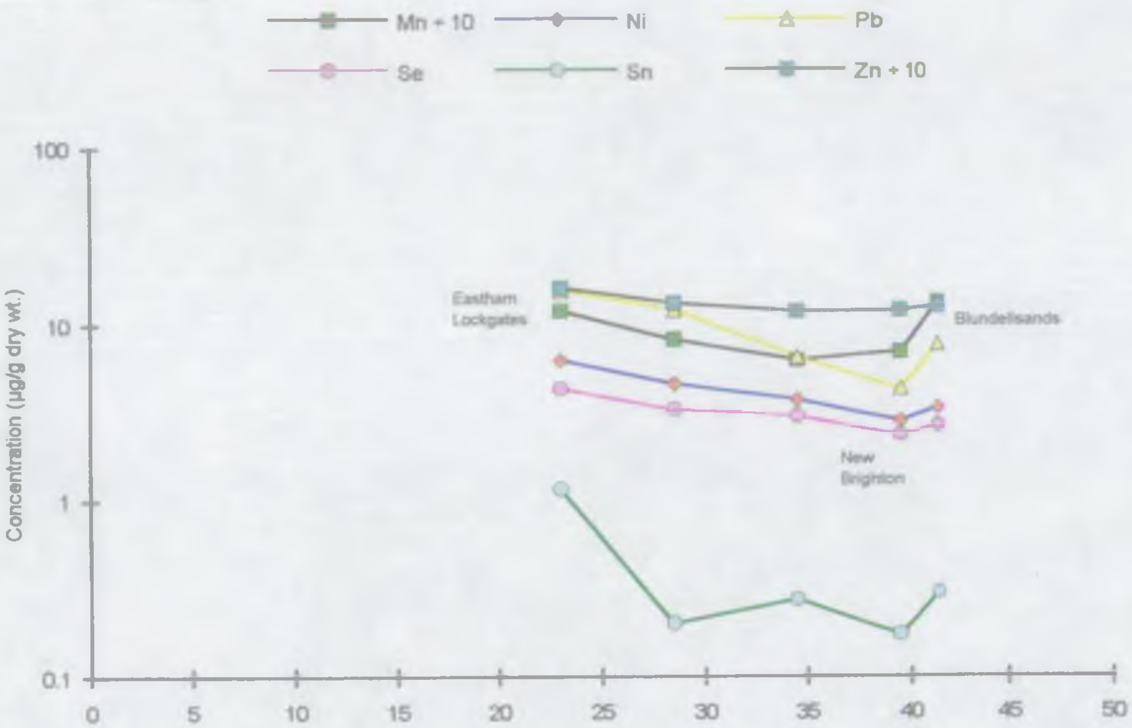
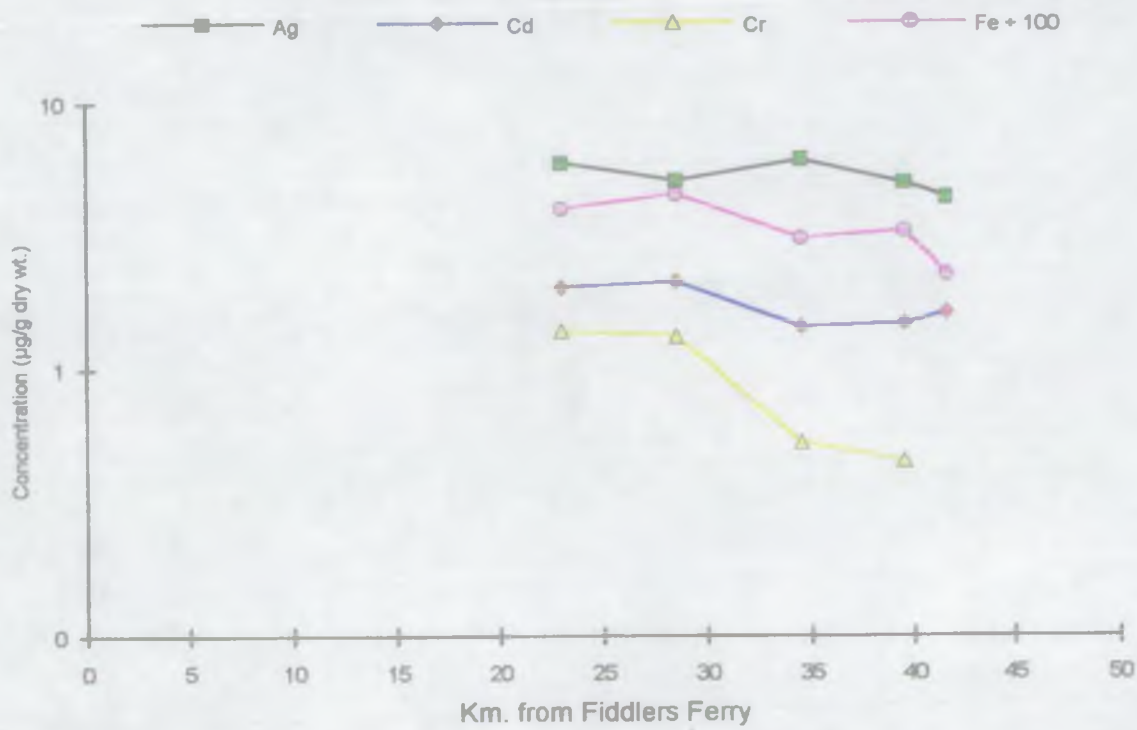


Figure 65. Spatial trends for Metals in Littorina littorea, 1993.

A. Mn, Ni, Pb, Se, Sn and Zn



B. Ag, Cd, Cr and Fe



Correlation analysis for metal concentrations in *Littorina littorea* in 1993 shows once again that there are common trends for several elements. Generally, for Mn, Ni, Pb, Se, Sn and Zn (Figure 65A) there are increases in body burdens upstream from New Brighton to Eastham Lockgates (the upstream limit for *Littorina littorea*). The magnitude of this increase varies, and in the case of tin, there are fairly constant levels within the estuary, and the higher levels at Eastham Lockgates may result from enhanced tin levels in the form of TBT in the canal region.

Additionally, all these metals show enhanced tissue concentrations at Blundellsands, although again, the magnitude of enhancement varies.

Trends for other metals (Ag, Fe, Cd, Cr) though sometimes less well defined, may be summarised as increasing upstream (Figure 65B).

Temporal trends

One of the advantages of biological monitoring is that organisms integrate metal bioavailability over a period of time, though as described above, *Fucus* tends to respond to episodic events more quickly than other species. In contrast, analysis of water or sediments may be subjected to considerable variability depending not only on the level of contamination at the time of sampling, but also on parameters such as grain-size and organic content (sediment) or salinity, freshwater run-off and tidal conditions (water), all of which can change significantly during a short time-span.

Several examples of long term trends in metal bioavailability in the Mersey estuary have emerged from the PML/MBA database, some of which have been described in greater detail in earlier reports (Langston, 1986; 1988; 1990). To briefly summarise earlier findings: major reductions in tissue concentrations of Hg and Pb occurred in most species during the early 1980's, probably as a result of control measures taken by the major industries involved with these metals. Efforts to curb inputs occurred principally in the mid-late 1970's for Hg and in the early 1980's for (organo-)Pb. Since 1984 tissue burdens of both elements declined at considerably slower rates and appeared to be approaching 'steady-state' concentrations - there were no significant changes in Pb or Hg levels between 1987 and 1991 in any of the species studied. Likewise the results of the present survey indicate that for Hg there have been no changes in average concentrations between 1991 and 1993. The persistence of Hg in sediments in particular may delay further reductions for many years. During the period between the two latest surveys lead in biota has likewise shown no significant change.

A pattern of declining Zn concentrations in *Fucus vesiculosus*, *Scrobicularia plana* and *Macoma balthica* during the earlier part of the study period also suggested that major reductions in inputs of this metal have coincided with those observed for Hg and Pb. The connections between these events, however, remain unknown. Between 1991 and 1993 there were no further significant changes in zinc in any of the species.

Between 1984 and 1989 marked decreases in As concentrations in sediments and biota were a consistent feature at sites in the middle and upper estuary. Since 1991 however there appear to have been significant increases in arsenic levels in *Nereis diversicolor*, *Mytilus edulis* and *Fucus vesiculosus*. Since As contamination in sediments has not changed, these increases may be related to reductions in phosphate levels in the estuary (or some other competing element/compound) as discussed earlier in this report.

The trend towards a reduction in Se concentrations appears to have stopped, with most species showing no change since 1991. An exception is *Macoma balthica* where a significant increase in Se concentration has occurred since 1991.

Reductions in tin burdens have also been observed since the mid-1980's and it seems likely that this is related to the decline in tributyltin (TBT) inputs following:

- Reduction of commercial shipping.
- Restrictions on their use in anti fouling paints during this period.

Since 1991 Sn concentrations have remained stable in most species.

Based on averaged data for the whole estuary there have been significant increases in silver and chromium in sediments since 1991, although this is not reflected in the concentrations measured in biota except in the instance of *Nereis diversicolor* at Stanlow where an increase in silver concentrations is apparent.

Until the 1989 survey, consistent changes in Cd contamination were not evident. Then in 1991 significant increases were noted for sediments and biota. The results of the present survey however show that this trend has reversed and concentrations have returned to a level similar to 1989.

For Fe and Ni neither long-term nor short-term (1991 - 1993) trends in contamination were apparent.

It is important to recognise that the above discussion relates principally to changes in mean concentration data (for all sites), and may therefore represent an oversimplification in view of the known variability between sites (see Results). Clearly localised events may be obscured by considering trends for the estuary as a whole.

<u>Comparisons with other estuaries</u>

As already described, metal levels in Mersey biota can be compared to data for other estuaries in two ways:

- Firstly, the mean tissue concentrations for a species can be compared, on a metal by metal basis with UK baseline data, to generate an **Enrichment Factor** for that metal in the particular species of interest. This does not however give any indication of how the degree of contamination relates to the highest levels encountered in UK estuaries, which leads to the second method for inter-estuary comparisons:

- **Relative Contamination Indices** have been discussed earlier in this report together with their limitations, but nevertheless by condensing the range of metals concentrations in organisms from UK estuaries to a scale of 0 - 100 (0 representing clean sites, 100 = most heavily polluted sites) it is possible to provide some idea of the relative degree of contamination in the biota of the Mersey estuary.

Enrichment Factors

Table 20 is a compilation of the enrichment factors for mean concentrations of metals in Mersey biota in 1993 (*Mya arenaria* has not been included since the PML/MBA UK database has limited records for this species). It can readily be seen from the shaded cells in Table 20 that in many instances Mersey biota contain average metal levels which exceed UK baseline data by a factor of 10 or more. As a further simplification, mean enrichment factors have been generated for each metal, and also for each species (geometric means have been calculated since the enrichment factors are in effect ratios of two values, not a simple number).

Table 21 is essentially similar to Table 20 except that the enrichment factors listed compare the highest Mersey concentrations measured in 1993 with UK baseline levels, in effect an expression of 'worst case' levels of contamination in the Mersey estuary for the current survey.

From the results shown in these two tables it is apparent that for As, Cu, Ni and Zn mean tissue concentrations in all biota analysed in 1993 were approximately within a factor of 3 of the UK baseline level (Table 20) while the worst case for any of these metals (Zn in *Fucus vesiculosus* from Eastham Lockgates) was only 13 times higher . The same can also be said for mean levels of Cd, Fe and Se, except that in these instances there are exceptions for some species. Thus, mean tissue concentrations of cadmium in *Nereis diversicolor* are over 10 times higher than UK baseline levels (Table 20), while worst case levels were nearly 50 times higher (in samples from Stanlow - Table 21). Mean levels of iron in *Fucus vesiculosus* are approximately 12 times higher than the UK minimum (Table 20) but may be up to 37 times higher (in samples from Garston - Table 21). Similarly, mean concentrations of selenium in *Fucus vesiculosus* are almost 18 times above baseline levels and 31 times higher at New Brighton.

Mean enrichment factors for Cr, Hg, Mn, Pb and Sn in all biological samples range from about 6 to 8.7 (Table 20), resulting from the increased incidence of high individual factors for several species.

- Mean chromium concentrations in *Nereis diversicolor*, *Littorina littorea* and *Fucus vesiculosus* are 28, 15.4 and 15 times higher than baseline levels respectively, but in the worst recorded cases in this survey exceed background by a factor of 123 (*Nereis*

Table 20. Enrichment Factors for Mean Metal concentrations in Mersey Biota, 1993.

Species	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn	Geo-mean
	Enrichment Factors													
Cerastoderma edule	11.91	1.56	1.23	4.43	1.18	2.75	2.83	19.26	2.57	4.97	1.26	1.39	2.27	2.87
Mytilus edulis	9.08	2.20	3.22	4.89	1.51	2.94	6.50	3.83	5.14	4.45	1.71	9.38	2.97	3.83
Nereis diversicolor	17.71	3.68	10.88	28.16	2.86	2.22	15.92	4.88	4.10	13.06	2.47	4.47	1.55	5.83
Macoma balthica	6.11	2.33	1.58	4.03	2.26	1.45	3.36	3.16	1.94	2.27	1.57	4.25	1.21	2.45
Scrobicularia plana	14.50	2.64	3.28	6.78	3.36	1.90	9.31	12.11	2.38	5.95	1.99	7.04	3.27	4.59
Littorina littorea	10.70	2.13	2.19	15.43	2.94	2.10	5.51	5.33	3.57	10.09	3.09	22.26	1.74	4.74
Fucus vesiculosus	8.39	3.11	3.24	14.80	2.92	12.27	6.11	5.73	3.45	17.66	17.88	16.90	8.43	7.51
Geometric mean	10.6	2.4	2.87	8.711	2.3	2.78	6.08	6.36	3.2	6.83	2.65	6.78	2.5	

- Shading highlights Enrichment Factors > 10x UK Baseline.

Ranking : Cu < As < Zn < Se < Fe < Cd < Ni < Hg < Mn < Sn < Pb < Cr < Ag

Table 21. Enrichment Factors for Highest Metal concentrations in Mersey Biota, 1993.

Species	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn	Geo-mean
	Enrichment Factors													
Cerastoderma edule	24.53	1.80	1.84	8.23	2.26	10.19	4.98	80.60	4.35	17.39	1.69	3.06	3.46	5.80
Mytilus edulis	14.73	2.85	5.96	11.31	1.75	4.26	11.69	6.91	9.39	5.99	1.97	19.43	3.53	6.00
Nereis diversicolor	68.60	5.02	49.28	123.13	8.18	7.10	50.47	13.19	6.93	30.65	4.24	17.73	2.95	15.79
Macoma balthica	10.40	3.09	2.16	7.64	3.17	4.37	5.55	8.88	2.62	5.54	1.96	18.07	1.79	4.52
Scrobicularia plana	24.13	3.35	5.13	13.81	6.95	3.94	20.59	32.67	3.59	8.26	3.01	19.16	4.98	8.31
Littorina littorea	12.31	3.02	2.68	23.17	3.39	2.79	7.82	7.58	5.38	16.98	4.29	61.16	2.14	6.80
Fucus vesiculosus	13.26	3.96	4.60	65.67	4.17	36.82	8.78	9.50	4.25	54.11	30.71	35.10	13.20	13.81
Geometric mean	19.3	3.2	4.96	21.06	3.7	6.6	11.3	14.8	4.8	14.5	3.78	18.6	3.68	

- Shading highlights Enrichment Factors > 10x UK Baseline.

Ranking : As < Zn < Cu < Se < Ni < Cd < Fe < Hg < Pb < Mn < Sn < Ag < Cr *diversicolor* at Hale), 23 (*Littorina littorea* at Eastham Lockgates), and 66 (*Fucus vesiculosus* at Garston).

- Average mercury burdens in *Nereis diversicolor* are nearly 16 times higher than UK baseline levels, and are over 50 times higher in worms from Stanlow.
- Manganese concentrations in *Cerastoderma edule* and *Scrobicularia plana* are on average 19.3 and 12.1 times higher than baseline levels, but increase to over 80 and 33 times higher in cockles from Blundellsands and clams from Eastham Lockgates.
- Mean lead levels in *Nereis diversicolor, Littorina littorea* and *Fucus vesiculosus* are approximately 13, 10 and 18 times baseline concentrations respectively, but increase to factors of 31 (*Nereis diversicolor* at Hale), 17 (*Littorina littorea* at Eastham Lockgates) and 54 (*Fucus vesiculosus* at Garston) in the worst cases recorded in the current survey.
- Enrichment factors for tin in several species in the Mersey tend to be fairly low (< 7) but for *Mytilus edulis, Fucus vesiculosus* and *Littorina littorea* reach values of 9, 17 and 22 respectively. However, it can be seen in Table 21 that in the worst case situations factors for all species except *Cerastoderma edule* reach values of 18 - 61, which in most cases are due to the levels recorded at the mid estuary sites of Garston and Eastham Lockgates.

Silver is the only metal, in 1993 for which the mean enrichment factor (for all species) is greater than 10, which is in turn due to high individual factors for most species of organisms as shown in Table 20. Overall, enrichment factors for silver range from 6 (*Macoma balthica*) to 17.7 (*Nereis diversicolor*), but these increase to 10.4 and 68.5 respectively in the worst case situations. These occur at Rock Ferry for *Scrobicularia plana, Cerastoderma edule* and *Macoma balthica*, Eastham Lockgates for *Fucus vesiculosus* and *Mytilus edulis*, Egremont for *Littorina littorea*, and at Stanlow for *Nereis diversicolor*.

Relative Contamination Indices

As mentioned earlier, enrichment factors only compare metal levels in biota to the minimum UK concentrations, and do not provide any information on the way in which mean tissue concentrations relate to the highest levels that have been measured in UK estuaries. In order that such comparisons may be made, albeit in a very simplified manner the Relative Contamination Indices (RCI's) for the 1993 data are compiled into a single matrix for all species as presented in Table 22. Within this table highlighted cells emphasise RCI's which are greater than 50%, i.e. the mean concentration of metal in a species is within a factor of 2 of the highest levels recorded in the PML/MBA database for UK estuaries (over 100,000 records). Figure 66 presents the RCI data in Table 22 in graphical format and serves to emphasise both the high and low values of the index for each species/metal combination.

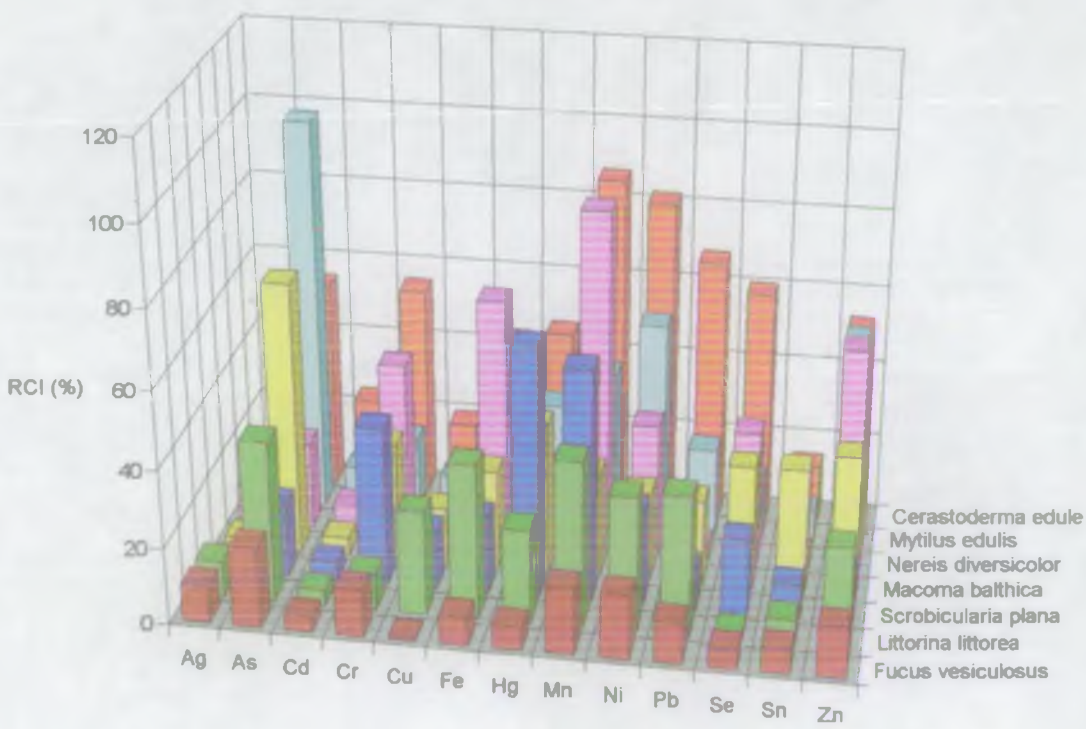
It is apparent that although mean concentrations of silver in most Mersey species showed considerable enrichment compared to UK baseline data, when the UK upper limits are also

Table 22. Relative Contamination Indices for Mersey Biota, 1993.

Species	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
	Relative Contamination Index (%)												
Cerastoderma edule	11	54	24	55	19	43	46	87	82	67	60	14	52
Mytilus edulis	1	102	11	20	11	32	32	41	55	23	16	9	55
Nereis diversicolor	10	23	7	46	3	64	22	89	35	4	35	4	58
Macoma balthica	3	71	5	31	15	26	39	27	23	22	32	32	37
Scrobicularia plana	3	19	5	41	15	20	65	60	25	11	20	9	13
Littorina littorea	9	42	4	10	27	40	24	43	35	36	2	7	26
Fucus vesiculosus	10	21	4	12	1	8	6	17	17	11	5	6	13
Geometric mean	5	40	7	26	9	28	28	45	34	18	16	9	31

- shaded cells highlight RCI's > 50%

Figure 66. Relative Contamination Indices for Mersey Biota, 1993.



taken into account the relative degree of silver contamination (means) in the Mersey compared to other estuaries, is considerably reduced (1 - 11% of maximum levels). Indeed, Table 22 shows that there are a number species/metal combinations in which the average metal concentrations are perhaps surprisingly low. For instance, the following combinations in Mersey samples are all <10% of worst-case UK examples (an order of magnitude lower):

Mytilus edulis	Ag, Sn
Nereis diversicolor	Cd, Cu, Pb, Sn
Macoma balthica	Ag, Cd,
Scrobicularia plana	Ag, Cd, Sn
Littorina littorea	Ag, Cd, Se, Sn
Fucus vesiculosus	Cd, Cu, Fe, Hg, Se, Sn

For these combinations, metal contamination in the Mersey appears to pose little threat compared with that, for example, in the highly polluted sites of SW. England

For cadmium, copper and tin the range of RCI values is higher (up to 32%) with maximum values occurring for *Cerastoderma edule* (24%), *Littorina littorea* (27%) and *Macoma balthica* (32%) respectively.

For all other metals there is at least one RCI value greater than 50%.

Again it should be stressed, however, that RCI's are calculated on estuary wide mean values, and ignore the fact that at individual sites, contamination may be significantly higher (Tables 20 & 21).

In summary, the Mersey estuary is subjected to varying degrees of contamination from a wide range of heavy metals. These are ranked on the basis of ascending enrichment in Tables 20 and 21. At the most contaminated sites Cr, Ag, Sn, Mn, Pb and Hg generally exceed baselines by an order of magnitude or more. For individual species, enrichment can be considerably higher - up to 123 for Cr in *Nereis diversicolor.* While significant reductions for many of these metals were observed over the last decade the rate of improvement of environmental quality has slowed, and in recent years the Mersey estuary remains impacted to a moderate or high degree for many metals.

Future research needs

A review of PML's commissioned research on metals in the NRA's NW. region is nearing completion and highlights a number of future research topics in the area of biological impact assessment. Specific needs which relate to the Mersey include:

1) The Mersey is relatively unique amongst UK estuaries in being contaminated by such a wide range of metals. Although the average degree of contamination can be described as 'moderate' for most metals, (with the possible exceptions of Cr, Fe, Mn and Hg, for which tissue burdens are close to their upper limits), it is unusual to find estuaries with such a 'cocktail' of elements. Continued surveillance of the estuary is clearly warranted in view of the suite of pollutants present. Current trends suggest there have been long-term improvements for As, Cu, Hg, Pb, Sn and Zn. In contrast, mean silver and chromium concentrations in sediments, together silver and manganese levels in some biota, have recently increased, notably from sites in the middle and lower estuary. Further surveys would be valuable in plotting the changes of these environmentally important elements and also determining the variability in expected values of other metals. Bi-annual surveys appear to remain a suitable time-span for the purpose of bioavailability studies, though some additional work on short term variability in a reduced number of samples would be valuable.

2) At present there is some evidence which links reductions of Hg and Pb inputs to the estuary with the long-term decline in tissue burdens in biota. A more rigorous attempt to correlate biological data with environmental concentrations (inputs; water and sediment concentrations) might provide a greater insight into the factors controlling metal burdens in the Mersey estuary and might assist in establishing meaningful water quality objectives. It would be valuable to link data on metals with the NRA's records on discharges and hence to fully assess the impact of recent changes in water quality, notably the introduction of major sewage treatment facilities.

3) The importance of metal speciation in the environment is now recognised as being a factor of major importance in determining both bioaccumulation potential and, ultimately, toxicity. Organometallic species are among the most biologically active forms and, in view of the known inputs of Hg and Pb (and Sn) in the Mersey, it would seem important to evaluate the distribution and persistence of organic forms of these metals and to examine their contribution to total metal burdens. Identifying sites and sources of mercury methylation in the estuary are seen as major priorities.

4) The restriction in distribution of many of the organisms to the lower reaches of the estuary may be due to a number of factors including strong tidal currents, sediment instability and salinity fluctuations. As a result, effective biological monitoring of the upper reaches of the Mersey (upstream of Eastham Lockgates/Garston) is severely limited in the region

which may possibly be most impacted. A combination of transplant and laboratory investigations, including sediment toxicity assessment using bioassay techniques (such as the *Microtox*® Solid-Phase Test) would be valuable in assessing the biological significance of such contamination. The possibility of pollutant-induced metal-tolerance in *Nereis* (and other species) would also merit investigation.

5) The gradual decline and disappearance, in recent years, of infaunal molluscs (*Scrobicularia plana* and *Macoma balthica*) from Egremont has coincided with increasing metal bioavailability. Since sediment-metal loadings have not changed significantly, the role of possible determinands of bioavailability, notably sulphides and pore-water metal concentrations, on metal uptake and survival in juvenile clams should be studied further.

6) Several newly developed biochemical, physiological and cytological techniques are now available for use on indigenous (and transplanted) species to determine their value in measuring biological responses to changing metal contamination (in the Mersey and elsewhere). Immunological parameters (differential blood-cell counts, phagocytotic activity), induction of detoxification systems (metallothionein), and physiological indices of condition (heart-rate, respiratory output) should be determined in conjunction with metal burdens, along gradients of contamination as possible indicators and predictors of biological response.

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Appendix 1. Silver in Mersey Samples, May 1993.

Site	Map reference	Ag (ug/g dry weight)							
		Fucus vesiculosus	*Cerastoderma edule*	*Mytilus edulis*	*Littorina littorea*	*Mya arenaria*	*Macoma balthica*	*Scrobicularia plana*	*Nereis diversicolor*
Fiddlers Ferry	SJ566867								0.652
Widnes	SJ514837								
Weaver Sluices	SJ494800								0.179
Hale	SJ483816								0.826
Ince	SJ458793								1.007
Oglet	SJ451819								2.670
Stanlow	SJ430777								5.206
Mount Manisty	SJ397791								1.038
Garston	SJ406828	0.408		0.190		0.597	2.423		0.415
Eastham Lockgates	SJ370812	0.570		0.383	6.953	1.533	2.371	1.925	0.667
Eastham	SJ365819	0.210							1.720
Rock Ferry	SJ340862	0.320	0.785	0.178	5.093	1.897	3.431	2.461	1.033
Egremont	SJ319924	0.290	0.420	0.348	6.093	1.290			0.901
New Brighton	SJ288938	0.371	0.094	0.108	4.968		1.672		
Blundellsands	SJ304988		0.227	0.207	4.382		1.335		
Hightown	SD295030							1.022	1.021
Hoylake	SJ216897						0.666	0.508	1.505
Mean value for 1993 data		0.361	0.381	0.236	5.298	1.329	2.016	1.479	1.346
UK minimum*		0.043	0.032	0.026	0.496	No data	0.330	0.102	0.076
UK maximum*		3.703	3.424	31.620	86.403	No data	76.625	61.686	13.632

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / MBA database (1993). See text for details.

Appendix 2. Arsenic in Mersey Samples, May 1993.

Site	Map reference	As (µg/g dry weight) *Fucus vesiculosus*	*Cerastoderma edule*	*Mytilus edulis*	*Littorina littorea*	*Mya arenaria*	*Macoma balthica*	*Scrobicularia plana*	*Nereis diversicolor*
Fiddlers Ferry	SJ566867								15.78
Widnes	SJ514837								
Weaver Sluices	SJ494800								16.85
Hale	SJ483816								18.84
Ince	SJ458793								17.13
Oglet	SJ451819								23.21
Stanlow	SJ430777								17.96
Mount Manisty	SJ397791								19.12
Garston	SJ406828	34.86		15.85		14.71	22.48	17.32	11.00
Eastham Lockgates	SJ370812	32.84		17.97	24.95	16.18	27.41	28.52	22.86
Eastham	SJ365819	20.96							14.54
Rock Ferry	SJ340862	26.11	12.65	13.08	14.24	10.26	24.74	26.33	21.27
Egremont	SJ319924	26.13	11.28	12.40	17.20	6.83			15.29
New Brighton	SJ288938	23.94	7.50	10.87	28.58		17.45		
Blundellsands	SJ304988		10.81	12.89	15.74		20.17		
Hightown	SD295030							19.66	11.21
Hoylake	SJ216897		12.42				12.09	20.70	14.07
Mean value for 1993 data		27.475	10.932	13.842	20.143	11.995	20.722	22.616	17.010
UK minimum*		8.81	7.02	6.30	9.46	No data	8.88	8.52	4.62
UK maximum*		139.77	27.14	19.90	57.78	No data	38.17	125.80	78.85

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / MBA database (1993). See text for details.

Appendix 3. Cadmium in Mersey Samples, May 1993.

Site	Map reference	Cd (ug/g dry weight) Fucus vesiculosus	Cerastoderma edule	Mytilus edulis	Littorina littorea	Mya arenaria	Macoma balthica	Scrobicularia plana	Nereis diversicolor
Fiddlers Ferry	SJ566867								0.344
Widnes	SJ514837								
Weaver Sluices	SJ494800								0.028
Hale	SJ483816								0.455
Ince	SJ458793								0.242
Oglet	SJ451819								0.916
Stanlow	SJ430777								1.577
Mount Manisty	SJ397791								0.327
Garston	SJ406828	0.550		3.044		1.054	0.236	0.149	0.053
Eastham Lockgates	SJ370812	1.011		5.293	2.022	2.682	0.259	1.191	0.144
Eastham	SJ365819	0.644							0.103
Rock Ferry	SJ340862	1.159	0.475	2.364	2.123	1.414	0.289	1.010	0.045
Egremont	SJ319924	1.170	0.392	2.469	1.441	0.763			0.160
New Brighton	SJ288938	1.402	0.497	1.705	1.478		0.224		
Blundellsands	SJ304988		0.281	2.289	1.620		0.189		
Hightown	SD295030							0.786	0.221
Hoylake	SJ216897		0.702				0.076	0.663	0.235
Mean value for 1993 data		0.989	0.470	2.861	1.737	1.478	0.212	0.760	0.348
UK minimum*		0.305	0.381	0.888	0.792	No data	0.134	0.232	0.032
UK maximum*		24.440	2.376	26.877	43.250	No data	4.684	16.432	4.888

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / MBA database (1993). See text for details.

Appendix 4. Chromium in Mersey Samples, May 1993.

Site	Map reference	Cr (µg/g dry weight) Fucus vesiculosus	Cerastoderma edule	Mytilus edulis	Littorina littorea	Mya arenaria	Macoma balthica	Scrobicularia plana	Nereis diversicolor
Fiddlers Ferry	SJ566867								0.622
Widnes	SJ514837								
Weaver Sluices	SJ494800								0.225
Hale	SJ483816								3.940
Ince	SJ458793								0.296
Oglet	SJ451819								0.625
Stanlow	SJ430777								0.933
Mount Manisty	SJ397791								0.313
Garston	SJ406828	15.498		7.726		5.690	4.805		0.432
Eastham Lockgates	SJ370812	1.978		4.698	1.390	12.899	3.213	7.555	0.457
Eastham	SJ365819	1.288							0.194
Rock Ferry	SJ340862	0.669	8.148	3.295	1.329	11.176	2.224	4.744	3.434
Egremont	SJ319924	0.505	1.494	1.345	0.530	3.024			0.391
New Brighton	SJ288938	1.020	1.162	1.052	0.455		1.244		
Blundellsands	SJ304988		6.723	1.935			3.237		
Hightown	SD295030							1.887	0.264
Hoylake	SJ216897						0.495	0.648	0.290
Mean value for 1993 data		3.493	4.382	3.342	0.926	8.197	2.536	3.708	0.901
UK minimum*		0.236	0.990	0.683	0.060	No data	0.629	0.547	0.032
UK maximum*		28.614	9.001	17.484	9.747	No data	8.894	9.860	2.002

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / MBA database (1993). See text for details.

Appendix 5. Copper in Mersey Samples, May 1993.

Site	Map reference	Cu (µg/g dry weight) *Fucus vesiculosus*	*Cerastoderma edule*	*Mytilus edulis*	*Littorina littorea*	*Mya arenaria*	*Macoma balthica*	*Scrobicularia plana*	*Nereis diversicolor*
Fiddlers Ferry	SJ566867								14.51
Widnes	SJ514837								
Weaver Sluices	SJ494800								10.61
Hale	SJ483816								32.60
Ince	SJ458793								21.65
Oglet	SJ451819								32.82
Stanlow	SJ430777								29.96
Mount Manisty	SJ397791								31.84
Garston	SJ406828	15.13		8.714		10.54	51.34	80.40	14.29
Eastham Lockgates	SJ370812	18.09	9.926	9.496	177.45	17.50	54.06	26.79	16.06
Eastham	SJ365819	9.63							27.36
Rock Ferry	SJ340862	13.18	4.997	9.215	172.33	15.83	70.08	45.39	19.82
Egremont	SJ319924	10.44	3.800	9.433	126.37	14.34			23.33
New Brighton	SJ288938	9.69	1.228	5.218	181.22		37.91		
Blundellsands	SJ304988		6.115	6.980	197.34		53.50		
Hightown	SD295030							24.87	17.20
Hoylake	SJ216897		5.143				33.68	16.64	60.16
Mean value for 1993 data		12.693	5.202	8.176	170,944	14.553	50.096	38.820	28.013
UK minimum*		4.34	4.396	5.431	58.21	No data	22.14	11.67	9.78
UK maximum*		1374.14	31.828	81.489	694.76	No data	363.89	268.66	925.70

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / MBA database (1993). See text for details

Appendix 6. Iron in Mersey Samples, May 1993.

Site	Map reference	Fe (ug/g dry weight) *Fucus vesiculosus*	*Cerastoderma edule*	*Mytilus edulis*	*Littorina littorea*	*Mya arenaria*	*Macoma balthica*	*Scrobicularia plana*	*Nereis diversicolor*
Fiddlers Ferry	SJ566867								354
Widnes	SJ514837								
Weaver Sluices	SJ494800								441
Hale	SJ483816								1622
Ince	SJ458793								382
Oglet	SJ451819								340
Stanlow	SJ430777								371
Mount Manisty	SJ397791								444
Garston	SJ406828	<u>2430</u>		<u>473</u>		208	233		394
Eastham Lockgates	SJ370812	1000	785	445	400	501	499	<u>1478</u>	332
Eastham	SJ365819	532							459
Rock Ferry	SJ340862	539	598	457	<u>454</u>	<u>517</u>	243	619	<u>1811</u>
Egremont	SJ319924	<u>169</u>	390	245	309	<u>123</u>			310
New Brighton	SJ288938	188	<u>241</u>	<u>139</u>	329		264		
Blundellsands	SJ304988		<u>4108</u>	200	<u>225</u>		<u>1395</u>		
Hightown	SD295030							502	<u>309</u>
Hoylake	SJ216897		524				<u>147</u>	<u>257</u>	359
Mean value for 1993 data		809.838	1107.799	326.473	343.270	337.261	463.714	714.117	566.229
UK minimum*		66	403	111	163	No data	319	376	266
UK maximum*		10712	2995	1146	1023	No data	2127	3967	1134

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / MBA database (1993). See text for details.

Appendix 7. Mercury in Mersey Samples, May 1993.

Site	Map reference	Hg (µg/g dry weight) *Fucus vesiculosus*	*Cerastoderma edule*	*Mytilus edulis*	*Littorina littorea*	*Mya arenaria*	*Macoma balthica*	*Scrobicularia plana*	*Nereis diversicolor*
Fiddlers Ferry	SJ566867								0.296
Widnes	SJ514837								
Weaver Sluices	SJ494800								1.624
Hale	SJ483816								0.329
Ince	SJ458793								0.734
Oglet	SJ451819								0.597
Stanlow	SJ430777								1.817
Mount Manisty	SJ397791								0.797
Garston	SJ406828	0.066		0.858		0.944	0.497	0.375	0.175
Eastham Lockgates	SJ370812	0.104		1.391	0.978	2.383	0.915	0.962	0.345
Eastham	SJ365819	0.104							0.179
Rock Ferry	SJ340862	0.121	0.827	0.600	0.817	1.160	0.628	0.842	0.223
Egremont	SJ319924	0.107	0.702	0.853	0.426	0.808			0.149
New Brighton	SJ288938	0.158	0.226	0.333	0.662		0.491		
Blundellsands	SJ304988		0.276	0.611	0.564		0.524		
Hightown	SD295030							0.418	0.229
Hoylake	SJ216897		0.318				0.269	2.069	0.533
Mean value for 1993 data		0.110	0.470	0.774	0.689	1.324	0.564	0.931	0.873
UK minimum*		0.018	0.166	0.119	0.125	No data	0.165	0.100	0.036
UK maximum*		1.796	1.194	2.329	2.967	No data	1.684	1.832	2.686

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / MBA database (1993). See text for details.

Appendix 8. Manganese in Mersey Samples, May 1993.

Site	Map reference	Mn (ug/g dry weight) *Fucus vesiculosus*	*Cerastoderma edule*	*Mytilus edulis*	*Littorina littorea*	*Mya arenaria*	*Macoma balthica*	*Scrobicularia plana*	*Nereis diversicolor*
Fiddlers Ferry	SJ566867								20.20
Widnes	SJ514837								
Weaver Sluices	SJ494800								20.73
Hale	SJ483816								72.44
Ince	SJ458793								30.06
Oglet	SJ451819								17.90
Stanlow	SJ430777								17.28
Mount Manisty	SJ397791								21.51
Garston	SJ406828	301.0		14.57		16.47	22.47	370.52	14.48
Eastham Lockgates	SJ370812	271.9	6.76	18.82	120.78	36.78	33.45	116.71	16.86
Eastham	SJ365819	108.3							18.53
Rock Ferry	SJ340862	206.7	35.07	26.33	82.71	30.25	20.47	89.17	61.66
Egremont	SJ319924	81.0	9.56	10.33	63.29	7.91			14.18
New Brighton	SJ288938	123.2	7.07	6.60	70.26		28.93		
Blundellsands	SJ304988		299.85	10.91	133.98		104.67		
Hightown	SD295030							53.95	29.07
Hoylake	SJ216897						13.64	86.16	20.02
Mean value for 1993 data		181.852	71.661	14.592	94.206	22.853	37.306	137.301	26.781
UK minimum*		31.7	3.72	3.81	17.68	No data	11.79	11.34	8.49
UK maximum*		1084.2	86.25	38.97	236.86	No data	148.73	240.00	35.68

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / MBA database (1993). See text for details.

Appendix 9. Nickel in Mersey Samples, May 1993.

Site	Map reference	Ni (µg/g dry weight)							
		Fucus vesiculosus	*Cerastoderma edule*	*Mytilus edulis*	*Littorina littorea*	*Mya arenaria*	*Macoma balthica*	*Scrobicularia plana*	*Nereis diversicolor*
Fiddlers Ferry	SJ566867								4.680
Widnes	SJ514837								
Weaver Sluices	SJ494800								1.538
Hale	SJ483816								3.092
Ince	SJ458793								3.803
Oglet	SJ451819								5.064
Stanlow	SJ430777								6.339
Mount Manisty	SJ397791								4.774
Garston	SJ406828	6.175		5.165		14.963	1.304		4.741
Eastham Lockgates	SJ370812	5.687	100.46	3.471	6.332	6.705	2.630	4.776	5.589
Eastham	SJ365819	7.181							0.998
Rock Ferry	SJ340862	6.585	106.66	2.563	4.637	15.074	2.434	4.502	2.043
Egremont	SJ319924	7.139	66.76	2.298	3.762	5.535			3.327
New Brighton	SJ288938	8.469	37.87	1.307	2.860		1.861		
Blundellsands	SJ304988		29.05	2.168	3.386		2.528		
Hightown	SD295030							2.876	3.688
Hoylake	SJ216897		36.70				0.932	0.534	2.902
Mean value for 1993 data		6.873	62.917	2.829	4.196	10.569	1.948	3.172	3.756
UK minimum*		1.992	24.53	0.550	1.177	No data	1.003	1.331	0.915
UK maximum*		42.983	101.58	8.679	13.172	No data	9.398	13.979	11.788

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / NBA database (1993). See text for details.

Appendix 10. Lead in Mersey Samples, May 1993.

Site	Map reference	Pb (µg/g dry weight)							
		Fucus vesiculosus	*Cerastoderma edule*	*Mytilus edulis*	*Littorina littorea*	*Mya arenaria*	*Macoma balthica*	*Scrobicularia plana*	*Nereis diversicolor*
Fiddlers Ferry	SJ566867								8.830
Widnes	SJ514837								
Weaver Sluices	SJ494800								8.276
Hale	SJ483816								12.994
Ince	SJ458793								3.673
Oglet	SJ451819								6.040
Stanlow	SJ430777								6.566
Mount Manisty	SJ397791								4.796
Garston	SJ406828	43.988		13.19		4.601	6.570	51.68	4.486
Eastham Lockgates	SJ370812	21.598	26.195	19.08	15.685	17.369	15.545	81.55	7.927
Eastham	SJ365819	7.874							3.509
Rock Ferry	SJ340862	7.408	4.975	17.61	12.257	8.106	6.713	29.92	6.554
Egremont	SJ319924	2.609	1.671	13.54	6.564	3.690			3.646
New Brighton	SJ288938	2.700	1.040	9.62	4.338		2.230		
Blundellsands	SJ304988		9.154	11.81	7.809		8.871		
Hightown	SD295030							39.33	2.070
Hoylake	SJ216897		1.900				1.332	13.84	1.182
Mean value for 1993 data		14.362	7.489	14.137	9.331	8.442	6.377	37.264	6.639
UK minimum*		0.813	1.506	3.18	0.924	No data	2.806	6.26	0.424
UK maximum*		131.935	12.656	54.32	26.640	No data	31.526	339.22	139.178

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / MBA database (1993). See text for details.

Appendix 11. Selenium in Mersey Samples, May 1993.

Site	Map reference	Se (ug/g dry weight) *Fucus vesiculosus*	*Cerastoderma edule*	*Mytilus edulis*	*Littorina littorea*	*Mya arenaria*	*Macoma balthica*	*Scrobicularia plana*	*Nereis diversicolor*
Fiddlers Ferry	SJ566867								4.732
Widnes	SJ514837								
Weaver Sluices	SJ494800								4.837
Hale	SJ483816								3.889
Ince	SJ458793								3.977
Oglet	SJ451819								8.327
Stanlow	SJ430777								7.044
Mount Manisty	SJ397791								3.976
Garston	SJ406828	0.015		4.148		3.706	4.176	0.797	6.178
Eastham Lockgates	SJ370812	0.319		4.342	4.342	5.714	4.774	5.578	6.311
Eastham	SJ365819	0.371							3.599
Rock Ferry	SJ340862	0.526	3.234	3.915	3.286	4.987	4.514	6.134	4.668
Egremont	SJ319924		2.863	3.681	3.025	3.343			2.165
New Brighton	SJ288938	0.645	2.336	2.690	2.350		3.737		
Blundellsands	SJ304988		1.274	3.805	2.663		3.558		
Hightown	SD295030							3.164	5.485
Hoylake	SJ216897		2.340				2.166	2.868	2.688
Mean value for 1993 data		0.375	2.410	3.764	3.133	4.438	3.821	3.704	4.848
UK minimum*		0.021	1.910	2.199	1.012	No data	2.438	1.866	1.966
UK maximum*		7.478	8.943	26.078	137.608	No data	14.347	20.608	18.926

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / MBA database (1993). See text for details.

Appendix 12. Tin in Mersey Samples, May 1993.

Site	Map reference	Sn (µg/g dry weight)							
		Fucus vesiculosus	*Cerastoderma edule*	*Mytilus edulis*	*Littorina littorea*	*Mya arenaria*	*Macoma balthica*	*Scrobicularia plana*	*Nereis diversicolor*
Fiddlers Ferry	SJ566867								0.069
Widnes	SJ514837								
Weaver Sluices	SJ494800								0.071
Hale	SJ483816								1.135
Ince	SJ458793								0.228
Oglet	SJ451819								0.259
Stanlow	SJ430777								0.194
Mount Manisty	SJ397791								0.448
Garston	SJ406828	1.088		0.443		13.799	0.463	2.472	0.257
Eastham Lockgates	SJ370812	0.700		0.777	1.162	8.901	0.701	0.732	0.165
Eastham	SJ365819	0.433							0.169
Rock Ferry	SJ340862	0.342	0.235	0.435	0.201	2.867	0.468	0.453	0.340
Egremont	SJ319924	0.285	0.154	0.211	0.276	0.426			
New Brighton	SJ288938	0.293		0.082	0.174		5.005		
Blundellsands	SJ304988		0.597	0.305	0.303		0.304		
Hightown	SD295030							0.681	0.275
Hoylake	SJ216897		0.101				0.095	0.202	0.104
Mean value for 1993 data		0.524	0.272	0.375	0.423	6.498	1.173	0.908	0.286
UK minimum*		0.031	0.198	0.040	0.019	No data	0.277	0.129	0.064
UK maximum*		8.293	2.082	4.424	6.257	No data	3.923	10.214	7.815

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / MBA database (1993). See text for details.

Appendix 13. Zinc in Mersey Samples, May 1993.

Site	Map reference	Zn (µg/g dry weight) *Fucus vesiculosus*	*Cerastoderma edule*	*Mytilus edulis*	*Littorina littorea*	*Mya arenaria*	*Macoma balthica*	*Scrobicularia plana*	*Nereis diversicolor*
Fiddlers Ferry	SJ566867								164.4
Widnes	SJ514837								
Weaver Sluices	SJ494800								116.4
Hale	SJ483816								325.6
Ince	SJ458793								156.9
Oglet	SJ451819								173.1
Stanlow	SJ430777								182.2
Mount Manisty	SJ397791								142.3
Garston	SJ406828	419.6		142.2		105.1	671.5	617.3	136.2
Eastham Lockgates	SJ370812	534.8	184.3	231.2	162.8	175.9	614.2	1366.3	154.8
Eastham	SJ365819	235.0							191.1
Rock Ferry	SJ340862	369.2	123.9	221.0	132.6	185.5	469.2	1273.0	234.1
Egremont	SJ319924	251.9	86.5	204.3	119.8	135.9			143.3
New Brighton	SJ288938	237.1	104.5	190.5	120.4		381.1		
Blundellsands	SJ304986		123.1	244.0	127.6		238.5		
Hightown	SD295030							735.7	151.9
Hoylake	SJ216897		101.8				227.9	496.3	134.0
Mean value for 1993 data		341.288	120.687	206.560	132.646	150.597	417.072	897.736	171.461
UK minimum*		40.6	53.2	69.2	76.1	No data	343.6	274.4	110.6
UK maximum*		2621.2	284.0	442.4	577.2	No data	1481.0	3241.6	406.7

Underlined values refer to minimum and maximum levels recorded in the Mersey 1993 survey

* - Refers to PML / MBA database (1993). See text for details.

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