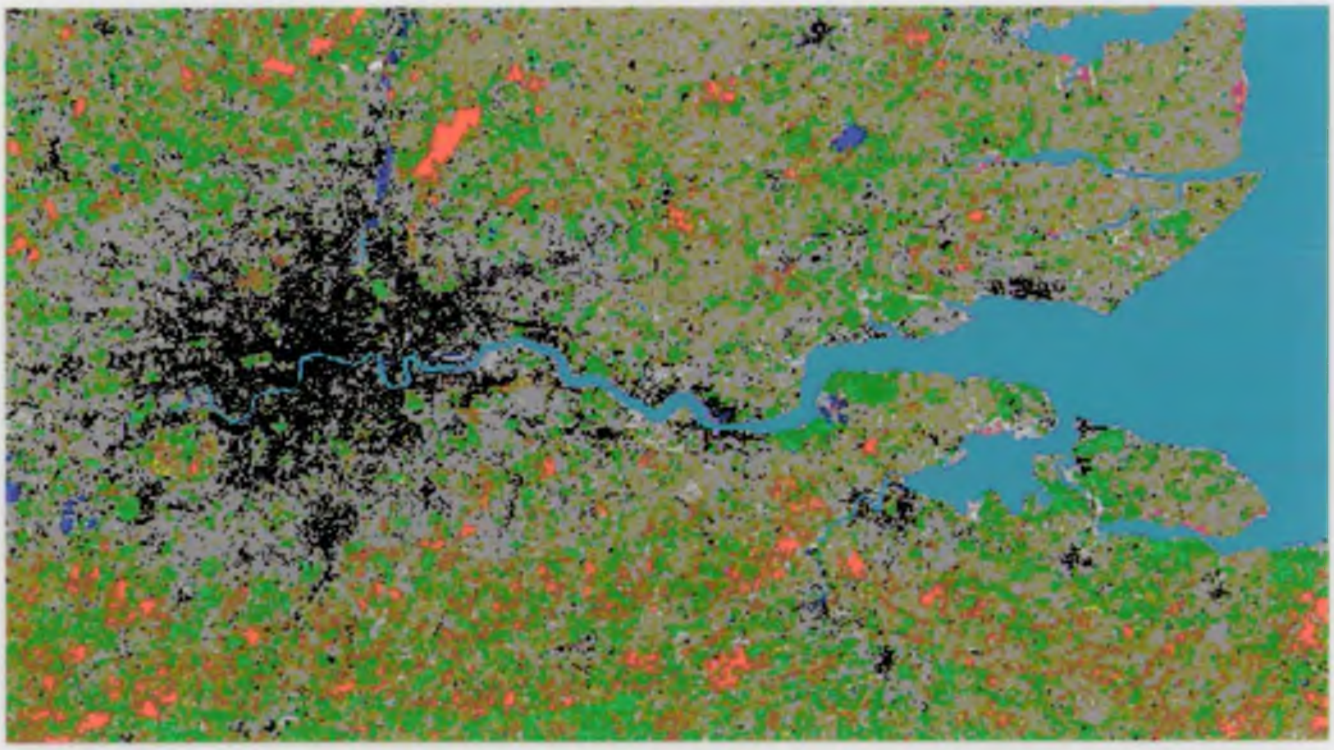
Bioaccumulation of metals in the Thames Estuary



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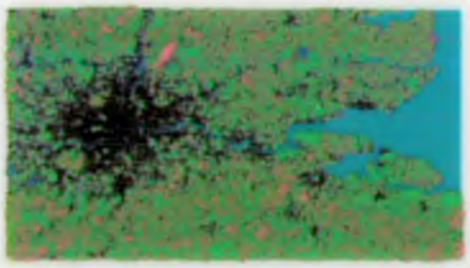

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Bioaccumulation of Metals in the Thames Estuary - 1997.

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A collaborative study between Plymouth Marine Laboratory and the Environment Agency (Thames Region)

Other Titles in 'Thames Estuary Environmental Quality Series':

Tributyltin (TBT) Impact in the Thames Estuary
Thames Estuary Environmental Quality Series, **1**, 67pp (March 2000).

SUMMARY

The primary objective of the current study was to determine the occurrence and bioavailability of metals in the Thames Estuary and to contribute to an in-depth assessment of contamination and impact in this major UK tidal waterway (see facing page - Thames Environmental Quality Series, No.1; others in preparation). The report will also serve as a reference document for future assessment studies.

Concentrations of silver (Ag), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), Copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), tin (Sn) and zinc (Zn) were determined in inter-tidal biota, sediments and water along an axial profile of the tidal Thames. Sampling took place during July 1997 at a total of 27 sites, from Teddington Lock seawards to Foulness on the northern shore of the outer estuary, and Shell Ness, on the Isle of Sheppey, to the south.

Water analyses represent a 'snapshot' of metal concentrations at the time of sampling, yet, despite this limitation, interesting features were revealed. Concentrations of most metals were elevated at inner- and mid-estuarine sites, though only copper and zinc consistently exceeded EQS values (5 and 40 $\mu g\ l^{-1}$, respectively). Even in the outer estuary, concentrations of several metals (Cd, Cu, Ni, Pb and Zn) were markedly higher than typical background values for the North Sea. Anthropogenic enrichment in the Thames was similar to that in other heavily industrialised European estuaries.

The profiles for dissolved metals gave some insight into the comparative estuarine behaviour of different elements. There was net removal of manganese to sediments in the estuary, particularly at low salinities, with, perhaps, a small degree of redox cycling in the middle reaches. Dissolved lead concentrations increased between Teddington and Kew; thereafter, concentrations declined seawards with little evidence of reactivity (similar behaviour was also observed for cobalt). Arsenic, zinc and, to a lesser extent, nickel profiles were characterised by an extensive mid-estuarine augmentation in concentrations, suggestive of diffuse inputs to the estuary, probably from sediments (pore waters). For silver and copper, peaks in concentrations occurred at one or more sites, suggesting that localised inputs could be important in influencing their distributions. The profile for dissolved cadmium was unusual in that concentrations increased in a seaward direction (opposite to the trend for Cd in sediments and biota). Inputs from the disposal grounds in the outer estuary are one possible reason for this gradient; in addition, there may be a salinity effect, since there is a tendency for Cd to form highly stable, soluble chloro-complexes in seawater .

For some metals, such as As and Ni, dissolved species were the dominant form in the water column. A significant proportion (>50%) of Cd, Ag and Zn was also present as dissolved metal. In contrast, Cu, Fe, Pb and Mn were transported in the water column predominantly as particulates. This variable pattern of partitioning behaviour for different elements was generally consistent with crude calculations of dissolved and particulate metal fluxes from the estuary. More extensive data is needed to confirm the spatial trends implied in the current survey and to determine, accurately, the budgetary significance for the North Sea.

Sediment metal-contamination patterns were fairly uniform, with concentrations decreasing, generally, in a downstream direction. The gradient was particularly marked for Ag, Cd, Pb, Se and Zn. These results imply that the influence of inputs was greatest towards the upper tidal limits. However, the significant co-variance between the majority of metals shows that their distributions may be determined to an extent by shared granulometric and geochemical factors, most important of which are the metal binding substrates that coat the surface of particulates, such as organic matter, and Fe oxyhydroxides.

Sediments, particularly those in the inner Thames, were significantly enriched in metals compared with deposits from the central North Sea, or from an 'unpolluted' reference estuary (Tweed). This was most obvious for silver (concentrations in Thames sediments 50-fold higher, on average, than those at reference sites), Cu and Hg (8-fold), Sn, Cd, Pb, Zn and Co (3-5-fold). Arsenic was the only element whose concentrations were not markedly higher. For most metals, the levels of contamination in sediments from the inner Thames were comparable to those of other industrialised estuaries bordering the North Sea (including the Humber, Tees, Tyne and Wear), whilst levels of silver and tin were higher. Since sewage treatment is one of the major vectors of contamination in the Thames, it may be that Ag and Sn act as tracers for this form of impact.

Extensive sediment-metal comparisons with other estuaries, countrywide, indicate that the mean value for Ag concentrations in the Thames was high - at around the 97th percentile of UK range (percentile = position within the normal distribution of UK sediment values, expressed as a percentage). 'Total' sediment loadings (concentrated HNO_3 - digests) were also important, nationally, for Cr, Sn, Hg, Cd, Mn, Co and Pb (>50th percentile), whilst Cu, Zn Fe and Ni ranged between the 25th and 50th percentiles. As and Se concentrations were ranked relatively low by comparison (< 25th percentile).

In addition to 'total' digests, sediment samples were extracted with 1M HCl as a measure of non-refractory metal (and a possible surrogate for the 'bioavailable' sediment fraction). Virtually all of the Pb in Thames sediments was extractable in 1MHCl, suggesting a high proportion was of anthropogenic origin - e.g. from urban run-off. Other elements with a high proportion in readily-extractable form (50-80% on average) were Cd, Mn, Zn, Sn, Cu and Co. At the other extreme, the value for Cr (16%) indicates that most of this metal was refractory in nature. The variability of these sediment associations influences the reactivity and bioavailability of metals in the estuary.

A **biomonitoring** strategy for the tidal Thames was developed. Using a multi-species approach, it was possible to provide a measure of bioaccumulation throughout all the sites. In the estuary proper, distribution ranges of monitoring organisms (seaweed *Fucus vesiculosus*; ragworm *Nereis diversicolor*; winkles *Littorina littorea*; clams *Scrobicularia plana* and *Macoma balthica*; cockles *Cerastoderma edule*; mussels *Mytilus edulis*) often overlapped and provided corroboration of trends in bioavailability. The amphipod crustacean *Gammarus zaddachi* was the only practical option for study in the inner, fresh water section; first impressions are that it may be a valuable bioindicator for several metals including Ag, As, Co, Cu, Hg, Se and Sn.

Scrobicularia plana (clam) *Macoma balthica* (clam) *Cerastoderma edule* (cockle) *Mytilus edulis* (mussel) *Littorina littorea* (winkle)

Molluscs used for bio-monitoring metals in the Thames Estuary

Patterns in bioavailability along the waterway were broadly similar for different metals, with impact *usually* increasing upstream, resembling trends in sediment contamination (Ag, Cd, Cr, Cu, Pb, Se and Sn) and, sometimes, water (Co, Ni and Pb). 1M HCl extracts were often more appropriate measures of bioavailable metal than total digests. However, there were various examples of how environmental and biotic factors influence body burdens. In certain organisms bioaccumulation of Ag, Cd, Pb and Se increased disproportionately upstream (*cf* sediment contamination), suggesting that bioavailability was promoted by conditions in the estuary. In contrast, increasing Fe in sediment reduced bioaccumulation of As, Pb, Cr, Cu, Mn, Ni, Zn and Se, complexation with particulate organic matter reduced bioaccumulation of Hg, and competition with dissolved phosphate appeared to inhibit arsenate uptake in *Fucus*.

Homeostasis of the essential metals Cu, Fe, Mn and Zn may have masked spatial trends in contamination to an extent. However, unusual features identified for Fe included high levels in *Nereis* and *Fucus* from Crossness and Beckton, which may signify atypically high Fe bioavailability at these sites.

Another biological feature which modified bioaccumulation was the selective ability to metabolise certain metal species. Thus, the known capability of *Mytilus* and *Littorina* to synthesise the metal-binding protein metallothionein probably accounted for the their comparatively high Cd burdens. Also, the high Sn concentrations in bivalve molluscs, relative to other taxa, may be attributed to the slow-degradation of bioavailable organotin species (notably, TBT). Allometric effects on metal burdens were relatively few because of the selection of similar-sized animals for analysis. However, the small size of *Nereis* from Foulness was responsible for elevated concentrations of Co and, to a lesser extent, Pb and Cr. Size effects were also observed for Cr in *Mytilus*.

Ag concentrations in Thames biota included some of the highest in UK estuaries, notably in molluscs from upstream sites. Se bioavailability was also disproportionately high here (often >90th percentile for UK Se data). Similar spatial trends were observed for Cd (more free-ion at low salinities, promoting bioavailability upstream) and the scale of Cd contamination in biota was moderate to high (upper values between 50th and 90th percentiles). Concentrations of Ni, Mn, Cu, Co, Sn, Fe, Zn, Pb and Hg in biota from the most contaminated Thames sites also ranked highly, in national terms (60th- 80th percentile, based on mean values across all species). However, at the least contaminated, outer estuary sites, rankings were considerably lower (all metals < 27th percentile, except Ag).

It is unlikely that levels of individual metals were acutely toxic to Thames biota, though EQS values were exceeded for Cu and Zn. Relatively little is known of possible subtle effects on sensitive life stages and the only evidence on which to assess impact is, therefore, circumstantial, based on published toxicity thresholds. On this basis Ag, Cd, Cu and Hg and Zn were *potentially* significant, with, perhaps, Mn, Ni and Pb posing a lesser toxic threat. Comparisons of Thames sediment data with OSPAR provisional ecotoxicological assessment guidelines for sediments indicates that concentrations of As, Cr, Cu, Hg, Pb and Zn (but not Cd) were within ranges where adverse biological effects could not be excluded. Equivalent comparisons for water suggest that concentrations of As, Cu, Pb, and Zn at a number of Thames sites are within the range where adverse effects would be expected.

There were significant negative correlations between the condition of clams *S.plana* and body burdens of Ag, Cd, Co, Cr, Hg, Pb, Sn and Zn, suggesting a link with poor performance. Levels of suspended Fe in the estuary were also similar to concentrations believed to reduce the nutritional status of filter feeders. It is therefore possible that metals are a contributory factor affecting the condition and distribution of Thames shellfish, but as yet these correlations are not proof of cause and effect.

Concerns over food chain magnification of toxic metals are considered to be marginal. The upper guideline value for Hg of 1 µg g^{-1} (dry weight), set for molluscs by OSPAR, compares with an upper limit of around 0.8 µg g^{-1} in Thames shellfish. Pb levels did not exceed current UK guidelines for food; however, a proposed EC regulation sets a limit of 2 µg g^{-1} wet weight (equivalent to approximately 10 µg g^{-1} dw) - similar to levels in cockles and mussels from the outer Thames and exceeded by two-fold in clams (non-commercial) from further upstream. The proposed threshold for Cd of 1.5 µg g^{-1} wet weight (~7.5 µg g^{-1} dw) was not exceeded. Incongruously, all shellfish samples in the Thames surpassed the UK limit for As in food of 1 µg g^{-1} wet wt (5 µg g^{-1} dw). However, this limit does not apply when contamination is deemed to come from 'natural sources'. In higher organisms, especially birds, there may be a fine-line between dietary levels of Se considered as essential (1 µg g^{-1}) and those regarded as potentially hazardous (>5 µg g^{-1}). Clams and worms from the inner Thames contained up to 10 µg g^{-1} Se, and winkles up to 35 µg g^{-1}, implying possible though, as yet, untested consequences for consumers at higher trophic levels.

Based on comparisons with a limited set of data for the mid-outer estuary from 1980, there appear to have been reductions in concentrations of As, Cd, Cr, Cu, Pb, Mn, Se, Sn and Zn in sediments (30%-80%). In certain biota, reductions of the same magnitude were observed for As, Cd, Co, Cr, Hg, Ni, Pb and Zn.

It is intended that many of the sites and sample types described in this report will form a reference set against which future trends in the Thames Estuary can be assessed. The information will assist decisions as to whether further improvements are necessary (or attainable) and to set appropriate environmental quality objectives. Hopefully this will ensure that the conditions in the estuary remain favourable for continued recovery.

CONTENTS

INTRODUCTION

Apart from information on trends in organic pollution loads (namely, from sewage inputs) there are few published records describing the incidence of persistent chemicals in the Thames Estuary. These are restricted, mainly, to small data sets on metals in sediments, and metals and selected chlorinated organic compounds in fish and shellfish (e.g. Rickard and Dulley, 1983; Attrill and Thomas, 1995; CEFAS, 1997). The paucity of data is extraordinary considering the importance of the Thames system. It constitutes one of the major water bodies feeding the North Sea and there are 12 million inhabitants in the catchment area of 9900 km^2, providing a diverse range of metal inputs. Principal sources of contaminants to the estuary are the River Thames itself, and the main sewage treatment plants such as those at Mogden, Kew, Crossness, Beckton, Riverside, Long Reach, Northfleet, Tilbury, Gravesend, Canvey and Southend (Figure 1). There are also periodic inputs from storm water run-off, particularly in central London, and various industrial effluents along the water course (including metal refineries, dockyards and marinas). Prior to cessation of sewage dumping in 1998, the Barrow Deep and South Falls sites in the outer estuary received large quantities of sludge (e.g. 4.5 million tonnes at Barrow in 1994 - CEFAS, 1997). Significant quantities of industrial wastes and dredge spoils have also been discharged in the outer Thames and are considered to be localised sources of, for example, cadmium and lead (at South Falls and Barrow, respectively; Figure 1) and probably other metals (Harper, 1988).

The primary objective of this study was to determine the distribution of particulate and dissolved metals and their bioavailability to a range of biota in the Thames Estuary. It is one of a series of collaborative projects between the Plymouth Marine Laboratory (PML) and the Environment Agency (EA) which will contribute to an in-depth assessment of contamination and impact in this major UK tidal waterway. Contemporary studies for TBT, and various indices of stress in benthic invertebrates and fish, were undertaken in parallel with the present work, to evaluate the 'health' of the Thames Estuary (e.g. Langston *et al.*, 2000a,b). This multi-tiered approach has seldom been applied in the field, but it is hoped it may form the basis of an improved strategy to interpret the status and trends in pollution, not only in the Thames, but eventually over much wider spatial and temporal scales. Principally, however, the results of the current project are intended to underpin the EA's role in understanding, forecasting and protecting the estuarine and coastal environment in the Thames region.

MATERIALS AND METHODS

Sampling sites, collection and distribution of indicator organisms

The Thames Estuary

Physical characteristics of the Thames Estuary include a mean river flow of 82 m^3 s^{-1} (range 9-210m^3 s^{-1}), a tidal range at the mouth of 3.5m (neaps) –5.1m(spring), and a flushing time of 20-75 days. It is well mixed, with little vertical stratification. Export of particulates amounts to an estimated 0.2 x10^6 tonnes per annum (Inglis and Allen, 1957; Veenstra, 1970; Turner *et al.*, 1991).

The current survey was designed to investigate the distribution of the metals silver (Ag), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), Copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), tin (Sn) and zinc (Zn) in biota, sediments and a limited set of water samples along the length of the tidal Thames Estuary. Sampling took place from Teddington Lock seawards to Foulness on the north bank of the outer estuary, and to Shell Ness, on the Isle of Sheppey, to the south. It was conducted in parallel with a survey of TBT (*see* Langston *et al.*, 2000a) and consequently, sites, types and timing of sampling were harmonised as far as possible, for obvious reasons of comparability and cost.

The major benthic sampling effort for biota and sediments was over a one week period in July 1997, although a preliminary selection of sites was undertaken shortly before this (June), in collaboration with Agency staff, who contributed valuable background knowledge of the estuary. Wherever possible, sites for the current project have been chosen to overlap closely with previous monitoring undertaken by the Agency and it's predecessors. Limited water sampling along an axial profile of the waterway was also undertaken in July 1997 to give an indication of the distribution of dissolved metals.

Figure 1 shows the distribution of sampling sites visited during July 1997. Material for metal determinations was collected from most, though not all, sites. Due to the size of the Thames estuary (117 km. from Teddington to Foulness/Shell Ness) and the logistical problems of travel, access to foreshore, and parking within Greater London, it was decided at an early stage in the planning of fieldwork that all water sampling, plus sediment and biota sampling at the upper and mid-estuarine sites, would be conducted from EA boats. Land-based sampling by vehicle was preferable for inter-tidal work at sites in the outer estuary (seawards from Coalhouse Fort).

Water Sampling

A collection of water samples (19 sites) along an axial profile of the Thames estuary was conducted on 16th July 1997 (a few days prior to sediment and biota sampling) using the EA pollution monitoring vessel *Thames Guardian.* Details of these samples, including locations, can be found in Figure 1 and Appendix 1.

Estuarine waters were sampled using the inert peristaltic pumping facility on board *Thames Guardian*. One litre samples were collected in glass-stoppered, acid washed bottles. Sub-samples (0.5l) were filtered on board (0.45 μm) using all glass vacuum filtration equipment (Sartorius) to represent the dissolved metal fraction in water. All filtered ('dissolved metal') and unfiltered ('total metal') samples were then acidified using 1 ml per litre of high purity nitric acid (Fisons *Primar*). Separate vials of water were also collected at each site for analysis of pH and salinity.

Benthic sampling

The principal survey work for sediments and benthic fauna and flora was conducted between 21-26th July, 1997 and covered some 27 sites in total. The first four days were boat-based in the upper- and mid-estuary, using the Agency vessels 'Abra' or 'Thames Dory'. These facilitated access to fairly inaccessible locations and also provided rapid transit between sampling sites. The final 2 days sampling in the outer estuary were shore-based, since this seemed most appropriate given the distance between sites and relative ease of access.

Figure 1. Map of Thames Estuary and sampling sites

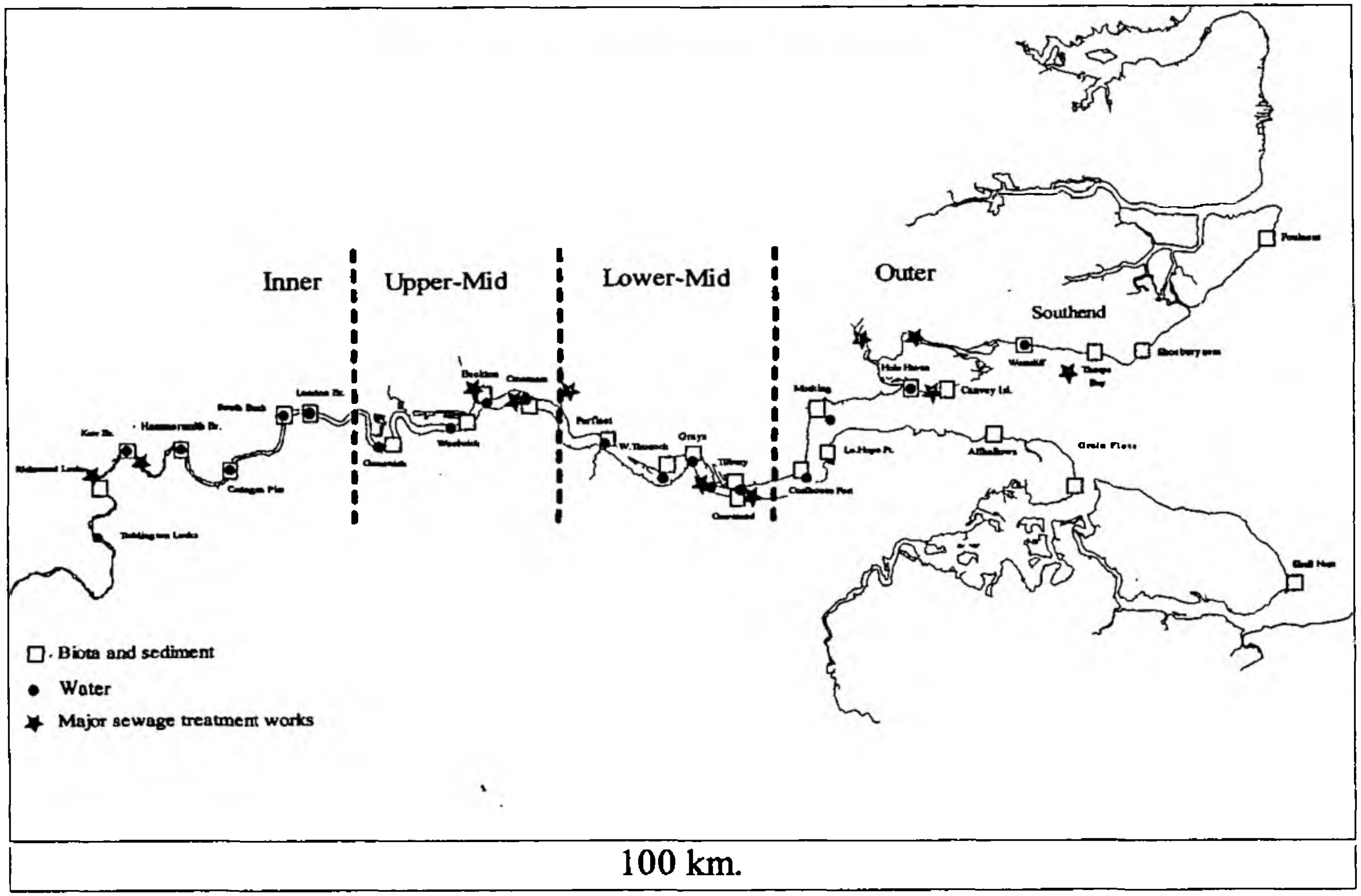


Table 1. Occurrence of indicator organisms, Thames Estuary 1997

N=numbers collected (and mean shell lengths of bivalves). {numbers collected in July survey but not analysed} ✓= *Fucus* collected but not enumerated

Site	Map Ref.	Distance	Bank	Date	*Gammarus*	*Nereis*	*Scrobicularia*	*Macoma*	*Fucus*	*Littorina*	*Mytilus*	*Cerastoderma*
Richmond Lock	TQ 168752	5.0	N	24-Sep-97	1052 {244}							
Kew Bridge	TQ 191779	9.0	N	24-Sep-97	522 {752}							
Hammersmith Bridge	TQ 230780	15.0	S	24-Sep-97	709 {1000}							
Cadogan Pier	TQ 276775	22.0	S	24-Sep-97	380 {1000}							
South Bank Centre	TQ 308804	27.0	S	24-Sep-97	504 {444}							
London Bridge	TQ 327805	29.0	S	24-Sep-97	380 {700}							
Greenwich	TQ 388783	37.0	S	24-Sep-97		69 {40}						
Woolwich	TQ 439798	44.0	N	24-Sep-97		124 {10}			✓			
Beckton	TQ 456817	47.0	N	22-Jul-97		55						
Crossness	TQ 492809	51.0	S	22-Jul-97		50			✓			
Purfleet	TQ 548786	58.0	N	23-Jul-97		65			✓			
West Thurrock	TQ 592770	64.0	N	23-Jul-97		30	2 (33.8)	1 (13.9)	✓			
Grays	TQ 614774	66.0	N	23-Jul-97		60	10 (31.6)		✓	67		
Tilbury	TQ 647753	70.0	N	24-Jul-97		90	44 (28.9)	3 (14.6)	✓	22		
Gravesend	TQ 648745	70.0	S	24-Jul-97		50	22 (24.6)	29 (12.7)	✓	13		
Coalhouse Fort	TQ 690762	75.0	N	24-Jul-97		110	10 (29.3)	60 (13.6)	✓			
Lower Hope Point	TQ 709776	77.0	S	26-Jul-97		90	18 (30.8)		✓	27		
Mucking	TQ 699807	80.0	N	25-Jul-97		160	22 (29.9)		✓	1		
Hole Haven	TQ 774821	87.0	N	25-Jul-97		90	40 (29.4)		✓	4		
Canvey Island	TQ 800824	90.0	N	23-Sep-97		100	24 (30.3)		✓	51	47 (37.0)	2 (30.4)
Allhallows	TQ 834789	91.0	S	26-Jul-97			67 (28.3)	20 (15.6)	✓	98	30 (38.1)	7 (25.0)
Westcliff	TQ 863852	97.0	N	25-Jul-97		60	62 (27.6)		✓	50	22 (39.3)	22 (33.3)
Grain Flats	TQ 894751	99.0	S	26-Jul-97		130	53 (30.6)	3 (13.4)	✓	31	18 (33.3)	
Southend (Thorpe Bay)	TQ 916844	102.0	N	25-Jul-97					✓	41	69 (26.3)	59 (23.2)
Shoeburyness	TQ 947852	106.0	N	25-Jul-97			19 (25.6)	74 (12.9)	✓	44	30 (29.8)	20 (24.0)
Shell Ness	TR 055682	117.0	S	22-Jul-97			21 (38.0)	17 (15.1)	✓	93	38 (25.8)	
Foulness	TR 036929	117.0	N	25-Jul-97		120 (small)	52 (25.3)		✓	60	43 (38.7)	

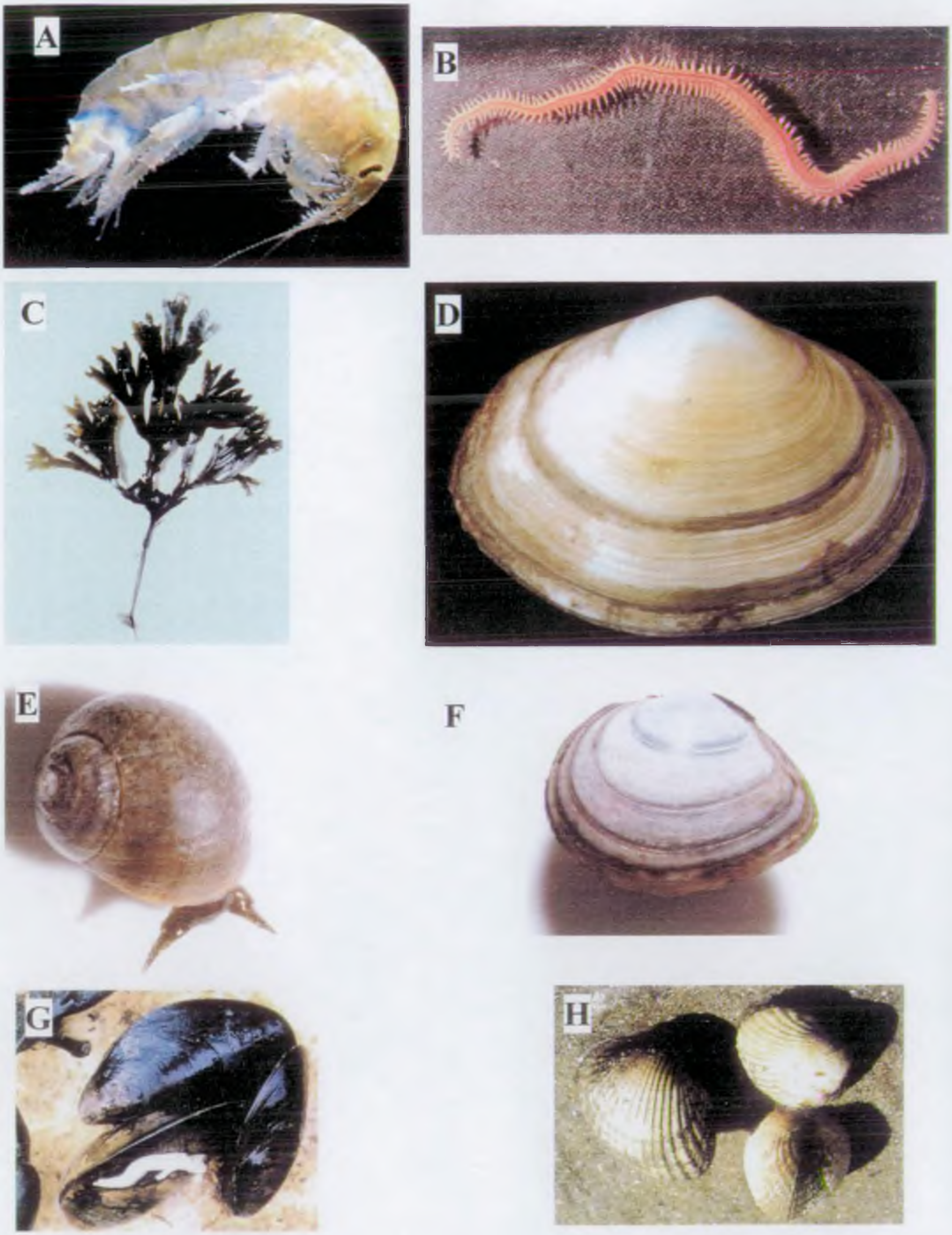


Plate 1. Biological indicator species, Thames Estuary. Gammarid shrimp, *Gammarus zaddachi* (A); Ragworm, *Nereis diversicolor* (B); Brown seaweed, *Fucus vesiculosus* (C); Clam, *Scrobicularia plana* (D); Winkle, *Littorina littorea* (E); Clam, *Macoma balthica* (F); Mussel, *Mytilus edulis* (G); Cockle, *Cerastoderma edule* (H).

Sediments
At each inter-tidal site, 100-200g oxidized surface sediment for metal analysis was scraped into a sealable polythene bag and temporarily stored on ice in a vacuum flask for transport back to the laboratory, where it was processed immediately.

Biota
The Thames is an extensive and diverse estuary, comprising a range of inter-tidal environments from almost liquid mud, through sand, gravel and stony shores to hard substrates of rock or clay. Furthermore, different sites are subject to a range of salinities from freshwater to almost fully saline conditions, and may support very different biological communities. From a contaminant-monitoring viewpoint, selection of a universal bioindicator is clearly impossible for the entire length of the tidal Thames. Therefore an appropriate strategy for any surveillance programme which attempts to address the issue of bioavailability/bioaccumulation must involve a multi-species approach.

Table 1 summarises the results of the main July survey, (combined with a smaller supplementary survey in September, *see below*) in terms of distributions of organisms recovered from each location. As a measure of abundance, numbers (and mean sizes) of biota collected over a sampling time equivalent to approximately 3 man hours is indicated. Note that where material was scarce, not all biological samples were analysed for every metal. Plate 1 illustrates the principal bioindicators sampled.

The amphipod *Gammarus zaddachi* was the most widespread species collected in the upper section of the tidal waterway (Richmond to London Bridge), although gastropods including *Potamopyrgus* and *Ancylus* were present at some locations, and the freshwater swan mussel *Anodonta cygnea* was found at the farthest upstream site, just below Richmond Lock. During the July survey, all amphipods died within 24 hours of collection, and had to be frozen prior to 'clean-up'. A repeat sampling of *Gammarus* was undertaken in September 1997 and, by transporting animals in dampened filter paper rather than water, extremely good survival rates were achieved. These latter samples were able to depurate successfully in clean water and consequently were used in the analytical studies.

Further downstream, the polychaete *Nereis diversicolor* was fairly common, although abundance and size varied between sites. Two individuals were found at the London Bridge site and probably represent the upstream limit of distribution for this species. It was notable that *Nereis diversicolor* samples from Greenwich and Woolwich were in very poor condition when returned to Plymouth following the July collection, and were immediately frozen. These two stations were re-sampled in September.

Downstream of West Thurrock the infaunal bivalves *Scrobicularia plana* and *Macoma balthica* were recovered from many sites, depending largely on whether or not suitable substrate (mud or muddy sand) was present. (At Thorpe Bay, Southend, for example, the substrate was probably too coarse for many of these infaunal indicators). Moving from mid- to outer-estuary, the incidence of biota typically associated with solid substrates also increased, including *Fucus vesiculosus* and *Littorina littorea*. *Mytilus edulis* and *Cerastoderma edule* were only found in the outer estuary, from Canvey Island seawards, indicating they are the least tolerant of low salinity estuarine conditions. (Note, the Canvey Island site was revisited in September since, due to tidal constraints, only limited sampling could be achieved in the July survey).

All biological samples were returned in cooling boxes to PML as quickly as possible and pre-treated as described in the next section, prior to freezing.

Not surprisingly for such an extensive field programme, some minor problems in sampling were encountered, as already indicated, though, overall, the survey was successful. A key objective was achieved, namely in identifying a practical option for a biomonitoring strategy which encompasses the whole tidal Thames. By adopting the above multi-species approach, it was possible to provide at least some measure of bioaccumulation at each site in the estuary, using one or more indicator organism. Ranges often overlapped, and should, therefore, provide confirmation of trends in bioavailability.

Experience has now been gained of the conditions at each site and the distribution of species, together with a knowledge of which sites are best sampled from a boat, and which may be most effectively sampled from the shore. It is hoped that many of the sites and sample types will form a reference set against which future trends might be assessed.

Pre-treatment of samples

Treatment of water samples

Water samples were screened for metals directly by flame and furnace atomic absorption spectrometry. Where concentrations were low or below limits of detection an extraction/pre-concentration procedure was used as described in the next section.

Treatment of sediment samples

In the laboratory the surface sediment samples were sieved through 100µm polypropylene mesh with 50% sea water (estuarine samples) or distilled water (riverine samples) and allowed to settle so that the water could be decanted. The resulting sediment slurry was well mixed before dispensing aliquots for metal analysis and determinations of water and organic content. Measurement of sediment organic matter was based on the loss in weight of dried (80°C) sediment after heating at 400°C for 6 h in a silica crucible. After both the preliminary drying and ashing stages, the sediment was allowed to cool for 1h in a desiccator before weighing. Since estuarine sediment had been treated with 50% sea water, and its water content was known, the results were corrected for errors due to the loss in weight of seawater salts at 400°C. No such correction was needed for riverine sediments.

Cleaning and treatment of organisms prior to analysis

***Fucus vesiculosus* (bladderwrack)**

Data for this brown seaweed are based on measurements on older parts of the plant about 50-100 mm behind the growing tips. Fronds from about 6 different plants were cleaned in running water and then cut into small pieces, avoiding the vesicles, and pooled to give a wet weight of about 12 g.

***Nereis diversicolor* (ragworm)**

To remove sediment from the body surfaces and the gut, ragworms were kept in acid-washed sand covered with 50% sea water for 6 days followed by one day in water. Pooled samples containing about 20 worms were used for analysis and, as far as possible, animals having a dry weight of 20 to 40 mg were used.

***Scrobicularia plana* and *Macoma balthica* (deposit-feeding clams)**

Clams were allowed to depurate in 50% aerated sea water for 7 days. Except where numbers were limited, each sample comprised the soft parts of five or six *S. plana* of about 40 mm shell length, or the soft parts of ten or more *M. balthica* of 12 to 18 mm length. The reason for using *S. plana* of constant size is that concentrations of some metals tend to be size dependent.

Other bivalve molluscs

To clean mussels *Mytilus edulis* and cockles *Cerastoderma edule,* specimens were kept in 50% and 75% sea water, respectively, for 2-3 days. Where possible, samples of 6-12 individuals of similar size were pooled for analysis.

***Littorina littorea* (winkles)**

Winkles were held in 50% sea water for 2-3 days. They were then usually frozen prior to removing the shell and operculum. Pooled samples usually contained 10 animals of 20-25 mm shell height.

Gammarus zaddachi

In the supplementary survey carried out in September, these small crustaceans were transported back to the laboratory in natural substrate from each site, dampened with filter paper. Clean-up was carried out in aerated freshwater for 2-3 days prior to analysis. As indicated above, survival was excellent compared to the heavy mortalities which occurred in July, following attempts to transport the animals in water. Cooler temperatures in September may have been a contributory factor in improved survival.

For each species, samples were dissected where necessary, and pooled individuals from each site frozen whole in clean glass beakers at -20°C, prior to freeze-drying at -80°C and 10^{-3} torr. All samples were then homogenised by grinding to a fine powder in a ceramic mortar and pestle, and stored in glass vials. Sub samples of freeze-dried homogenate were extracted for metal analysis, using the procedures outlined below.

Analysis of heavy metals

Water

Elevated aqueous concentrations of Mn, Fe , Zn and Cu were measured by flame AAS. Other metals were analysed by graphite furnace atomic absorption spectrometry (Varian 300 Zeeman). Ag was measured directly in water whereas, for low levels of Cu, Pb, Cd, Ni and Co, 100ml subsamples were extracted using the method of Danielsson *et al.,* (1982). Briefly, metals were sequestered using a mixed buffer/complexing reagent (APDC/DDDC), extracted into Freon-TF, and back extracted into nitric acid solution for analysis by Flame or Graphite Furnace Atomic Absorption (GFAA) techniques. Thus, low levels of metals were separated from the saline matrix, and concentrated by a factor of 20, prior to analysis. Extraction of spiked seawater samples had previously shown this method to give recoveries >90% for Cu, Pb, Cd, Ni and Co. Arsenic was determined by hydride generation, after reducing any As present in the water samples to As^{3+} in 5% hydrochloric acid (HCl) and 1% potassium iodide (KI) solution at 70°C. Metal concentrations in waters are expressed as µg/l.

Sediment

'Total' sediment metals (except Ag) were determined following microwave digestion of an aliquot of sediment (0.5g) with 5mL 16M HNO_3 (Primar) for 15 min at ~170°C in a pressurised teflon bomb. Water content of the sediment slurry was determined on a separate sub-sample to enable expression of results on a dry weight basis. For Ag, an aliquot of sieved sediment was dried and then approximately 1 g was placed in a 100 ml conical flask with 20 ml of nitric acid, covered with a glass bubble and digested for 2-3 days. After evaporating the acid, the residue was dissolved in concentrated hydrochloric acid with warming and diluted to give 1M HCl. Prior to analysis the solution was decanted into a test tube and any particles allowed to settle.

This operationally-defined 'total' sediment metal extract (concentrated nitric acid digest) may include residual, strongly-bound forms which are not assimilated by organisms. Therefore, an aliquot of sediment from each site was leached with weaker extractant (1M hydrochloric acid) as a possible surrogate for the 'bioavailable' sediment fraction. Each sample was continuously stirred with 1M HCl for two hours at room temperature, during leaching, and the extract separated by pressure filtration through a 0.45µm membrane filter, prior to metals analysis.

Most analyses for Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn were carried out by flame atomic absorption using an air-acetylene flame (Varian AA20). Background correction was employed for all metals except Cu, Fe, Mn and Zn. Interferences encountered during the analysis of Cr in sediment were overcome by using standard additions or by employing a nitrous oxide-acetylene flame. Low concentrations of metals such as Ag and Cd were determined by graphite furnace atomic absorption using standard addition methods (Varian 300 Zeeman).

As, Se and Sn were analysed by flameless atomic absorption (Perkin-Elmer MHS-20 system) using sodium borohydride to produce volatile hydrides. Hg was measured by cold vapour atomic absorption (Perkin Elmer MHS-20) using stannous chloride as the reductant (see Langston *et al.*, 1994a).

Biota

For most metals, pooled freeze-dried soft-tissues of each species (0.5g aliquots) were subjected to microwave digestion with 5ml 16M HNO_3 (Primar), as described for sediments. Digests were diluted to 25ml with distilled water, prior to analysis. For Ag, dried tissues were slowly digested in conical flasks with nitric acid (20 ml per gram), evaporated, and made up in 1M HCl in almost the same way as sediment samples. For As analyses, subsamples of tissue were mixed with 15 ml of ashing slurry (10g magnesium oxide and 6 g of magnesium nitrate per 100 ml distilled water) in 100 ml pyrex beakers (Langston *et al*, 1994a). After drying, the material was ashed at 500°C in a muffle furnace. The residue was dissolved in 25 ml of 50% hydrochloric acid and diluted to 50 ml with distilled water. This solution was used for the determination of As using the Perkin-Elmer MHS-20 hydride system.

Quality control

Appropriate quality assurance measures were taken to ensure the data were reliable. Certified Reference Materials SLEW (water), PACS-1 (sediment) and DORM-2 (tissue) were run with each batch of samples as an analytical control, by testing whether determinations fell within confidence intervals of the assigned values.

Data Processing and Analysis

Data from the analyses described above were input to MICROSOFT EXCEL 97 spreadsheets. Statistical analyses were performed using STATISTICA.

Comparisons with other estuaries

In order to make comparisons with other UK estuaries, the minimum, mean and maximum metal concentration in Thames sediment samples, and in each species, was compared to equivalent data for other UK estuaries, contained in our database (Langston *et al.*, 1994b). Thus, Thames data may be ranked in comparison to the rest of the UK and expressed as **percentiles** of the values present in the database. These data values follow a near normal distribution with, at the extremes, UK minimum and maximum values. If current Thames data are included in this set, and the data sorted into ascending order, then each individual value may be ranked from 1 to *n* (where *n* is the total number of data) and ascribed a percentile value of its position within this normal distribution. Thus, this method takes into account the whole data set irrespective of *n*. However, it must be remembered that these databases are not comprehensive and are subjected to the following caveats:

- The data for other UK estuaries, though extensive in coverage, were assembled over more than two decades. Conditions at some sites will be different now.
- The 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 percentile figures provide a broad impression of the scale and biological significance of metal contamination in the Thames estuary.

Comparison with earlier data

As indicated in the introduction, previous data on Thames biota is scarce, making assessment of temporal trends difficult (one of the aims of the current work is to establish a comprehensive baseline against which future changes may be measured). However, we have analysed a limited amount of material from an earlier survey (conducted in 1980) consisting of sediments, *Macoma, Scrobicularia, Fucus, Mytilus, Nereis* and *Cerastoderma* from six sites in the mid-outer estuary (Grays, Tilbury, Coalhouse Fort, Hole Haven, Westcliffe and Thorpe Bay). Where similar material has been analysed in the current survey, comparisons have been made using a paired Students 'T' test (α=0.05) as a guide to possible changes since 1980.

Table 2: (A). Dissolved metal levels (means and ranges, µg l^{-1}) in different salinity zones (see Fig. 1) of the tidal Thames. (B) Baseline values for the North Sea (Laslett, 1995) and EQS values for metals in marine waters.

A

Estuarine zone	Salinity (‰)	Ag µg/L	As µg/L	Cd µg/L	Co µg/L	Cu µg/L	Fe µg/L	Mn µg/L	Ni µg/L	Pb µg/L	Zn µg/L
INNER Teddington - London Bridge	(freshwater) 0.14- 1.96	0.12 (0.02-0.25)	3.55 (2.6-4.4)	0.05 (0.03-0.09)	0.31 (0.23-0.4)	12 (9-12)	31.2 (25-37)	14.29 (7.9-30.4)	8.10 (6.8-8.6)	1.55 (0.4-2.5)	53 (34-75)
UPPER-MID Greenwich- Crossness	(low salinity) 4.47 - 11.79	0.23 (0.09-0.38)	5.42 (5.1-5.7)	0.16 (0.08-0.26)	0.24 (0.22-0.26)	11.25 (9-17)	42.25 (37-47)	4.98 (3.5-6.2)	8.06 (7-8.8)	1.28 (0.5-1.8)	63.75 (59-70)
LOWER-MID Purfleet- Gravesend	(intermediate) 14- 19.2	0.15 (0.03-0.4)	5.30 (5-5.4)	0.23 (0.18-0.34)	0.11 (0.09-0.13)	12.2 (10-14)	17.2 (12-27)	6.18 (3-12.1)	9.46 (8.9-10)	0.64 (0.5-0.9)	57.6 (47-64)
OUTER Coalhouse Fort- Southend	(high salinity) 21.1- 31.58	0.16 (0.09-0.21)	4.38 (3.9-5)	0.21 (0.16-0.25)	0.07 (0.04-0.12)	ns	ns	1.6 (0.8-2.6)	7.71 (5.1-9.3)	0.33 (0.2-0.6)	41.75 (19-67)

ns= no sample

B

	Salinity (‰)	Ag µg/L	As µg/L	Cd µg/L	Co µg/L	Cu µg/L	Fe µg/L	Mn µg/L	Ni µg/L	Pb µg/L	Zn µg/L
North Sea offshore areas (1991-2)[1]	35.94	na	na	0.017 (0.004-0.051)	na	0.44 (0.20-0.83)	na	1.4 (0.25-3.4)	0.42 (0.18-1.0)	0.044 (0.013-0.071)	0.6 (0.11-2.2)
EQS[2]				2.5		5			30	25	40

na= not analysed

[1] Laslett (1995)

[2] EQS; see appendix 11 for details

RESULTS

Water

The complete data set for dissolved and total metal concentrations in water samples collected along an axial transect of the Thames Estuary on 16th July 1997 are presented in Appendix 1. This data can be summarised by dividing sites according to salinity zones, as indicated in Table 2.

Concentrations of most metals were highest at inner- and mid-estuarine sites, though only Cu and Zn consistently exceeded EQS values of 5 and 40 $\mu g\ l^{-1}$ respectively (see Table 2, Figure 2, and EQS details in Appendix 11). Even in the outer estuary, concentrations of several metals (Cd, Cu, Ni, Pb and Zn) were elevated compared to background values reported for the North Sea (Table 2B, data from Laslett, 1995) and those for Cu and Zn remained at or slightly above the EQS. In contrast, Mn values at the mouth of the Thames were comparable to average values for the North Sea.

The high Cu concentrations would be expected to harm biota if the metal were uncomplexed. However, in view of the strong affinity of Cu for dissolved organic matter, much of the 'dissolved' Cu is presumed to be in complexed form in the estuary. The most obvious sources of this organic matter are the humic and fulvic acids in river water and the major sewage discharges along the tidal waterway.

In Figure 2 the data for dissolved Cd, Cu, Mn, Ni, Pb and Zn concentration ranges in different sections of the Thames are plotted alongside published (Laslett, 1995) ranges for other North Sea estuaries (including the uncontaminated Tweed) and for the open North Sea. This indicates the elevated metal status of much of the Thames Estuary, at the time of sampling. These high concentrations are probably of anthropogenic origin and are on a par with (and sometimes exceed) levels found in other heavily industrialised European estuaries such as the Mersey, Severn, Elbe and Rhine (reviewed in Laslett, 1995; Power *et al.*, 1999). Again the one exception is Mn which is significantly enhanced at some of the sites in the Humber, Tyne, Tees and Wear Estuaries compared with the Thames Estuary. Mn is not generally associated with anthropogenic inputs and, in estuaries, is more likely to originate from benthic sources, especially when combined with oxygen minima (usually at the turbidity maximum). More extensive data is needed to confirm the important spatial trends implied in the current data set and should be extended to include analysis of suspended particulate loads. The Thames is presumably a significant source of metals to the North Sea but the budgetary significance of this has received comparatively little attention in comparison with other macrotidal estuaries bordering the North Sea.

Comparisons with available published material on metals in Thames Estuary waters in recent years confirm a similar level of contamination to that found in the current survey: Harper (1988) indicated the range of dissolved Cd to be <0.03-0.07 $\mu g\ l^{-1}$ (0.03-0.34 this survey) and Pb <0.03-0.11 $\mu g\ l^{-1}$ (0.03-0.34 this survey); Power *et al.*, (1999) report unfiltered 'model' values of 0.17$\mu g\ l^{-1}$ for Cd (0.08-3.05 this survey), 6.01$\mu g\ l^{-1}$ for Ni (0.8-14), 8.92$\mu g\ l^{-1}$ for Pb (1.75-31) and 37.48$\mu g\ l^{-1}$ for Zn (24-117). Their value for total Cu (11.4$\mu g\ l^{-1}$) was lower than in our survey (111-384). However, in view of the transient nature of water samples, such discrepancies - particularly in unfiltered samples - are not unexpected.

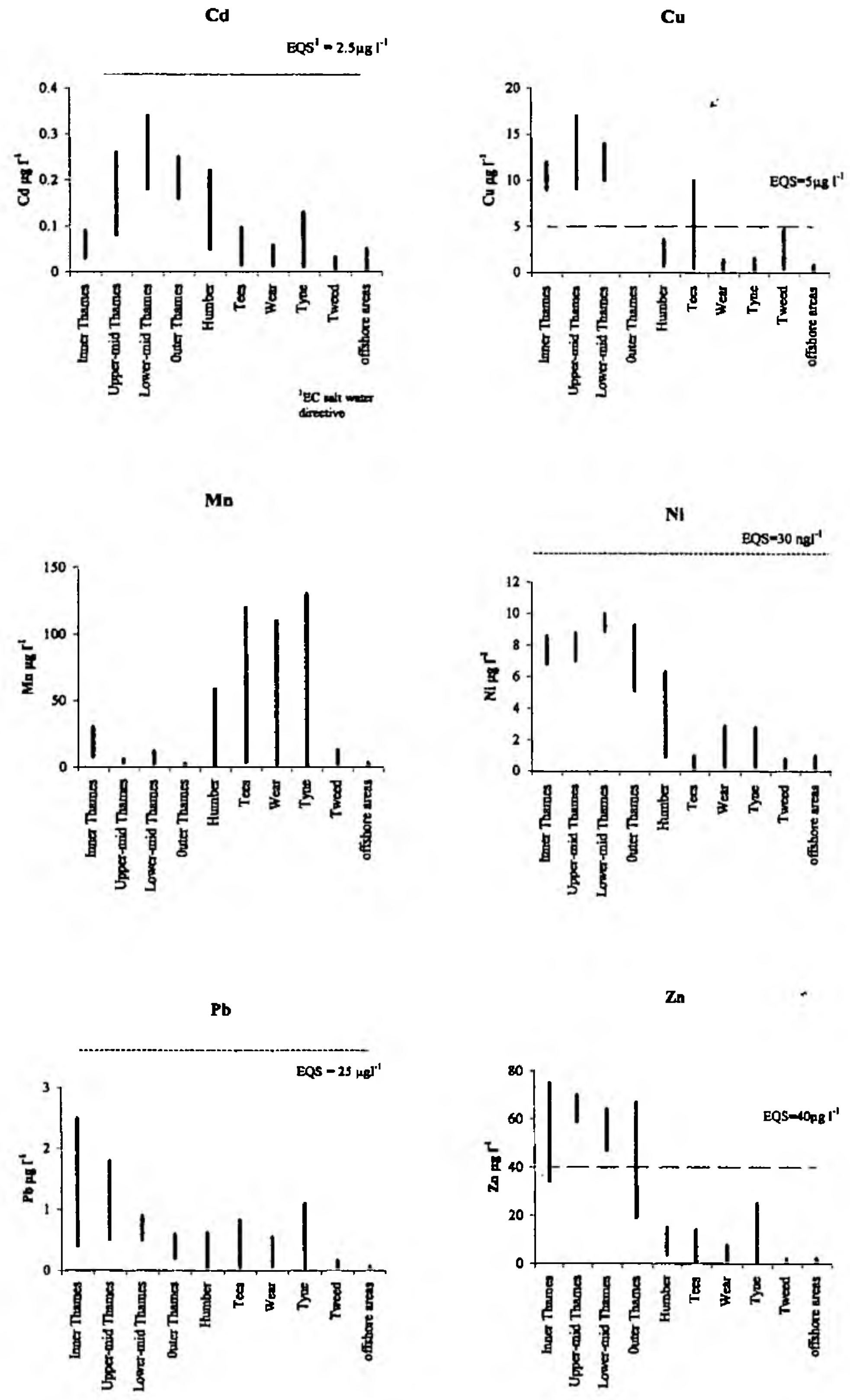


Figure 2. Comparison between dissolved metal concentration ranges for the Thames Estuary (current study) and published values for other N. Sea estuaries and offshore areas (Laslett, 1995). See Figure 1 for Thames zonation.

Long-term observations by the NRA /EA reveal that metal levels in the estuary have responded to water quality improvements in the last two decades and that, overall, loadings in the water column have been declining, though perhaps not on as great as scale as might have been anticipated. Thus, Power *et al.*, (1999) estimate that between the mid 80's and 90's concentrations have fallen by 63-68% for Cu, Hg, Ni and Zn, but by only 39% for Pb and 24% for Cd. There may even be some reversal of the trend for Pb in recent years, attributable to a combination of increased motor vehicle usage (and resultant road run-off) together with periodic rainfall patterns (drought-induced increases in Pb concentrations are conceivable). Unfortunately, spatial resolution in the EA's historic data-set (unfiltered samples only) is acknowledged to be poor and perhaps misleading. For example, the hypothesis that 'the urban area, not the upstream freshwater sections of the Thames, is the major source of metals found downstream' (Power *et al.*,1999) seems open to debate for some metals. Clearly, the spatial and temporal variability of dissolved and particulate metals needs to be studied in more detail, particularly with respect to tidal conditions and flow rates. This would help to evaluate the significance of the current major inputs to the estuary (natural and anthropogenic). The development and use of model simulations might also be considered with a view to explaining how effluent composition and quantity (from the major sewage treatment plants) influences metal profiles and water quality in the estuary.

Estuarine profiles showing metal concentrations in filtered and unfiltered water samples, plotted as a function of distance downstream from Teddington, are shown in Figure 3. Salinity and pH are illustrated in Figure 4. Filtered and total metal measurements were made on separate subsamples which might explain why some of the filtered samples appear slightly higher than unfiltered water. It is important to reaffirm that water samples represent only a transient signal of conditions at the time and site of collection. Nevertheless, there are some systematic features which can be to indicate the likely processes controlling the behaviour of individual metals:

Manganese concentrations in the Thames Estuary generally decreased downstream as riverine waters were diluted by less contaminated seawater (Fig.3). When data for dissolved Mn are plotted against salinity (Fig. 4), departure from the theoretical dilution line (a line drawn between concentrations in the extreme fresh water and saline end-members) suggests that there may be net removal of Mn to sediments in the estuary (apart from the water body sampled in the Purfleet region, where a small input of Mn is indicated). This overall pattern for Mn may be partly driven by redox-related conditions, as suggested above. In reducing conditions, $Mn^{(2+)}$ predominates and is relatively soluble, but will oxidise to insoluble $Mn^{(4+)}$ following contact with oxygenated sea water and become associated with particulates. As these are deposited and buried, reduction to $Mn^{(2+)}$ and further re-solubilisation takes place in anoxic conditions. This cycling may explain the peak in Mn near the Purfleet reach of the estuary, since injection of Mn (from interstitial to surface waters) is likely to be enhanced in the region of the turbidity maximum (Figure 4).

In contrast, the lead profile shows little evidence of reactivity. Dissolved Pb concentrations increased between Teddington and Kew, thereafter, levels declined uniformly towards the sea (Fig 3). Similar behaviour was observed for Co.

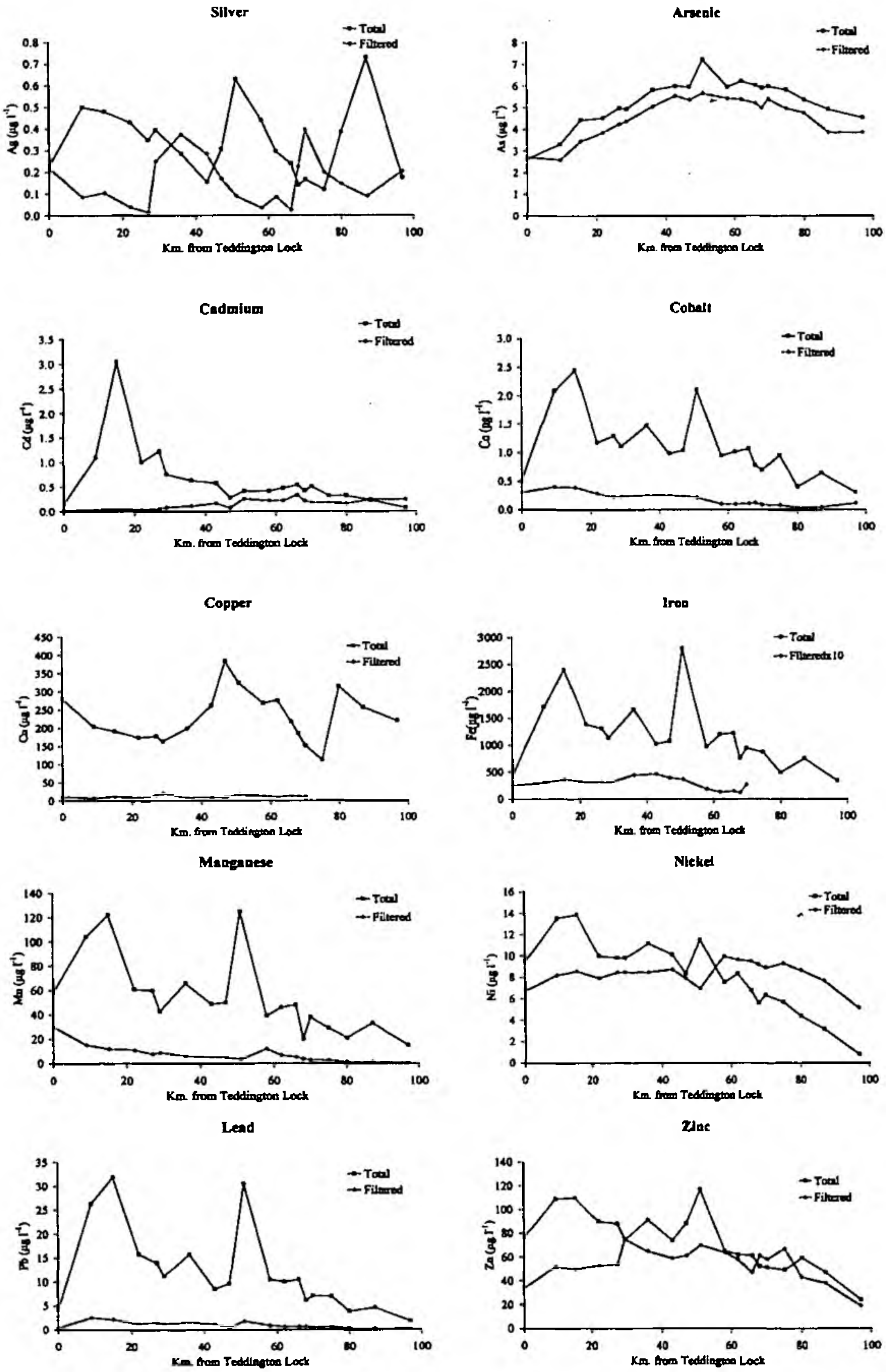


Fig. 3. Metal profiles in water (µg l^{-1}), Thames Estuary, July 1997 (note values for dissolved Fe are multiplied by ten).

The distribution of dissolved Cd is unusual in that concentrations increase in a seaward direction (Fig. 3). The dumping grounds in the outer estuary are a possible reason for this gradient: unlike many metals, Cd is unlikely to be bound strongly to particulates in the estuary and is more readily solubilised. Furthermore, there is an tendency for Cd to form highly stable, soluble chloro-complexes in seawater due to the higher levels of chloride ion. Similar Cd behaviour (increasing concentrations of dissolved metal towards the sea) has been observed in other estuaries such as the Gironde, Rhone, Huanghe, Forth and Tay (Elbaz-Poulichet *et al.*, 1987, and review in Laslett, 1995).

Arsenic, zinc and nickel profiles were all characterised by an extended mid-estuarine 'hump' in (dissolved) concentrations (Fig. 3), suggestive of diffuse inputs to the estuary, probably from sediments. This departure from conservative behaviour (depicted by deviation from the theoretical dilution line), is most clearly demonstrated for arsenic by plotting concentrations of dissolved As as a function of salinity (Fig 4). Similar profiles have been observed in the other tidally-energetic estuaries such as the Tamar (Langston, 1983).

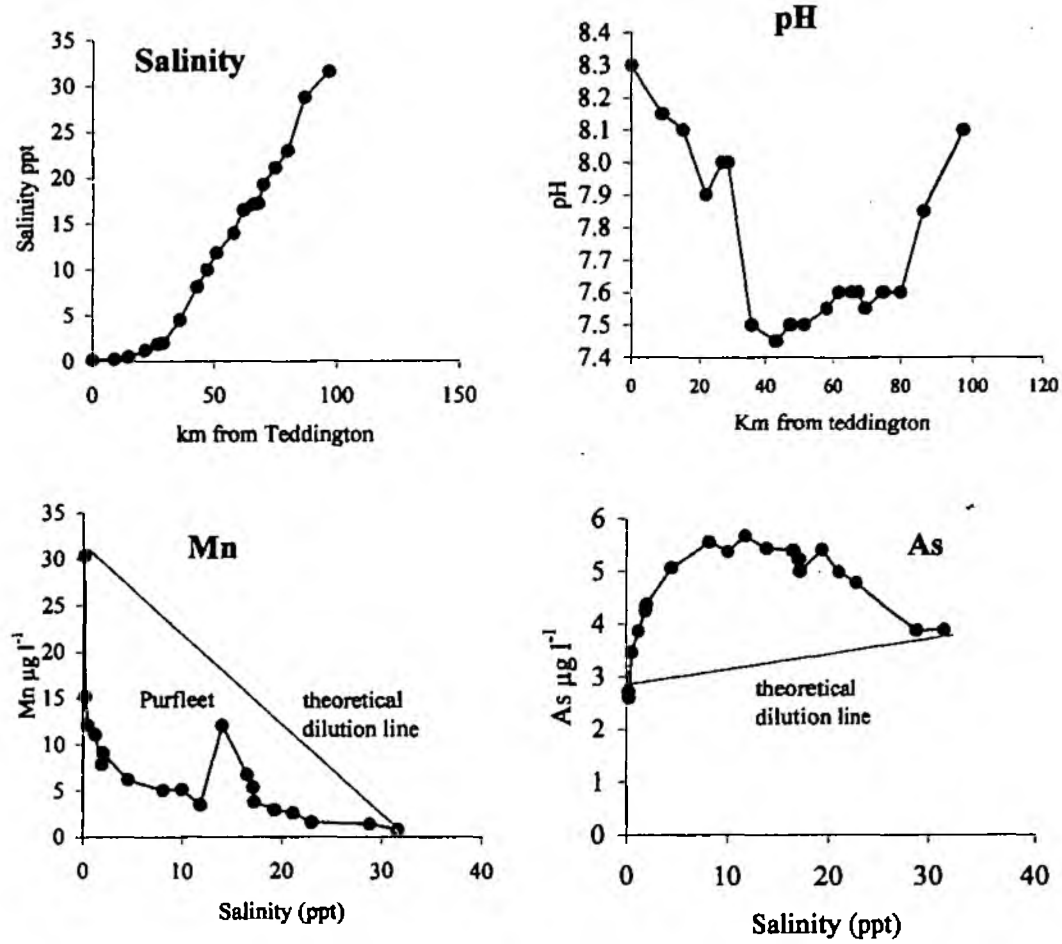


Figure 4. Plots of salinity and pH along the Thames Estuary (upper) and dissolved Mn and As as a function of salinity (lower), July 1997. Deviation of dissolved metals from the theoretical dilution line in lower figures illustrates removal and addition of Mn and As, respectively, during estuarine mixing.

Dissolved Fe in the Thames appears to deviate from it's typical, non-conservative behaviour in estuaries. Because of the relative insolubility of Fe^{3+} in seawater, strong removal of Fe from solution would be expected to occur with increasing salinity (producing a profile similar to that of Mn in Figure 4). However, in the current survey such a pattern of Fe removal was not observed (Figure 3). Typical behaviour may have been masked by additional inputs from point-source discharges, or diffuse, redox-mediated, sedimentary sources along the estuary.

For Ag and Cu, peaks in concentrations occurred at several sites (Fig. 3) making it difficult to describe the overall reactivity in the estuary, and suggesting that localised inputs could be important in influencing distributions. In the current survey peak values for Ag occurred at Greenwich and Gravesend, and for Cu at London Bridge and Crossness.

The matrix in Table 3 summarises the correlation statistics for all dissolved metals, salinity and distance. Highlighted r values are significant ($P<0.05$). These results confirm that Mn, Co and Pb decreased, progressively, towards the sea (negative correlations with distance) whereas, unexpectedly, As and Cd showed the reverse trend. Correlations for other metals were not statistically significant. These trends against distance are generally mirrored by relationships with salinity. The exceptions are As (not significant), and Fe (negatively correlated with salinity).

Correlations between individual dissolved metals determined in this single survey varied in accordance with the distribution patterns described above. They were significant, for example, for As *vs* Cd, Ni, or Zn and for Co *vs* Fe, Mn or Pb. Ag was not significantly related to other metals; Cu was only (weakly) correlated with Zn. A more detailed temporal study of estuarine behaviour is needed to determine the consistency of the observed profiles, to identify the origin and magnitude of possible metal sources and to model their influence on metal distributions.

Table 3. Correlation matrix for dissolved metals, salinity and distance in Thames water samples, July 16th 1997. Highlighted r values are significant ($P<0.05$)

	Distance	Salinity	Ag	As	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Distance	1.0000											
Salinity	0.9762	1.0000										
Ag	0.0838	0.0807	1.0000									
As	0.5077	0.3481	0.1919	1.0000								
Cd	0.8066	0.7774	-0.0890	0.5812	1.0000							
Co	-0.9042	-0.8716	-0.0262	-0.5466	-0.7479	1.0000						
Cu	0.1994	0.1310	-0.0024	0.2459	0.3337	-0.2828	1.0000					
Fe	-0.4235	-0.5404	0.3769	-0.0317	-0.4695	0.6063	-0.1465	1.0000				
Mn	-0.7996	-0.6849	-0.1170	-0.6212	-0.6028	0.6256	-0.1675	-0.0624	1.0000			
Ni	0.0126	-0.1037	-0.0967	0.4807	0.1304	-0.2207	-0.0090	-0.4963	-0.1051	1.0000		
Pb	-0.6960	-0.7378	-0.1794	-0.2741	-0.4733	0.7876	-0.0648	0.6003	0.2878	0.0646	1.0000	
Zn	-0.2084	-0.3687	0.1499	0.5501	-0.0731	0.0927	0.4832	0.2253	-0.1323	0.6010	0.3669	1.0000

$P<0.05$ @ r= 0.456

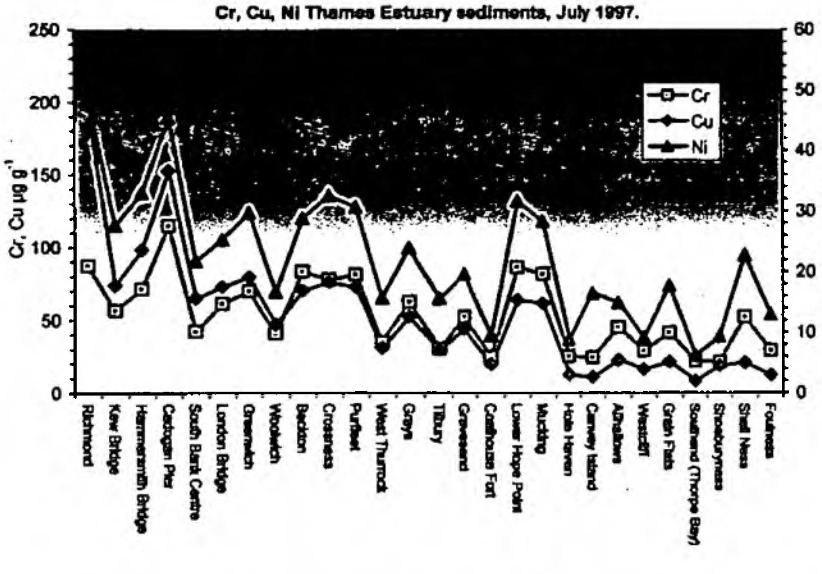
As indicated from comparisons of metal concentrations in filtered and unfiltered water samples, dissolved forms represent a variable proportion of the total concentration in the water column, depending on the metal in question (see profiles, Fig 3.). Table 4 summarises the mean percentage of the dissolved component, for all water samples. For some metals dissolved species were the principal form (As and Ni). A significant proportion (50% or more on average) of Cd, Ag and Zn was also present in dissolved form. (Note that for Cd, Ni and, to a lesser extent, Zn the proportion in solution increased in a seaward direction). In contrast, Cu Fe, Pb and Mn were predominantly transported in the water column as particulates. For Mn and Fe the proportion bound to suspended sediments increased with increasing salinity, reflecting the relative insolubility of oxidised species.

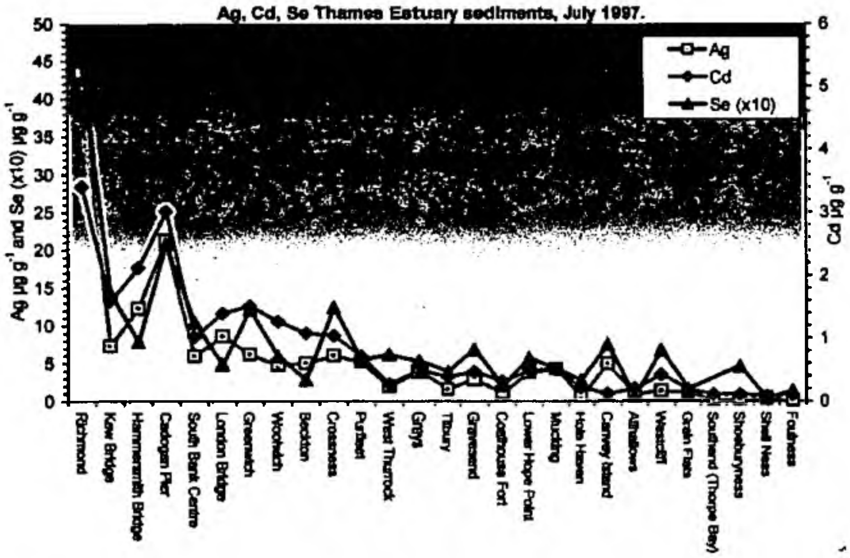
Table 4. Percentage of total metal in water column present in dissolved form.

Ag	As	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
73	86	50	19	5	2	14	115	9	79

Sediments

Data for total (concentrated HNO_3-extractable) and 1M HCl extractable- sediment metals are presented in appendices 2 and 3, respectively. Profiles of total metal concentrations and percentage organic content of sediments along the estuary are depicted in Figure 5. The determinants in these figures are grouped according to similarity in contamination trends. However, although variations between elements were evident, there was a common trend of decreasing concentrations in a downstream direction, towards the sea. This pattern is particularly marked, for example, for the pollutant metals Ag and Cd and implies that the influence of inputs is greatest towards the upper tidal limits.





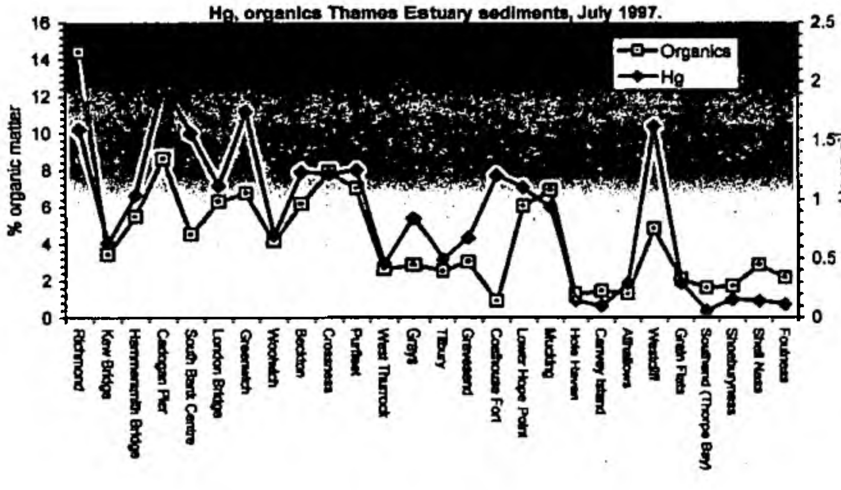
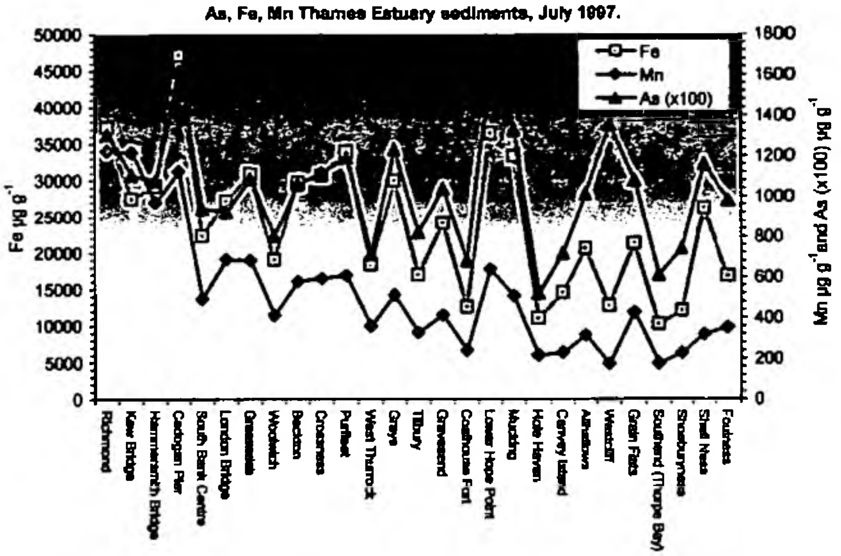
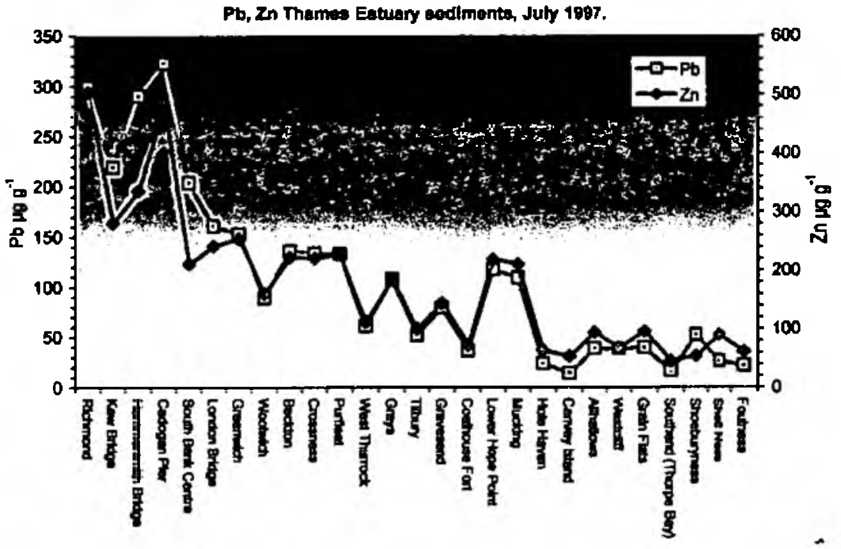
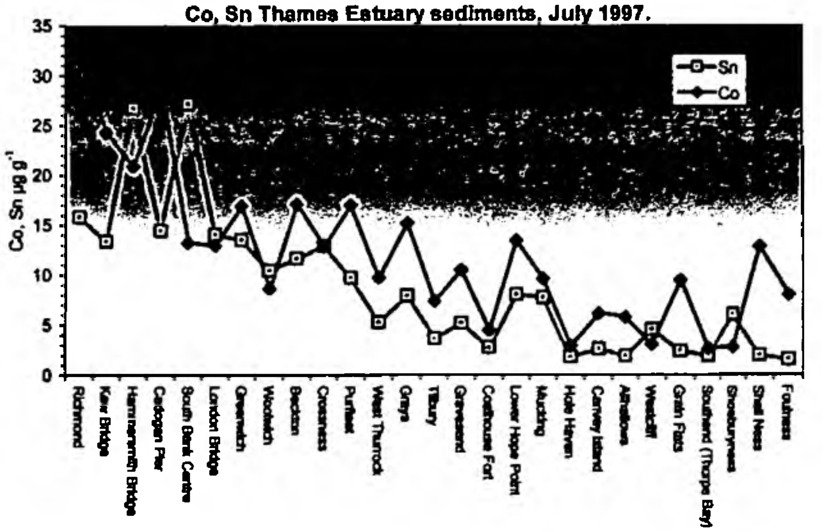


Figure 5. 'Total' sediment metal concentrations (<100µm fraction), Thames Estuary ....cont.







(cont)....Figure 5. 'Total' sediment metal concentrations (<100µm fraction), Thames Estuary

The correlation matrix in Table 5 confirms that all of the measured determinants in sediments, except As, decreased significantly ($P<0.05$) towards the open sea (negative correlations with distance from the most upstream site, Teddington). The coefficients also demonstrate that nearly all of the elements in HNO_3 digests co-varied: instances where correlations were particularly strong ($R>0.9$) are highlighted. Of a possible 91 combinations of metal pairs 89 were found to be significantly correlated ($P<0.05$).

Table 5. Correlations between Thames Estuary sediment metals (HNO_3 digested 'totals'), organic content and distance downstream from Teddington, July, 1997.

	Distance	Organics	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
Distance	1.0000															
Organics	-0.6541	1.0000														
Ag	-0.6760	0.8331	1.0000													
As	-0.2614	0.6311	0.4073	1.0000												
Cd	-0.8620	0.8148	0.8941	0.4478	1.0000											
Co	-0.7905	0.7614	0.7917	0.6094	0.8747	1.0000										
Cr	-0.5941	0.8060	0.5873	0.7931	0.6925	0.8154	1.0000									
Cu	-0.8148	0.9103	0.9173	0.5778	0.9493	0.9133	0.8210	1.0000								
Fe	-0.5959	0.7786	0.6002	0.8157	0.6900	0.8546	0.9800	0.8238	1.0000							
Hg	-0.6724	0.7444	0.5391	0.5944	0.6885	0.5934	0.6690	0.7145	0.6369	1.0000						
Mn	-0.8371	0.7318	0.7704	0.5649	0.8905	0.9533	0.7674	0.8958	0.7964	0.5590	1.0000					
Ni	-0.7146	0.8766	0.7809	0.7157	0.8276	0.9272	0.9349	0.9309	0.9494	0.6548	0.8797	1.0000				
Pb	-0.8927	0.7641	0.7821	0.5265	0.9328	0.9047	0.7603	0.9266	0.7702	0.7053	0.9279	0.8616	1.0000			
Se	-0.6613	0.7743	0.9384	0.3637	0.8353	0.7439	0.4751	0.8498	0.5058	0.5410	0.7254	0.7024	0.7189	1.0000		
Sn	-0.8371	0.5822	0.5175	0.2943	0.7181	0.6545	0.5249	0.6883	0.5262	0.6459	0.6821	0.6288	0.8572	0.4814	1.0000	
Zn	-0.8443	0.8658	0.8605	0.6161	0.9506	0.9417	0.8556	0.9849	0.8633	0.7166	0.9378	0.9423	0.9611	0.7826	0.7250	1.0000

correlations are significant ($P<0.05$) for r values of 0.381 and above
shaded cells signify r values >0.9

The significant co-variance between the majority of metals suggests that their distribution was determined to some extent by shared granulometric and geochemical factors – particularly the metal binding substrates such as organics and Fe oxyhydroxides that coat the surface of particulates. In fact, there were significant relationships for all metals with both Fe and organic matter, as shown in the comparison of r values in Table 6. Correlations were significant at $P<0.001$ except Se, Sn *vs* Fe, and Sn *vs* organics ($P<0.01$). Overall, relationships with organics or Fe were equally strong as indicated by the similarity of mean r values in Table 6 (comparison of r values by paired 2 sample t-test; $p>0.05$). Individually, however, some metals were associated more strongly with organics (e.g.Cu, Fig 6), and others with Fe - (e.g. Cr, Fig 6).

Table 6. Comparisons of r values for relationships between metals in sediments and Fe or organic matter. All significant at $P<0.001$ except * ($P<0.01$)

	Fe	%Organics
Ag	0.6002	0.8331
As	0.8157	0.6311
Cd	0.6900	0.8148
Co	0.8546	0.7614
Cr	0.9800	0.8060
Cu	0.8238	0.9103
Hg	0.6369	0.7444
Mn	0.7964	0.7318
Ni	0.9494	0.8766
Pb	0.7702	0.7641
Se	0.5058*	0.7743
Sn	0.5262*	0.5822*
Zn	0.8633	0.8658
Mean	0.7982	0.7928

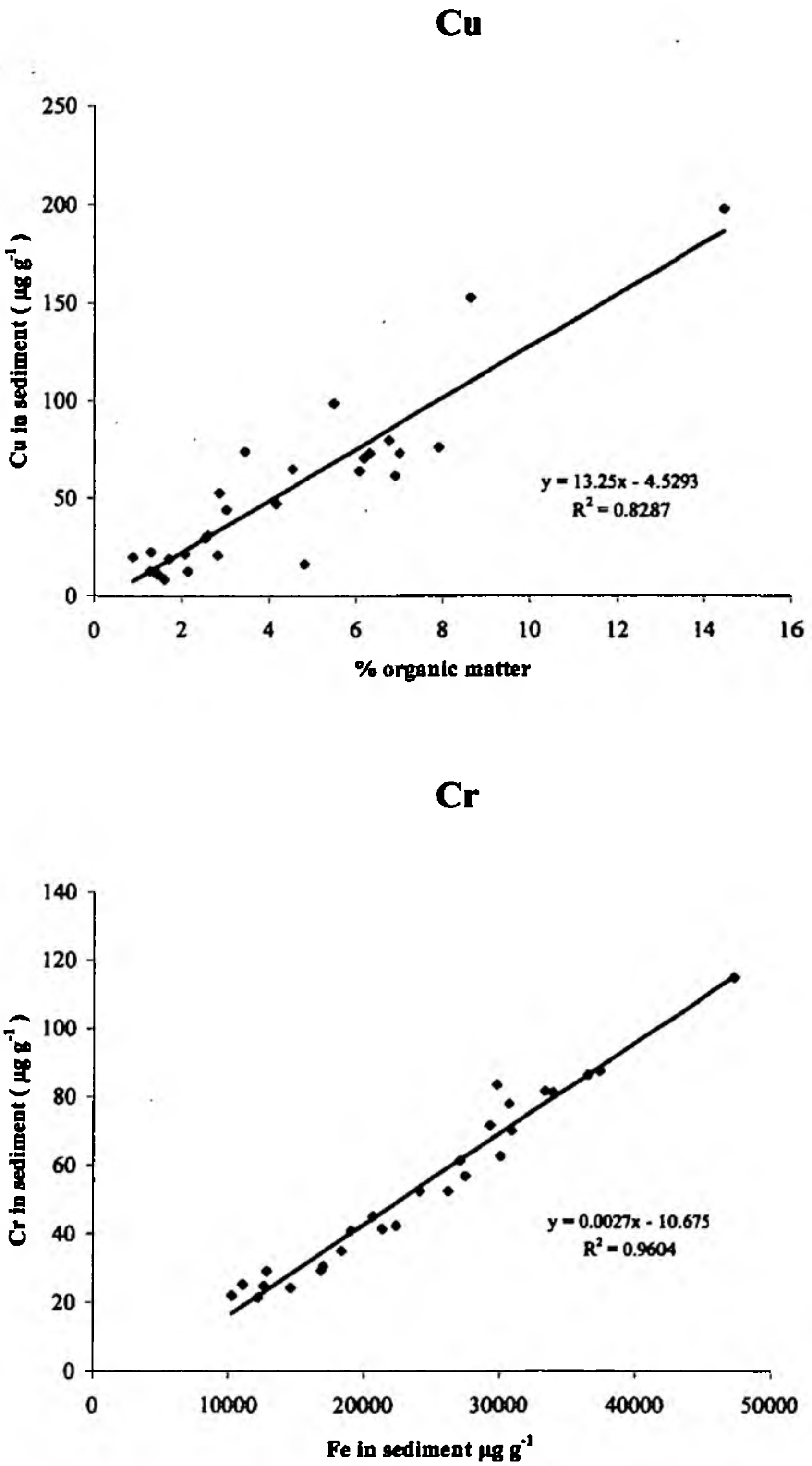


Figure 6. Relationships between Cu and organic matter (top) and Cr and Fe (bottom) in Thames sediments, July 1997

For 1M HCl sediment extracts, there were somewhat fewer significant correlations between metals (44 out of 66 combinations, see Table 7) - presumably because this fraction represents a more significant proportion of adsorbed/anthropogenic metal (of varied origin), and less of the common geological component, than that present in the 'total' sediment metal digest. As a consequence, compared with total sediment loadings, metal distributions in weaker extracts are less likely to be dominated by common, geogenic properties.

Nevertheless, nearly all metals in 1M HCl extracts were significantly (negatively) correlated with distance downstream from Teddington (Table 7). The one notable exception was 1M HCl-extractable As, which increased in concentration seaward - in contrast to the trend for total As. (This may have significance for patterns of bioavailability of As, as discussed later). Individually, for other elements, the ratios of 1M HCl extractable/ total ($HN0_3$ digests) were fairly consistent over the length of the estuary, though proportions extracted were highly element specific. Such properties are undoubtedly a major influence on the re-mobilisation, flux and bioavailability of metals from sediments during estuarine transport, as indicated in subsequent sections.

Table 7. Correlations between Thames Estuary sediment metals (1M HCl extracts), organic content and distance downstream from Teddington, July 1997.

	Distance	Organics	Ag	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sn	Zn
Distance	1.0000													
Organics	-0.6541	1.0000												
Ag	-0.7579	0.5791	1.0000											
As	0.4948	-0.0741	-0.1281	1.0000										
Cd	-0.8594	0.8422	0.6791	-0.3729	1.0000									
Co	-0.3177	0.1673	0.1557	-0.2090	0.2285	1.0000								
Cr	-0.3860	0.7557	0.5666	0.2727	0.4461	0.1046	1.0000							
Cu	-0.8248	0.8323	0.7716	-0.0863	0.9207	0.2449	0.5814	1.0000						
Fe	-0.5828	0.8102	0.6238	0.1788	0.5693	0.1800	0.8413	0.6739	1.0000					
Mn	-0.8781	0.7226	0.7032	-0.2469	0.8213	0.2976	0.5246	0.8317	0.7024	1.0000				
Ni	-0.5433	0.4790	0.4033	-0.2663	0.4560	0.8996	0.4266	0.4679	0.5007	0.5034	1.0000			
Pb	-0.8700	0.6650	0.7391	-0.2584	0.8090	0.2513	0.4494	0.8523	0.6850	0.8624	0.4881	1.0000		
Sn	-0.7773	0.4661	0.6992	-0.2425	0.6958	0.2527	0.3069	0.7701	0.4679	0.8197	0.3748	0.9082	1.0000	
Zn	-0.9077	0.8492	0.7572	-0.2327	0.9111	0.2681	0.6126	0.9250	0.7913	0.9129	0.5477	0.9352	0.8084	1.0000

correlations are significant ($P<0.05$) for r values of 0.381 and above

shaded cells signify r values >0.9

Thus, by performing geochemical 'normalisation' procedures (e.g. relating metals to the appropriate metal-binding components, such as Fe and organics), and by use of selective extractants, it is possible to explain much of the residual variation in Thames sediments. In future studies, it would also be useful to normalise sediment metals with respect to a geogenic component such as Al or Li. This combination should establish a procedure which provides better comparisons of sediment contamination between sites or different sea areas, and will help to define the anthropogenic component.

Comparisons of metal concentrations in Thames sediments and other N Sea sites

Because sediment concentrations are influenced by factors such as granulometry and geochemical composition, direct comparisons with other studies is difficult unless the processing techniques (sampling, sieving, digestion etc.) were similar. Bearing in mind these caveats, current results are illustrated alongside published values for Thames sediments in Figure 7. Concentration ranges in the present study were, in fact, remarkably consistent with those reported for sediments from a similar range of sites in the Thames, collected in 1989, by Attrill and Thomas (1995) (Figure 7). The latter authors analysed freeze-dried, HNO_3 - H_2O_2 digested samples (<63μm fraction) by ICP-OES. It seems likely the choice of fine fractions for analysis in these two surveys is responsible for the similarity in metal concentrations. The results also imply there has not been a substantial change in sediment contamination over the last decade.

In Figure 7, comparisons are also made with metals in sediments from other major UK industrial estuaries entering the North Sea (Humber, Tyne and Wear), an 'uncontaminated' reference estuary (the Tweed) and samples from offshore (Dogger Bank). These data were all generated by our laboratory, using identical methodology (see methods) thereby reducing inter-laboratory anomalies.

Thames sediments, particularly those in the inner estuary, were, as expected, significantly ($P<0.05$) enriched with metals compared to those in the central North Sea (Dogger Bank). This was most obvious for Ag (average enrichment factor~50), Cu, Hg (8), Sn, Cd, Pb, Zn and Co (3-5). Arsenic was the only element whose concentrations were not markedly higher than those at the Dogger Bank. A similar pattern of enrichment is also seen when Thames sediment data are compared with the Tweed reference site (Figure 7).

Generally, the levels of contamination of most elements in sediments from the inner Thames were on a par with those of other industrialised estuaries bordering the North Sea (Fig 7), though, occasionally, hotspots occured in the north-east group (e.g. Hg and Cr in the Tees and As in Humber and Tees). However, it is notable that Ag and Sn were significantly elevated in Thames sediments - a feature which was also indicated in the study by Attrill and Thomas (1995).

Since sewage is probably the major source of contamination to the Thames, it would appear from current results that Ag and Sn are potentially important tracers for this form of impact. However, the fact that Sn (as triorganotin compounds) has also been used in antifouling preparations, wood-preservatives and fungicides may detract from it's value as a marker for sewage. For example, a direct major spillage of TBT in to the River Bourne, a tributary of the Thames, occurred in the late 1980's and could have influenced sediment concentrations in the estuary (Dowson *et al.*, 1996; see also Langston *et al.*, 2000a for review of TBT distributions in the Thames Estuary). Other diverse usages of organotins which may have affected the overall distribution of Sn in sediments include incorpoation of dibutyltin as a stabiliser in PVC.

Among the alternative sources of these and other metals in the estuary are the fresh waters of the River Thames and the various tributaries that enter the water course in central London, run-off via storm drains and direct inputs from adjacent industry. Nevertheless, discharge from major treatment plants must be regarded as a potential prime source and it would be interesting to investigate the possible role of both Ag and Sn as tracers for sewage-related influence in sediments.

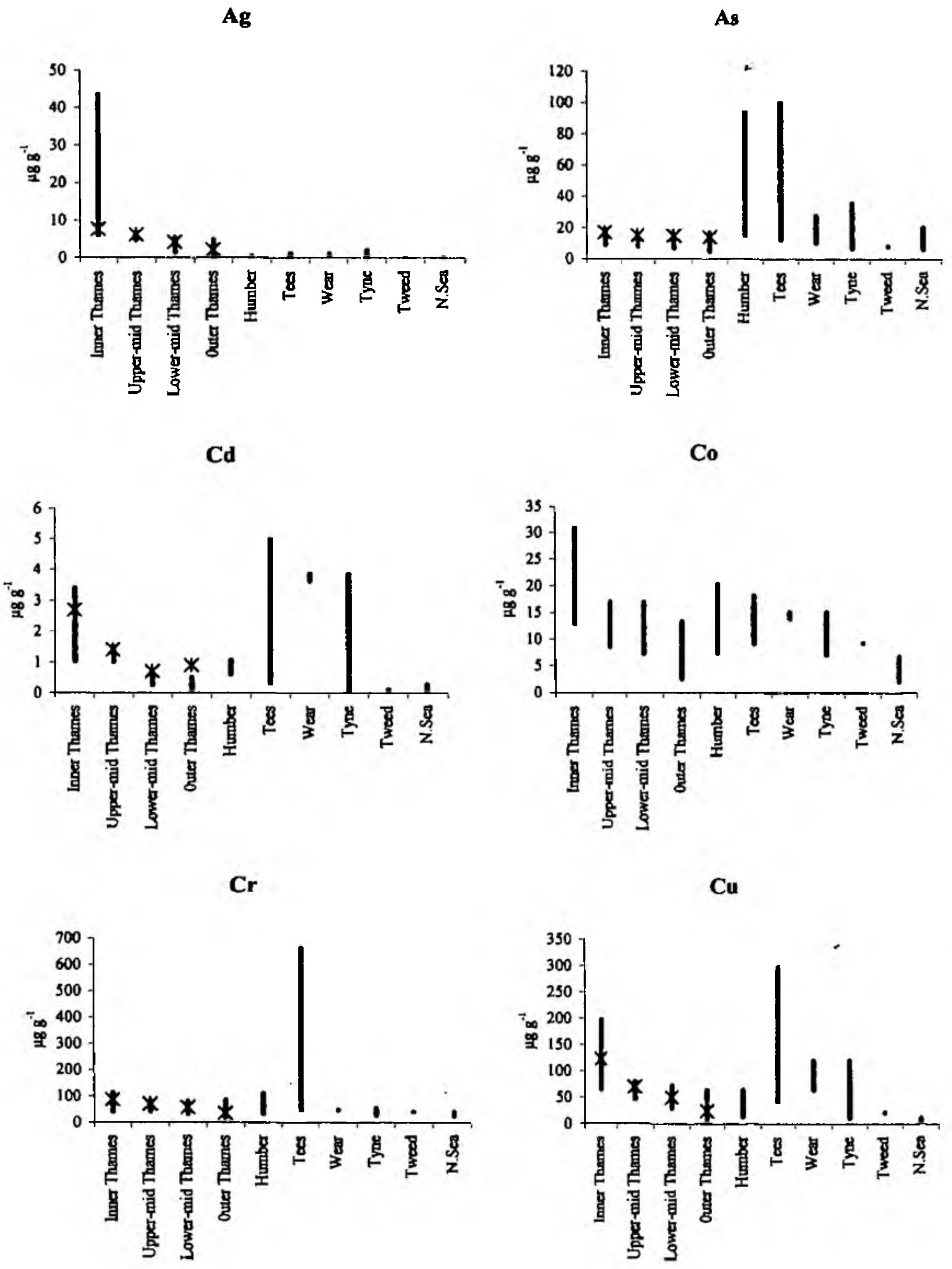


Figure 7. Comparison of sediment metal concentration ranges for the Thames Estuary and N. Sea estuaries (bars - current survey and data from Bryan and Langston, 1992; Langston *et al.,* 1999. ✳= means for samples collected in 1989, by Attrill and Thomas (1995)) …….(cont)

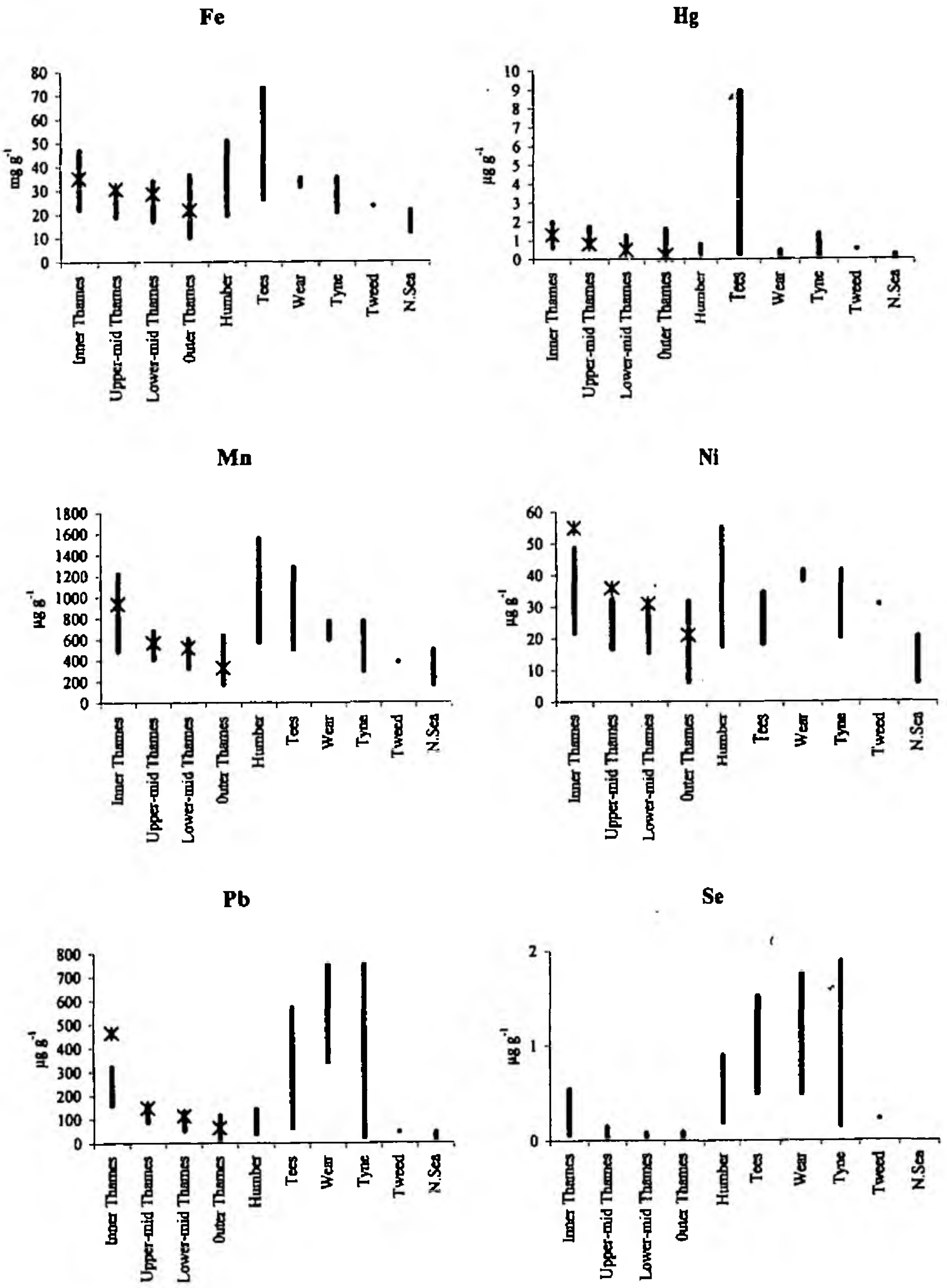


Figure 7 (cont). Comparison of sediment metal concentration ranges for the Thames Estuary and N. Sea estuaries (bars - current survey and data from Bryan and Langston, 1992; Langston *et al.*, 1999. ✳= means for samples collected in 1989, by Attrill and Thomas (1995)) ....(cont)

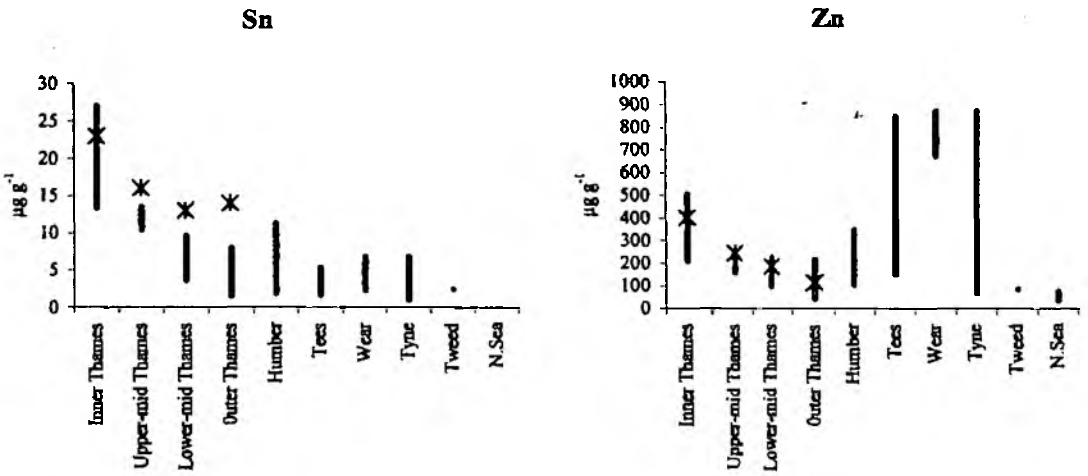


Figure 7 (cont). Comparison of sediment metal concentration ranges for the Thames Estuary and N. Sea estuaries (bars - current survey and data from Bryan and Langston, 1992; Langston *et al.*, 1999. ✳= means for samples collected in 1989, by Attrill and Thomas (1995)) …….(cont)

Attempts were made to correlate levels of dissolved metals in the Thames with those in sediments, hence, to try and explain some of the observed distributions patterns. Significant relationships were established between levels in sediments and overlying waters for Co ($r=0.7284; P<0.001$), Mn ($r=0.8491$; $P<0.0001$) and Pb ($r=0.7501$; $P<0.001$) - some of the more particle-dominated metals (Table 4) - implying that distributions might be governed by benthic fluxes. Relationships for Ag, Cu, Fe, Ni, Zn and As were not significant, though this may partly reflect the transient nature of water sampling and need not rule out a possible contribution from particulate sources.

Cadmium was unusual in that sediment concentrations were *inversely* correlated with levels of dissolved metal ($r= -0.7345$; $P<0.001$), whose concentrations increased in a seaward direction (Figure 3). The high proportion of total sediment-Cd which was present in readily-extractable (1M HCl) form, particularly in the lower estuary (85%; see Table 10) suggests it may have been easily desorbed from sediments. This, together with chloride complexation, would favour solublised forms at high salinities

Comprehensive comparisons of metal levels in Thames sediments and broad range of UK estuarine sites is described in the following section, alongside biota. In this later analysis of data, Thames sediments (min, max and mean values for each metal) are ranked in comparison to the rest of the UK, as percentiles (see 'methods, data analysis' for further explanation). A summary of the sediment comparisons, (for minimum, maximum and mean values in the Thames sites), is shown in Table 8. On a UK-wide basis, contamination with Ag was confirmed as most significant: the mean value for Thames sediments was equivalent to the 97th percentile, nationally. In descending order, Cr, Sn, Hg, Cd, Mn, Co, and Pb were also important (>50th percentile), whilst Cu, Zn Fe and Ni means ranged between the 25th and 50th percentiles. As and Se in

Thames samples were below the 25th percentile indicating that total sediment concentrations of these two metalloids were relatively low.

However, it is obvious from Table 8 that extreme values for most metals in Thames sediments displayed considerable variability. At the most contaminated Thames sites Ag, Co, Cr, Cd, Ni, Pb, Mn and Sn were all > 90th percentile; Fe, Hg and Zn > 75th percentile; Cu and As > 50th percentile, and Se > 40th percentile. In the least contaminated sediments - usually the more sandy sites at the mouth of the estuary - most metals were below the notional baseline of the 5th percentile. Minimum values for Ag, Sn and Mn were ranked slightly higher (5th - 10th percentile).

Clearly, metal contamination of sediments is significant for much of the Thames, as might be expected for any major urbanised estuary. However, it is important to bear in mind the extreme variability in concentrations along its length. This is typified by the fact that the estuary contains some the highest (e.g. Ag), as well as the lowest (e.g. Se) values encountered in estuarine sediments from England and Wales.

Table 8. Thames sediments (min, max and mean values for each metal, expressed as percentiles*) ranked in comparison to the rest of the UK.

	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
mean	97*	23	59	53	69	44	29	66	55	28	53	4	68	33
min-max	7-100	4-52	4-94	1-98	5-95	3-70	3-89	2-86	7-92	1-94	1-92	0-43	10-90	2-76

e.g. the 97th percentile for Ag indicates that 97% of the values for this variable in the PML data set for English and Welsh estuaries fall below the mean value for Thames sediments (see text for further explanation).

Estimated fluxes of particulate metals from the Thames Estuary

Crude estimates of the annual supply of particulate metals from the Thames to the North Sea have been calculated from sediment metal concentrations, using the sediment discharge figure of 0.2×10^6 t a^{-1} derived by Veenstra (1970). Though these are only approximations, the fluxes presented in Table 9 have been calculated for three sediment ranges - based on high sediment metal concentrations in the inner estuary (Teddington-London Bridge), low outer estuary values (Coalhouse Fort seawards) and whole estuary means, to give an idea of type of variability which might be expected to occur as a result of varying particle composition in the region (i.e. worst-case, best-case and average scenarios).

Similar calculations are shown in Table 10 for 1M HCl-extractable metals (equivalent to adsorbed and easily reducible metals, and a possible surrogate measure of anthropogenic loadings). As indicated in Table 10, it would seem than all the Pb in sediments and, hence, the particulate Pb flux to the North Sea, was extractable and potentially labile. A high proportion of this may have come from urban run-off from Greater London. Other elements with a high proportion in readily-extractable form (50-80%) were, in descending order, Cd, Mn, Zn, Sn, Cu and Co. This compares with

Table 9. Estimated fluxes of particulate metals from the Thames Estuary (tonnes per annum). A range of estimates is given, based on total (conc HNO_3) sediment metal concentrations in the inner estuary (high values), outer estuary (low values), and whole estuary (mean values), and assuming a sediment discharge of 0.2×10^6 t a^{-1} (Veenstra, 1970).

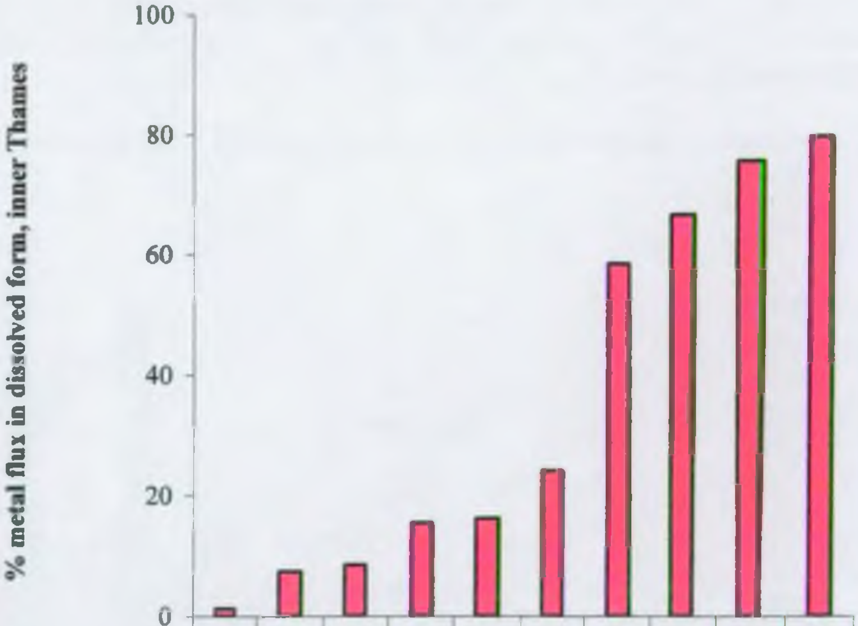
	inner estuary (high)		whole estuary (mean)		outer estuary (low)	
	total metal µg g^{-1}	flux t a^{-1}	total metal µg g^{-1}	flux t a^{-1}	total metal µg g^{-1}	flux t a^{-1}
Ag	16.5	3.31	5.79	1.16	1.63	0.33
As	11.6	2.33	10.3	2.07	9.88	1.98
Cd	2.10	0.42	0.84	0.17	0.24	0.05
Co	21.8	4.37	12.1	2.42	6.75	1.35
Cr	72.4	14.5	53.8	10.8	40.2	8.05
Cu	110	22.0	53.8	10.8	24.1	4.82
Hg	1.32	0.26	0.84	0.17	0.51	0.10
Fe	31769	6354	24170	4834	19011	3802
Mn	954	191	520	104	319	63.8
Ni	33.7	6.73	22.4	4.47	15.7	3.13
Pb	249	49.9	110	22.0	44.5	8.91
Se	0.21	0.04	0.10	0.02	0.04	0.01
Sn	18.6	3.71	8.68	1.74	3.58	0.72
Zn	342	68.5	178	35.6	93.6	18.7

Table 10. Estimated fluxes of non-refractory particulate metals from the Thames Estuary (tonnes per annum), based on 1M HCl-extractable sediment metal concentrations in the inner estuary (high values), outer estuary (low values), and whole estuary (mean values), and assuming a sediment discharge rate of 0.2×10^6 t a^{-1} (Veenstra, 1970). Hg and Se were not measured because of the low levels present in these extracts.

	inner estuary (high)			whole estuary (mean)			outer estuary (low)		
	1MHCl µg g^{-1}	%total (%)	flux t a^{-1}	1MHCl µg g^{-1}	%total (%)	flux t a^{-1}	1MHCl µg g^{-1}	%total (%)	flux t a^{-1}
Ag	3.03	28	0.61	1.68	47	0.34	0.60	50	0.12
As	2.03	19	0.41	2.92	27	0.58	3.77	33	0.75
Cd	1.51	75	0.30	0.61	80	0.12	0.21	85	0.04
Co	7.87	39	1.57	5.43	52	1.09	3.16	50	0.63
Cr	9.91	14	1.98	8.97	16	1.79	7.05	16	1.41
Cu	56.6	56	11.3	28.2	56	5.64	14.6	58	2.92
Fe	9199	30	1840	7505	32	1501	6066	33	1213
Mn	641	71	128	366	72	73.2	227	72	45.4
Ni	9.74	31	1.95	6.76	31	1.35	3.43	21	0.69
Pb	218	91	43.7	102	100	20.4	45.5	107	9.11
Sn	15.3	81	3.06	6.69	70	1.34	2.56	64	0.51
Zn	233	73	46.6	125	73	25.1	67.4	73	13.5

25 and 50% for Ag, Fe, Ni and As and only 16% for Cr (i.e. most of this metal was refractory in nature). The variable nature of these sediment associations will influence reactivity and bioavailability in the estuary, as indicated elsewhere in this report. Salinity exerted only small effects on these patterns. Thus, whilst the proportion of Ag, As and Co in extractable form was slightly higher at seaward sites, for other metals this fraction did not change significantly along the estuary.

It is possible to give an approximation of the relative importance of particulate *vs* dissolved metal fluxes from the Thames. Based on the percentages of metal present in the water column in dissolved form (Table 4), transport as soluble metal would be anticipated to more important for e.g. As, Ni and Zn than for particle seekers like Fe and Pb. Crude estimates of dissolved fluxes - based on an annual flow of 82 m^3s^{-1} (Inglis and Allen, 1957) and low salinity metal concentrations for the inner estuary, determined in the current study (Table 2) - support this general hypothesis, as summarised in Figure 8. It should be remembered, however, that these figures are derived from results for the inner estuary (high values) during a single survey and are only intended as relative guidelines. More focussed efforts are required to produce accurate simulations of fluxes under different conditions, which take into account different reactivities of the elements.



	Fe	Pb	Ag	Co	Mn	Cd	Cu	Zn	Ni	As
dissolved metal flux t/a	81	4.0	0.3	0.8	37	0.1	31	137	21	9.2
particulate metal flux t/a	6354	49.9	3.3	4.4	191	0.4	22	68	6.7	2.3
total metal flux t/a	6434	53.9	3.6	5.2	228	0.6	53	206	28	11.5
% flux as dissolved metal	1	7	9	15	16	24	58	67	76	80

Figure 8. Relative importance of dissolved and particulate metal fluxes* from the Thames Estuary. [* estimates based on inner estuary values and a mean annual flow of 82 m^3s^{-1} (Inglis and Allen, 1957)].

Biota

The extensive range of habitats and salinities which are represented along the tidal Thames support a variety of different biological communities. Any surveillance programme which attempts to address the issue of bioavailability/bioaccumulation along the entire waterway must, therefore, involve a multi-species approach.

The distribution trends for biota in Table 1 illustrates that ranges of the selected indicator species were usually continuous over a number of adjacent sites (spanning kms or even tens of kms) and often overlapped. Together, they were sufficiently extensive to provide adequate confirmation of trends in bioavailability along the whole estuary. Metal data, for individual species, are presented in full in Appendices 4-10. Results are discussed on a metal-by-metal basis below.

Silver

Sediment data for Ag showed that the Thames is subjected to considerable contamination by this toxic metal. Thames biota reflect Ag contamination in different ways, highlighting the fact that responses to metals are often dependent on the physiology of the organism, routes of assimilation and habitat. Accordingly, Ag magnification in tissues of the bioindicators studied, relative to environmental levels, varied by as much as two orders of magnitude. Concentration Factors (tissue÷water concentrations) and Bioaccumulation Factors (tissue÷sediment concentrations), for different species, are shown in Figure 9.

Ag Concentration/Bioaccumulation Factors from water/sediment

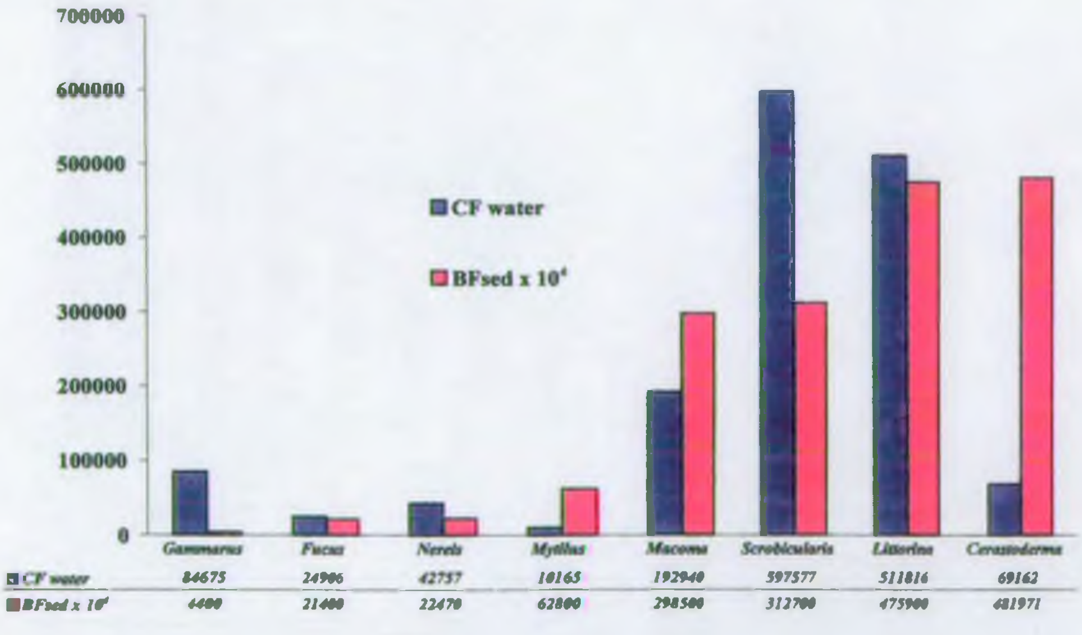


Figure 9. Silver in Thames biota: Concentration Factors [CF = concentration in organism (μg g^{-1}) ÷ concentration in water (μg g^{-1})] and Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment]. Note BFs are multiplied by 10^4 in order to plot on same scales as CFs.

Ag concentrations in *Gammarus* were in fact lower than in surrounding sediment (BF <1). Some magnification of Ag was evident in *Fucus, Nereis* and *Mytilus* (BFs 2-7), though the snail *Littorina* and sediment-dwelling bivalves *Scrobicularia, Macoma* and *Cerastoderma,* were by far the most important accumulators of Ag (BFs 30-48). The composition of the latter group suggests that sediments were an important route for Ag uptake and, judging by the sharp gradient in body burdens (Fig 10), Ag bioavailability was exceptionally high in Thames particulate matter. Previous observations have indicated that enhancement of this kind occurs in estuaries where sewage is prevalent; in these conditions bioaccumulation in deposit feeders becomes disproportionately high, as contamination of particles increases (see review by Bryan and Langston, 1992). Experimental work on the uptake of Ag from iron oxide particles in *Macoma* has shown that the presence of bacterial exudates promotes uptake from particulates (Harvey and Luoma, 1985) and it is hypothesised that high levels of such material, in estuaries having major sewage inputs, is the cause of disproportionately high body burdens in sediment feeders. In view of the potential toxicity of Ag this phenomenon needs to be examined further in the Thames.

The presence of high Ag levels in *Littorina* may also reflect an element of sediment uptake, since the winkle grazes over mudflats at many of the Thames sites. *Littorea littorea* contains a complex array of metal-binding ligands -including several types of metal storage granule, and the metal-binding proteins metallothionein and haemocyanin - all of which may contribute to the retention of considerable quantities of pollutant metals such as Ag (Langston *et al.*, 1998).

Comparable inter-species variability was evident from Ag Concentration Factors (CF = Ag in tissue ÷ Ag in an equivalent weight of water). CFs ranged from 1×10^4 in *Mytilus* to 6×10^5 in *Scrobicularia* (Fig. 9). These values were, however, based on fewer observations, and may be subject to more variability, than sediment BF's.

Correlations between body burdens and dissolved Ag and were not statistically significant, partly because of the limited and variable nature of the water samples. However, there were positive relationships between Ag in sediment (totals) and both *Macoma* ($r=0.9298$; $P < 0.05$) and *Mytilus* ($r=0.83$; $P<0.05$). Such relationships were even more common for 1MHCl-extractable Ag - implying a sediment vector for uptake in *Littorina* ($r=0.7059$; $P<0.01$); *Macoma* ($r=0.9088$; $P<0.05$); *Scrobicularia* ($r=0.66$; $P<0.05$) and even *Fucus* ($r=0.57$; $P<0.05$). It may seem incongruous that an autotrophic macroalga such as *Fucus* - normally considered to be a prime choice of indicator for dissolved metals - should reflect sediment Ag. However, similar observations have been made by Luoma *et al.*, (1982) who suggested that scavenging from sediments could occur where algal tissues are in contact with sediments (suspended or deposited). Metals most likely to be scavenged are those whose binding strength to algal tissue components (e.g. polyphenols) exceed the strength of binding to particles, and include Ag (together with As, Cu, Pb and Zn). This does not detract from the use of macroalgae as indicators of dissolved metals, since it is likely that in many cases sediments directly control solute concentrations, via partitioning behaviour.

In some estuaries, certain forms of sediment organic matter can *reduce* the bioavailablity of Ag (Bryan and Langston, 1992). This was tested for the Thames, by normalising sediment Ag with respect to organic content, but correlations with body burdens were not improved. Bioavailability appears to be enhanced in the estuary by the unusual nature of Ag in sediment - most likely promoted by sewage-derived products.

Spatial trends for Ag in the different bioindicator species are plotted in Figure 10 to provide an overall picture of bioavailability along the estuary. The principle bioaccumulators - sediment dwelling clams and *Littorina* - were all restricted to the mid-lower estuary (below Grays). This distribution pattern is presumed to be determined by salinity or substrate tolerances. However, because of the steep gradient in Ag burdens in clams and winkles, relative to sediments and other organisms, it is difficult to avoid speculating whether or not Ag bioaccumulation and toxicity may contribute to their inability to penetrate further upstream. This would be an interesting topic for further work. in view of the toxic nature of this metal.

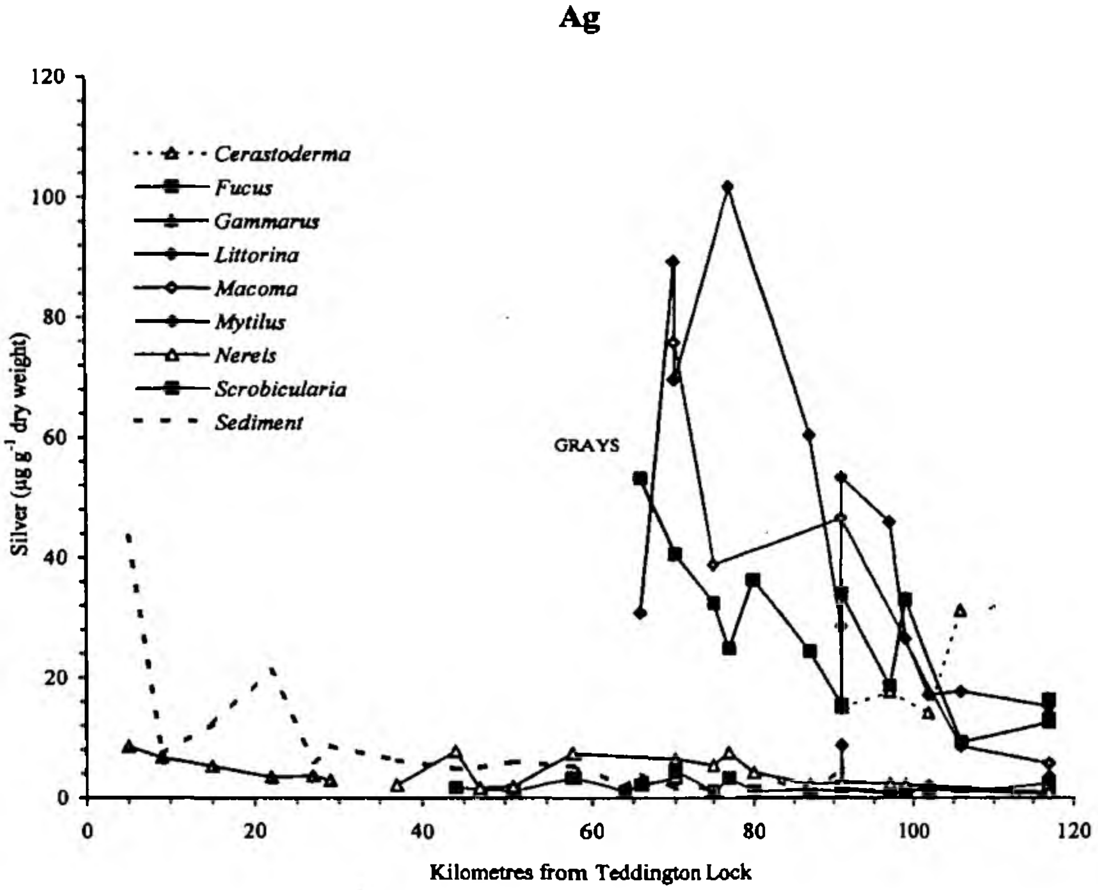


Figure 10. Silver concentrations in organisms and sediments from the Thames Estuary (July, 1997). Values in *Littorina*, *Macoma*, *Scrobicularia* and *Gammarus* are significantly (negatively) correlated with distance P<0.005, <0.05, <0.005 and <0.005, respectively).

The most extensive distributions in the estuarine zone were those of *Nereis diversicolor* and *Fucus vesiculosus*, and, in the inner fresh-water region, that of *Gammarus zaddachi*. Results for these bioindicators are plotted, on expanded scales, in Figure 11. Although all three species were less spectacular accumulators of Ag than clams and winkles the trends were similar, with higher burdens upstream. This was most obvious for *Gammarus*, where the gradient in Ag concentrations was steep (r = 0.9641, P<0.005).

Several secondary peaks were superimposed on the general pattern for Ag in *Fucus* and *Nereis* along the estuary (Fig 11), which may reflect localised inputs or subtle changes in bioavailability: thus Ag profiles for the two species were significantly correlated (r= 0.7232; P<0.01). There were a number of other strong relationships between Ag burdens in different species, most notably between *Littorina* and *Macoma* (r=0.99), *Littorina* and *Nereis* (r=0.93) and *Macoma* and *Scrobicularia* (r=0.98).

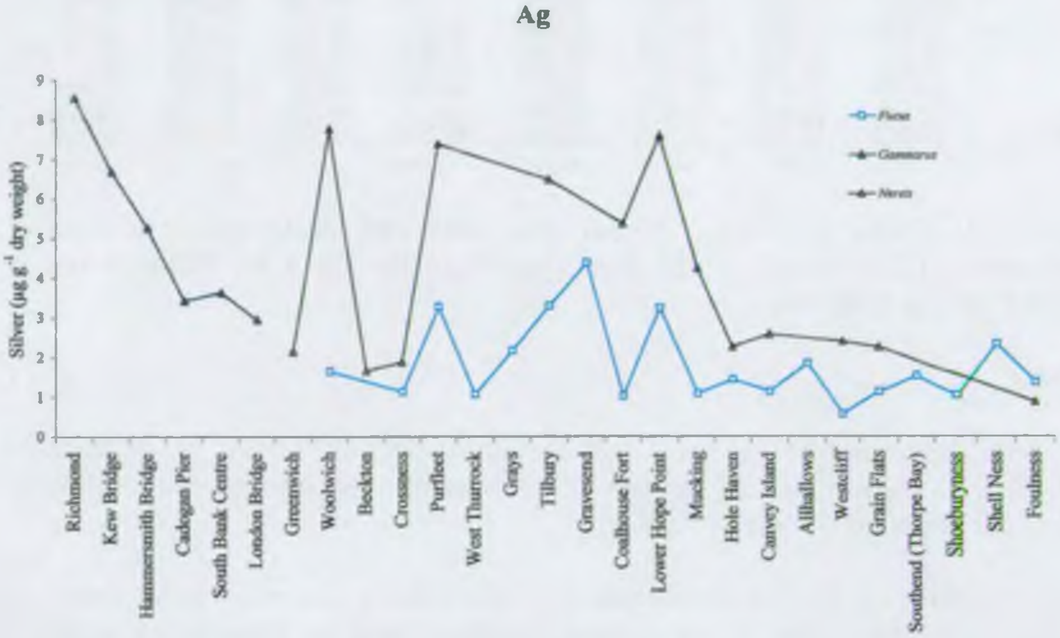


Figure 11. Silver concentrations in *Gammarus zaddachi Nereis, diversicolor* and *Fucus vesiculosus*.

Minimum, maximum and mean values for Ag in Thames biota, expressed as a percentile of the range in our own data-base for the UK, are shown in Figure 12. Bearing in mind that this comparison is only intended to give a broad indication of the scale of contamination (see 'Methods'), Figure 12 illustrates that values for Ag in the Thames include some of the highest in UK estuaries. This is particularly notable for cockles, *Cerastoderma edule*, where even the lowest values exceed those in other estuaries. Indeed, the minimum value for each of the species is at, or above, the 50th percentile, indicting the widespread nature of Ag contamination in the Thames.

Comparing results for *Macoma, Scrobicularia, Fucus, Mytilus, Nereis, Cerastoderma* and sediments, from six sites in the mid-outer reaches (Grays, Tilbury, Coalhouse Fort, Hole Haven, Westcliffe and Thorpe Bay), with similar data from an earlier survey (1980), suggests there have been no significant changes in Ag contamination in this part of the estuary (P>0.05, Students 'T' test).

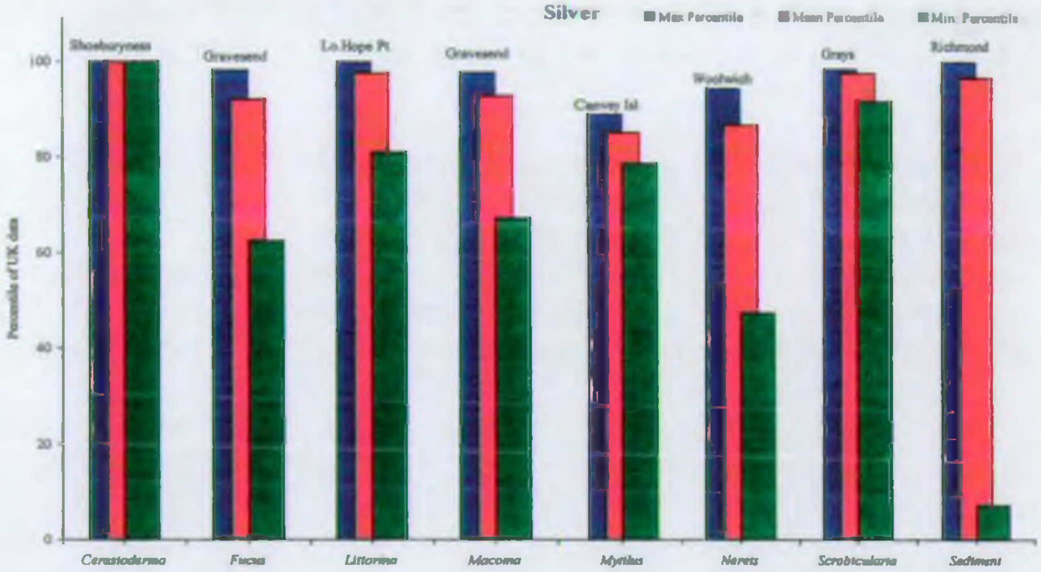


Figure 12. Silver in Thames biota: min, max and mean values expressed as percentile of the range in our own data-base for the UK. Thames site with highest values indicated.

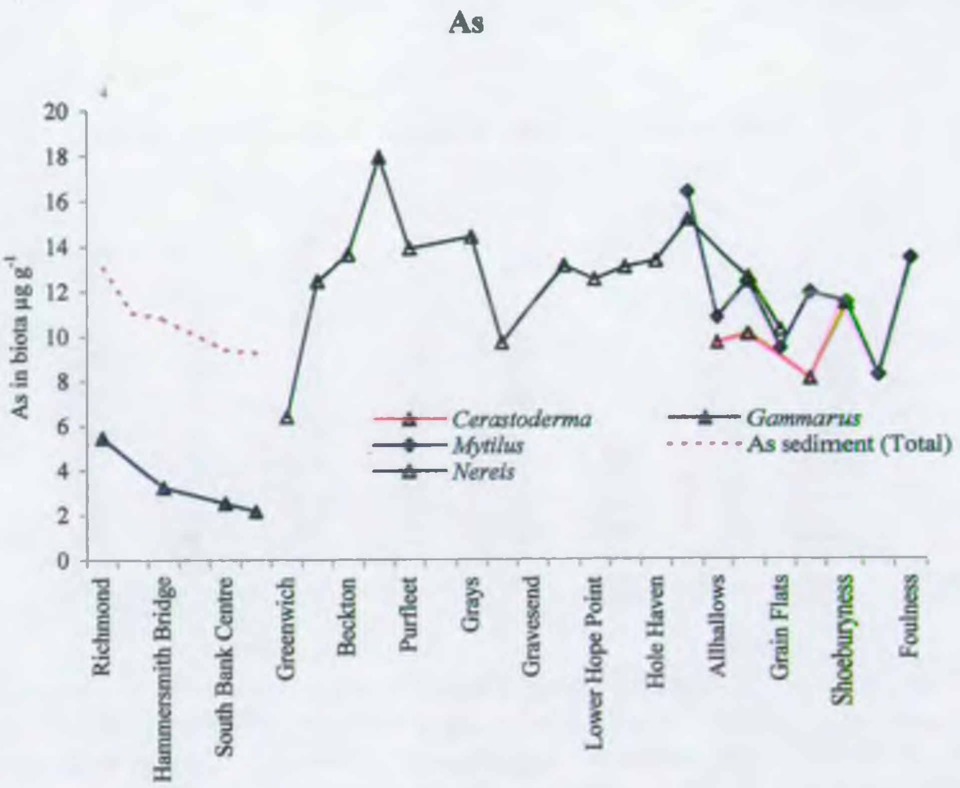
Arsenic

Sediment analyses have indicated that contamination with arsenic is not particularly high in the Thames estuary. In fact concentrations were comparable with those in sediments from the central North Sea.

The absence of significant contamination in the Thames was reflected by that fact that total As in sediments displayed no clear gradient along the estuary as a whole. This absence of any distinct range of As contamination probably explains why tissue As burdens for a number of species (*Cerastoderma, Littorina, Mytilus, Nereis*) were not statistically related to total As sediment concentrations (Figure 13). There was one exception, for the freshwater section of the waterway, where in fact As concentrations in *Gammarus* were a function of total As in sediment ($r=0.9924;P<0.01$. Fig. 13, upper figure). At this group of sites in the upper reaches, between Richmond and London Bridge, As concentrations decreased in a downstream direction.

Arsenic in 1M HCL sediment extracts - in contrast to total arsenic - gradually increased lower down the estuary, towards the open sea (see earlier discussion on sediment metals, and data in Appendix 2). This 'bioavailable' As fraction in sediments was reflected in As profiles in *Scrobicularia*, *Littorina, Macoma* and *Fucus* which also displayed a trend towards higher concentrations in a seaward direction (Fig 13, lower figure). Sediment-tissue relationships for *Scrobicularia*, *Littorina*, and *Fucus* were improved significantly when 1M HCl sediment values were 'normalised' with respect to similarly-extracted Fe ($r=0.68$, 0.85, 0.74; $P=0.01$, 0.001, <0.001, respectively). The As/Fe profile in 1M HCl sediment extracts, is shown in Fig 13. It is thought that increasing amounts of Fe in sediments may modify the availability of certain metals, including As, either through competitive interactions or by moderating the equilibrium concentrations of dissolved As in surrounding surficial/pore waters (Langston *et al.*, 1998).

Significant correlations between As body burdens in different species were observed in several instances; notably *Fucus* vs *Nereis* and *Scrobicularia*; and *Nereis* vs *Mytilus*.



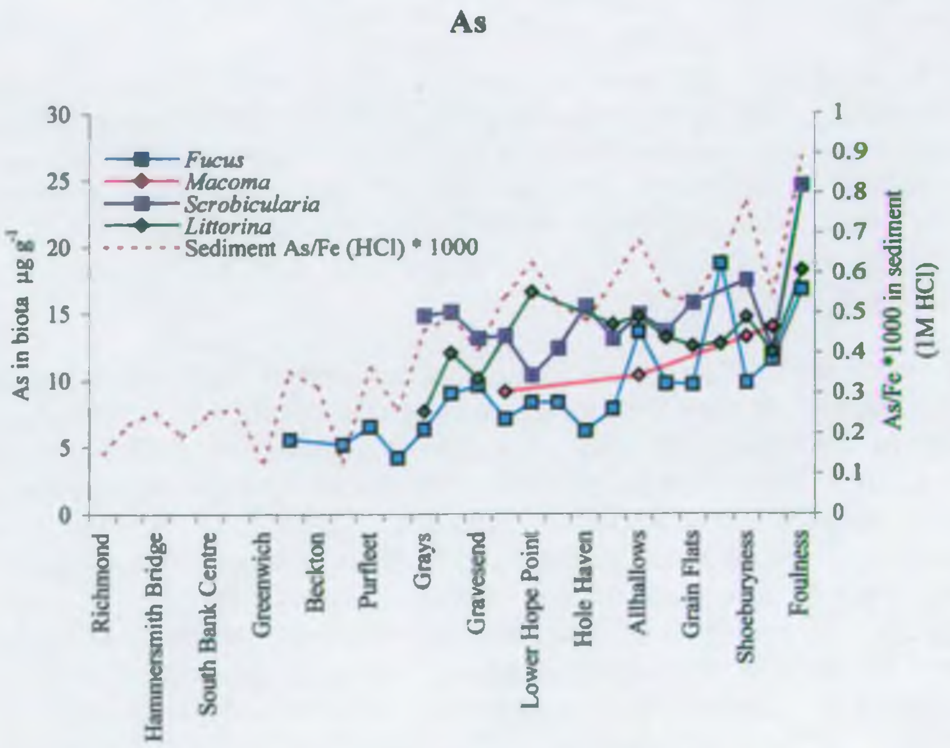


Fig 13 Arsenic concentrations in organisms and sediments along the Thames Estuary (July, 1997).

Arsenic Concentration Factors (tissue concentrations, relative to water) ranged from 1×10^3 - 3×10^3 and Bioaccumulation Factors (tissue concentrations, relative to sediment) from 0.3 -1.6 (Figure 14). These were generally lower, and showed far less inter-species variation, than corresponding values for the pollutant metal Ag.

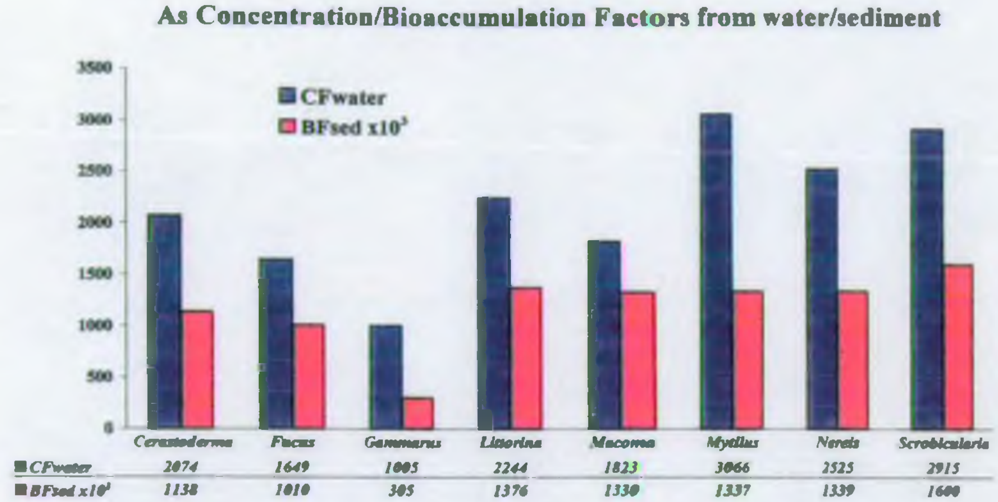


Figure 14. Arsenic in Thames biota: Concentration Factors [CF = concentration in organism ($\mu g\ g^{-1}$) ÷ concentration in water ($\mu g\ g^{-1}$)] and Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment]. Note BFs are multiplied by 10^3 in order to plot on same scales as CFs.

Minimum, maximum and mean values for As in Thames biota, expressed as a percentile of the range in our own data-base for the UK are displayed in Figure 15. Although there were occasional elevated As values at individual sites, average values for the whole estuary rarely exceeded the 50th percentile for any species, and minimum values seldom exceeded the 20th percentile. These statistics imply that As contamination in the Thames can be considered as relatively insignificant for such a major industrial estuary.

Arsenic concentrations in *Fucus* (min, max and mean) were of particularly low ranking, compared to other species, and may be due to the presence of high levels of phosphate in the estuary: phosphate is known to out-compete arsenate for uptake in algae. A similar phenomenon of reduced As bioavailability has been observed at other UK sites subjected to phosphate discharges (Langston *et al.*, 1997). Arsenic concentrations in *Fucus* from the section of the estuary between Woolwich and West Thurrock were in fact some of the lowest recorded in the UK. In view of the discharges to this region from the major sewage treatment plants at Beckton and Crossness, it would be interesting, in future, to look at phosphate distributions and sources, and their influence on metal/metalloid bioavailability and toxicity.

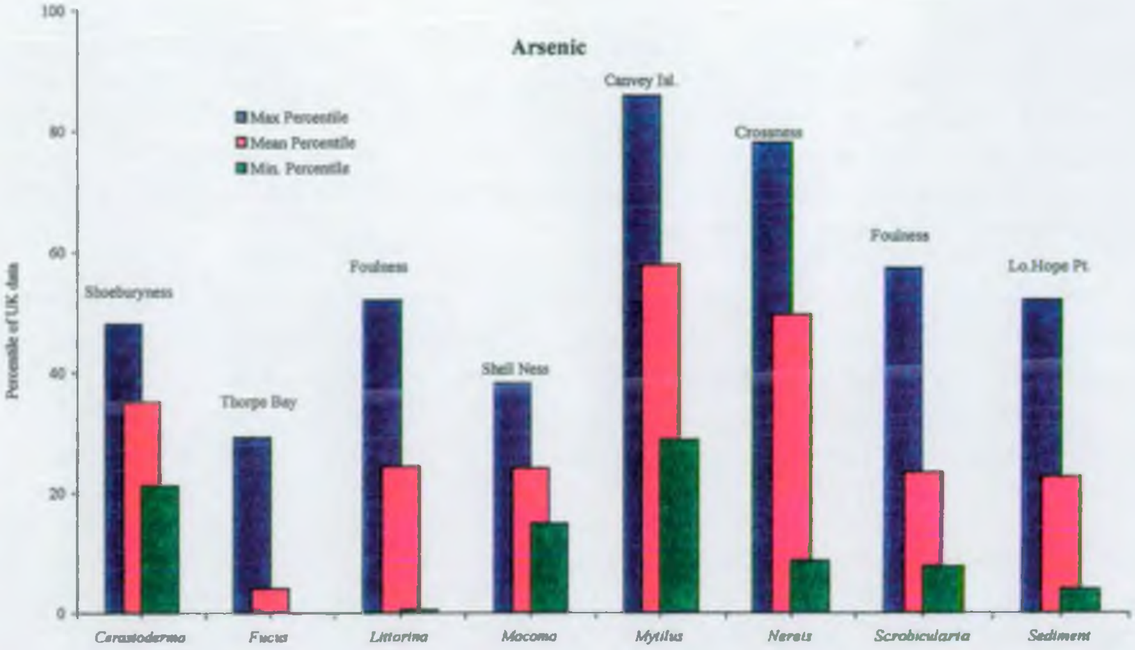


Figure 15. Arsenic in Thames biota: min, max and mean values expressed as percentiles of the range in our own data-base for the UK.

The absence of any remarkable arsenic body burdens in Thames biota implies that the major potential sources of contamination - sewage inputs - are not a significant contributor to As bioaccumulation in estuarine organisms. Toxic effects would not be expected to arise from As contamination in the Thames, based on present levels.

It appears incongruous, therefore, that all shellfish samples in the Thames surpass the UK limit for arsenic in food of 1 μg g^{-1} wet wt (5 μg g^{-1} dw equivalent). However, this limit does not apply when contamination is deemed to come from natural sources. It would be difficult to exclude the possibility of a contribution from industrial origin to the As burden of Thames biota, though present indications suggest this is likely to be minimal; in either case the limit value for As in shellfish would appear to be set too low.

Comparisons of results from 1980, with current data, for six sites in the mid-outer reaches, shows that there have been some reductions in As contamination (and bioavailability) in this part of the estuary. Small but significant decreases were observed for As concentrations in sediment (42% and 45% in total and 1M HCL extracts, respectively), *Fucus* (41%), *Nereis* (15%) and *Scrobicularia* (30%) ($P>0.01$, Students 'T' test).

Cadmium

Sediment analyses revealed a wide range of Cd concentrations in the Thames, ranging from some of the highest in the UK to some of the lowest. The sediment gradient decreased seawards, in contrast to the pattern for dissolved Cd concentrations, which increased gradually with increasing salinity. The pattern of bioavailability in the majority of estuarine species (decreasing downstream, Figure 16) was therefore more comparable to sediments than to water.

In fact, the distribution of dissolved Cd did not correlate with tissue Cd in any of the bioindicator species, whereas relationships between Cd in tissues and total Cd in sediments were statistically significant for *Littorina*, *Scrobicularia* and *Fucus* ($r=0.73$, 0.65, 0.59, respectively: $P<0.01$). The use of 1M HCl sediment extracts, or normalisation with respect to organics and Fe, did not improve these relationships noticeably. The disproportionately steep upstream increase in Cd in some organisms, compared to sediments, was similar to the pattern observed for Ag. It is possible that Cd lability and bioavailability is promoted because of the nature of coatings on sediment particles, as suggested for Ag, though the effect for Cd was less pronounced and may involve different explanations.

Thus, although sediments appear, superficially, to be the principal determinant of Cd in Thames biota, mechanistically, uptake routes remain equivocal. There may be several confounding factors which modify Cd availability, particularly speciation. Published literature indicates that the proportion of Cd present as the highly bioavailable free-ion should increase upstream in estuaries, resulting in increased assimilation of dissolved Cd - in agreement with observed bioaccumulation trends. Chloro-complexes, present in increasing propotions at higher salinities, are likely to be less available for uptake (e.g. Cross and Sunda, 1985). Dissolved Cd speciation might, therefore, determine observed body burden profiles even though total dissolved Cd concentrations apparently do not. More evidence is needed to distinguish whether sediments or water are the most significant vector for uptake.

Giblin *et al.*, (1980) determined that Cd levels in the suspension-feeding bivalve *Modiolus demissus* were enhanced in salt marsh plots contaminated with sewage-sludge fertiliser (implying a sedimentary route), though this coincided with high diffusion from sediment, and some metal may have been desorbed. Rapid dissolution of Cd from particulate phases (including sewage and sewage sludge) has also been noted by Radford *et al.*, (1981). It may be that pore-water concentrations, as much as sediment particles themselves, are responsible for enhanced uptake of this readily-mobilised metal. Harvey and Luoma's (1985) series of experiments on availability of sediment-bound and dissolved metal to *Macoma balthica* came to a similar conclusion. As they had shown for Ag, Cd was available in sediments amended with bacterial extracellular polymers, though for Cd a significant dissolved component remained. It is likely that both sediments and waters provide a source of Cd uptake for Thames biota, as is probably the case in many UK estuaries (Bryan and Langston, 1992).

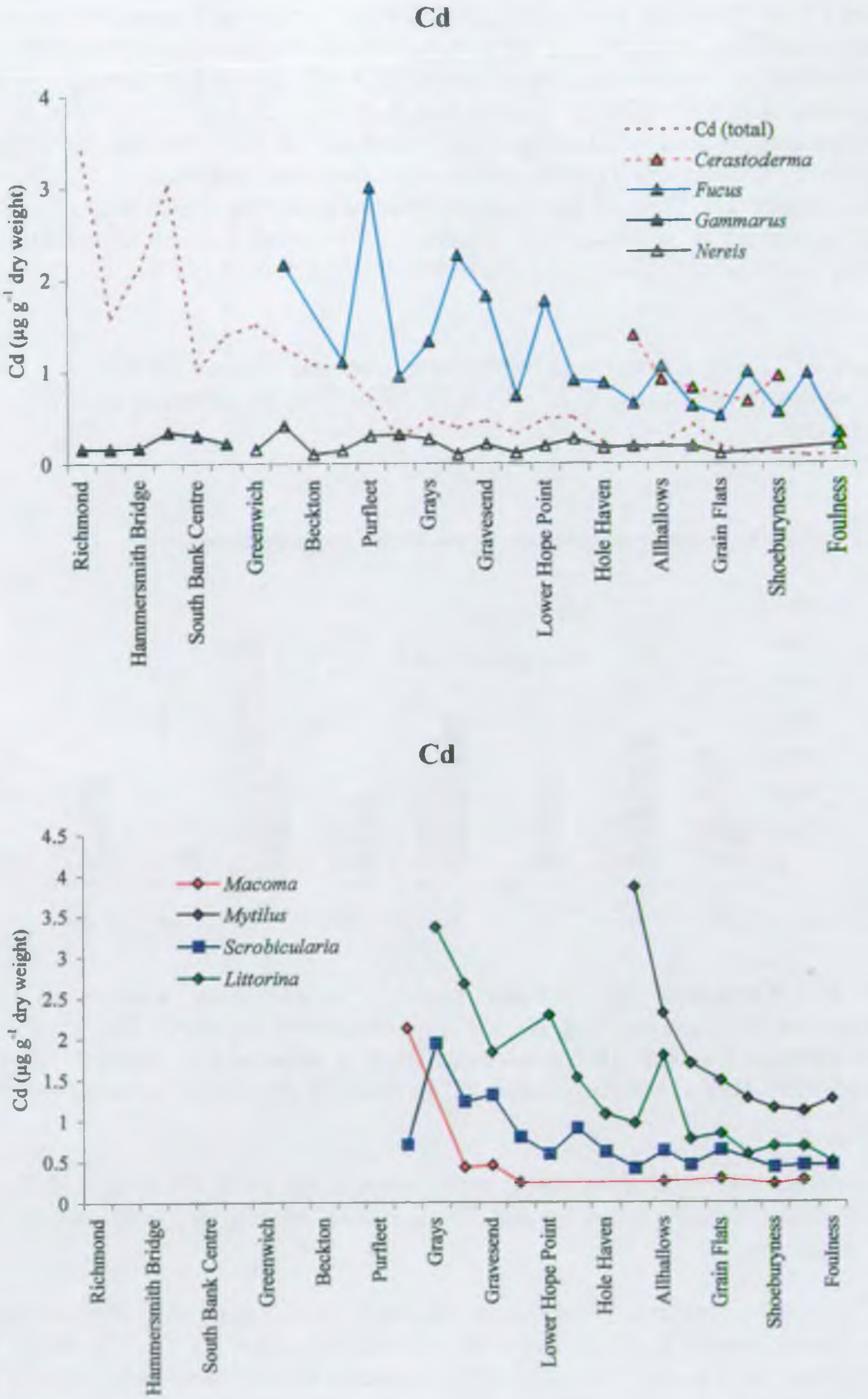


Fig 16. Cadmium in organisms and sediments, Thames Estuary (July, 1997)

Low body burdens in *Gammarus* and *Nereis* meant that there were no obvious spatial trends for Cd in these two species (Fig 16). Cd burdens in the Thames worms were inversely related to size [Cd $_{\text{Nereis}}$ µg g^{-1}= -4.8005 dry weight (g) + 0.3562; r =0.63, P<0.01] though this parameter would cause, at most, a two fold variation in Cd concentration and was unlikely to have had a major influence on profiles in the Thames. Judging by the low Bioaccumulation Factors (<1) these two species are poor accumulators of Cd in the Thames, relative to other taxa, particularly *Mytilus* and *Littorina* (Figure 17). Both of the latter molluscs contain the metal-binding protein metallothionein which is capable of retaining accumulated Cd almost indefinitely, explaining their higher Cd concentration factors (Langston *et al.*, 1998).

The mean CF_{water} for Cd in *Fucus vesiculosus* from the Thames Estuary of 7 x 10^3 was in the centre of the range (2.7 -14 x 10^3) described by Bryan *et al.* (1985) for other field sites.

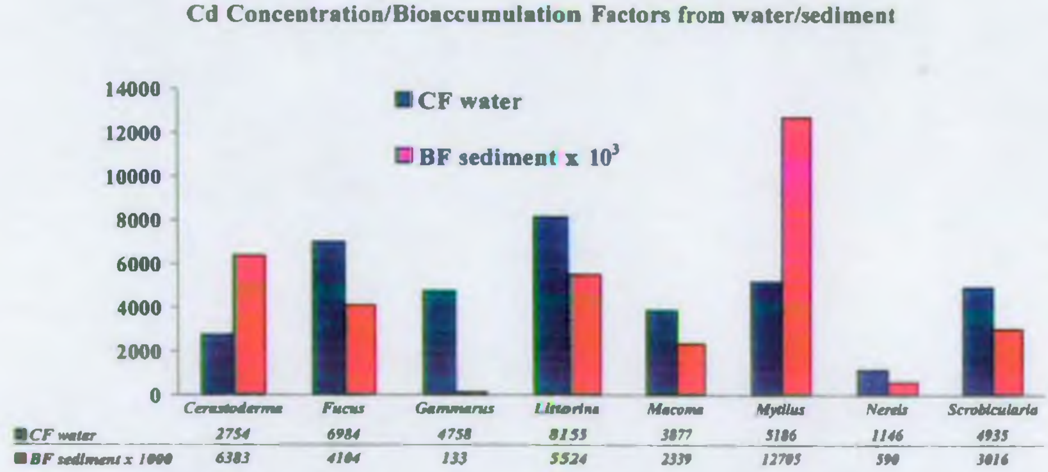


Figure 17. Cadmium in Thames biota: Concentration Factors [CF = concentration in organism (µg g^{-1}) ÷ concentration in water (µg g^{-1})] and Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment]. Note BFs are multiplied by 10^3 in order to plot on same scales as CFs.

There were several significant correlations between Cd body burdens in different species, notably *Fucus vs Littorina* and *Scrobicularia*; *Mytilus vs Cerastoderma*; and *Nereis vs Macoma*.

Figure 18 displays minimum, maximum and mean values for Cd in Thames biota, expressed as a percentile of the range in our own data-base for the UK. Mean Cd concentrations for the whole estuary rarely exceeded the 50th percentile, though, for most species, there were a small number of moderately high values at individual sites. Minimum Cd concentrations in the Thames rarely exceeded the 20th percentile for UK sites. The most notable exception was that of the cockle *Cerastoderma,* where maximum, mean and minimum values were all ranked highly, at the 83rd, 70th and 47th percentile, respectively. However, it should be noted that this somewhat elevated ranking may be partly due to the number of *C.edule* samples in the data-base - which, at 129, is smaller than all other sample types. Also, *C.edule* has usually been sampled at outer estuary sites which are generally the least contaminated.

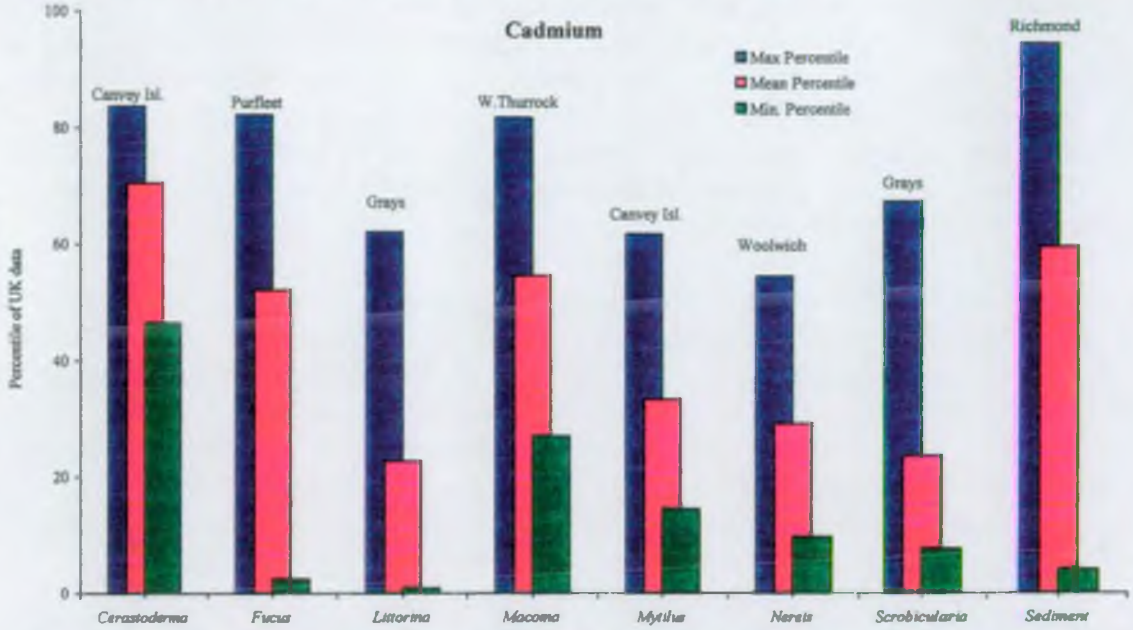


Figure 18. Cadmium in Thames biota: min, max and mean values expressed as percentiles of the range in our own data-base for the UK.

Despite its appearance as a priority chemical in various 'Black Lists', Cd is not so directly toxic to aquatic organisms as, for example, Cu. This is partly due to the presence of detoxifying systems such as metallothionein which, though capable of storing Cd (thus presenting a possible hazard to consumers), renders the metal relatively harmless to the organism itself. There is also evidence that in estuaries subjected to multiple contaminants, Cd uptake is reduced by competition from other metals including Zn and Mn. Certainly, it would seem unlikely that the dissolved Cd concentrations currently present in the Thames would effect the distribution of organisms. However, work on bivalves *Corbicula* in San Francisco Bay has shown that an increase in sediment Cd from 0.1-0.4 $\mu g\ g^{-1}$ coincided with a decrease in condition of these clams (Luoma *et al.*, 1990). As Cd concentrations in much of the inner and mid part of the Thames exceeded this upper value, the possibility of similar sub-lethal impact from sediments should not be dismissed.

A draft EC Regulation proposes a limit of 1.5 $\mu g\ g^{-1}$ wet weight (equivalent to approximately 7.5 $\mu g\ g^{-1}$ dw) for Cd in food. None of the molluscan species analysed in the Thames Estuary exceeded this value, though levels up to half the limit were measured in winkles and mussels.

Between 1980 and 1997 there appear to have been significant decreases in Cd concentrations in sediment (total* and 1M HCL extracts**), *Fucus***, *Littorina**, and *Scrobicularia** (*$P<0.05$, **$P<0.01$, Students 'T' test), based on the six mid-outer estuary sites described earlier. The scale of these reductions ranged from ~50% in sediments up to 78% in *Littorina*.

Cobalt

Cobalt is considered to be an essential trace element for most organisms (for example in vitamin B_{12} enzymes) and, in estuarine biota, has not been as extensively studied as the more toxic metals. It was included in the current survey to help fill this gap in knowledge, with the premise that, in excess, even essential metals can be toxic. Elevated cobalt concentrations in the environment may arise from a number of anthropogenic sources - in addition to mining - namely, through its usage in alloys, electroplating, catalysts, pigments, enamels and glazes. Its principal routes to the sea are likely to be rivers and pipelines.

Results for sediments and water indicate that the major source(s) of Co enrichment in the Thames Estuary originate upstream - either the River Thames or discharges close to the tidal limit. Dissolved Co concentrations in the inner estuary (mean = 0.31μg l^{-1}) were significantly higher, by an order of magnitude, than those at the mouth of the estuary, and levels probably continue to decrease offshore. Tappin *et al.*, (1995) reported values as low as 0.009 μg l^{-1} in central North Sea waters, increasing to 0.05 μg l^{-1} at sites closest to the Thames, similar to our mean outer estuary value of 0.07 μg l^{-1}.

There was a similar gradient in Co concentrations in Thames sediments, with concentrations ranging from in excess of 30 μg g^{-1} upstream (among the highest encountered in the UK) to between 2 and 8 μg g^{-1} in the outer estuary and the central part of the N.Sea (own, unpublished data). This distribution pattern, and the low percentage of Co in dissolved form in estuarine water samples (mean = 16%), is indicative of the particle reactive nature of the element. Much of the Co in sediments is closely correlated with Fe or Mn and probably resides in associated oxyhydroxide and crystalline (geogenic) phases. Studies by Kremling and Hydes (1998) and Tappin *et al.*, (1995) have indicated that the behaviour of Co may be similar to that of Mn, perhaps because of coupled redox reactions.

According to results from experimental exposures, cobalt concentrations in *Fucus* are directly proportional with those in water,; macroalga are, therefore, usually acceptable indicators for dissolved Co (Bryan *et al.*, 1985). There is some experimental evidence of suppression of Co uptake by elevated levels of Mn and Zn, and such interactions may have modified profiles observed in the Thames, though, generally, Co levels in *Fucus* displayed the anticipated significant reduction towards the open sea (Fig 19).

Of the invertebrate species studied, *Gammarus*, the sole bioindicator from the inner estuary (Figure 19), also reflected dissolved Co gradients reasonably well (r=0.6577), even though concentrations were comparatively low. Further downstream, r values for *Macoma* and *Scrobicularia vs* dissolved Co were fairly high (0.67 and 0.71, respectively), but not significant. Because of the small range of samples, however, these results should only be taken as a preliminary guideline, and should not be considered a rigorous test of bioindicating ability. Nevertheless, they suggest that water, as well as sediment, could be a significant source for Co uptake in infaunal species. Similar observations were made by Luoma and Bryan (1982) with reference to *Scrobicularia* and *Nereis*.

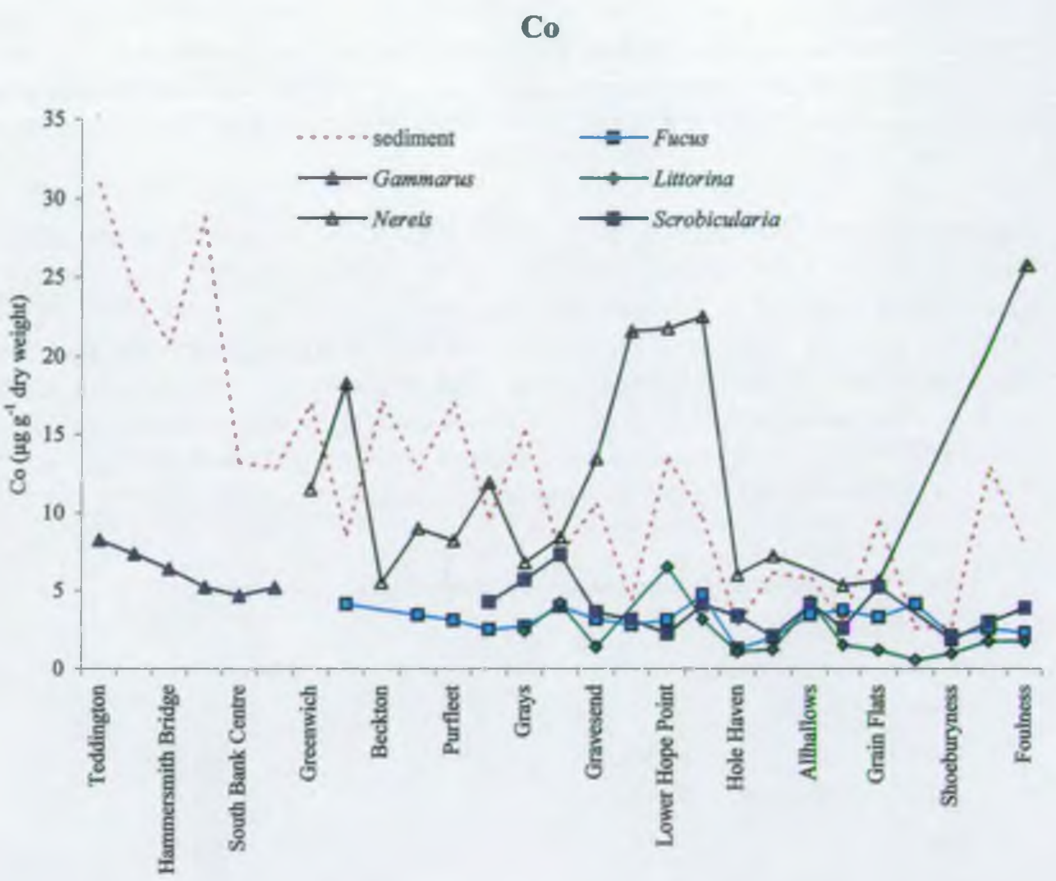


Fig 19. Cobalt concentrations in organisms and sediments along the Thames Estuary (July, 1997).

Cobalt levels in *Gammarus* were closely related to sediment concentrations (r= 0.70), as well as dissolved Co, at freshwater sites above London Bridge (Figure 19). Further investigation of the potential of this crustacean as a bioindicator is clearly warranted since it appears to be one of the few species in the Thames whose Co body burdens were related directly to environmental levels.

Several polychaete species and the clam *Scrobicularia plana* have been proposed as promising (direct or indirect) indicators of sediment-bound Co, at least in multi-estuary studies where a large range of contamination levels exists (Bryan *et al.*, 1985). The best of these is anticipated to be *Nereis diversicolor* because of its extensive distribution and relatively high Co body burdens (Figure 20). However, for Thames *Nereis* samples, correlations with sediment Co (totals and 1MHCl extracts) were non-significant. Highest Co concentrations were in fact found in worms from Foulness, at the mouth of the estuary, where the Co concentration in sediment was comparatively low (Fig 19). This anomaly is almost certainly a size-related effect. The worms here weighed 3mg dw on average compared to some 34 ± 9mg at other Thames sites. A further Co peak was evident in *Nereis* (and in *Littorina*) in the Lower Hope Reaches (Fig 19). Clearly, there may be other factors which determine Co burdens in Thames Estuary biota besides sediment concentration *per se.*

There were few discernible trends for Co in other estuarine benthic invertebrates (i.e. *Cerastoderma, Mytilus*), either because their distributions were restricted to the lower end of the estuary - where concentration gradients were less marked - or because body burdens of this essential element were successfully regulated over the concentration range found here.

Concentration Factors for Thames biota, relative to water, ranged over an order of magnitude, from $9x10^3$ for *Mytilus* up to 13×10^4 for *Nereis* (Fig 20). BFs (relative to sediment) ranged from 0.2 in *Macoma* and *Mytilus* up to 1.5 in *Nereis* (Fig 20). The latter species was the only one studied in which Co tissue concentrations were magnified compared to those in sediments. The diversity in accumulating ability between taxa may reflect individual species' requirements for this essential element. It may also explain why body burdens in different species were seldom significantly related (the exception being Co in *Littorina* and *Cerastoderma* -$r=0.918;P<0.05$).

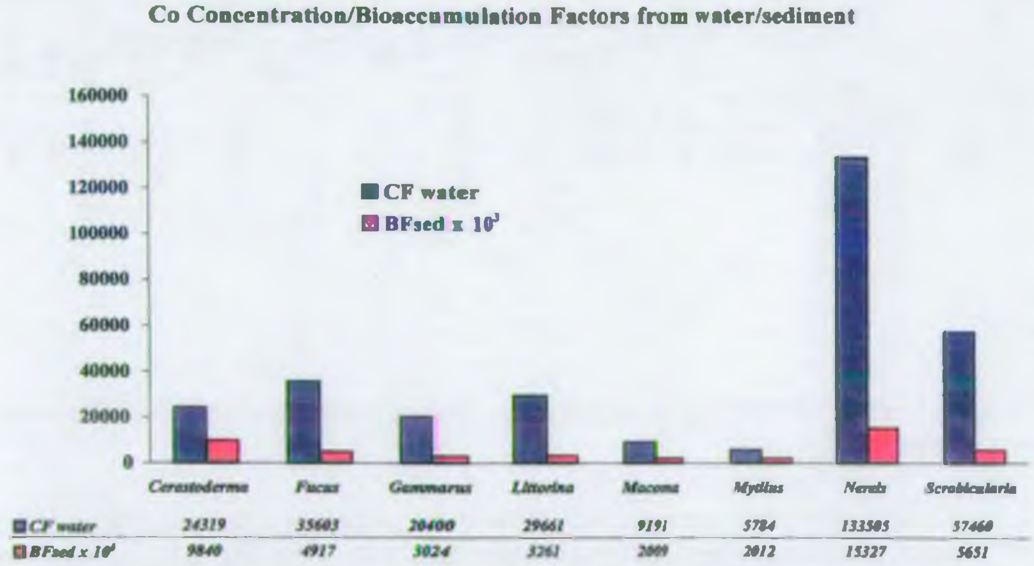


Fig. 20. Cobalt in Thames biota: Concentration Factors [CF = concentration in organism (μg g^{-1}) ÷ concentration in water (μg g^{-1})] and Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment]. Note BFs are multiplied by 10^3 in order to plot on same scales as CFs.

The range of cobalt contamination in UK estuaries is not extensive. Some of the highest values tend to be associated with metal mining sources, such as those in south west England. Nevertheless, the Thames Estuary was enriched in Co, relative to background levels, as reflected in concentrations in several organisms and sediments (Fig 21). However, rankings for the Thames biota varied considerably between species: based on mean values these ranged from 14th (*Scrobicularia*) to 97th (*Nereis*) percentiles, nationally. The latter value implies that the form of Co in the Thames was extremely bioavailable to ragworms, and included the highest concentration measured in UK estuaries. Even minimum values for *Nereis* ranked highly in national terms (71st percentile). There were also some notably high Co values in cockles, mussels and winkles at selected sites (Figure 21).

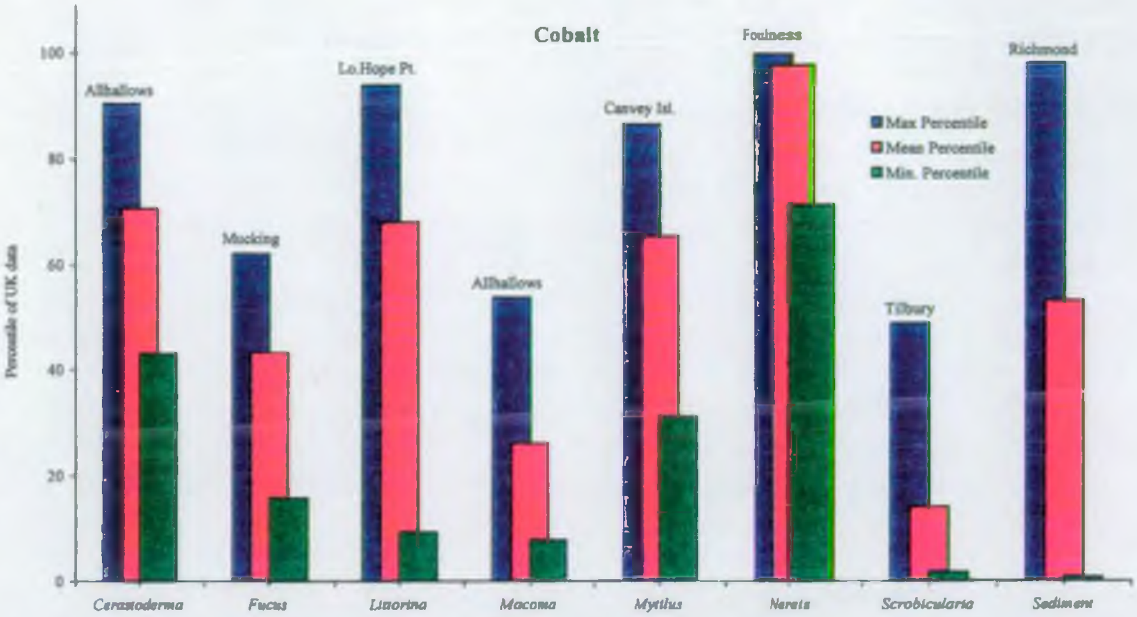


Figure 21. Cobalt in Thames biota: min, max and mean values expressed as percentile of the range in our own data-base for the UK.

It is uncertain whether these represent deleterious levels, though this seems unlikely as Co is probably one of the least toxic metals. Acute experiments with *Nereis* indicate an LC_{50}(192h) of around 170 µg ml^{-1} and a corresponding lethal body burden of 2000 µg g^{-1} - far in excess of Thames values. However, relatively little is known of possible subtle effects thresholds in sensitive life stages of estuarine organisms.

There was no evidence of significant change in Co concentrations in biota or sediment at the mid-outer estuary sites since 1980, other than in *Scrobicularia* where body burdens have decreased by 50% ($P<0.01$),

Chromium

Chromium, like Co, has been designated as an essential element for some organisms though it may be toxic and carcinogenic in excess. Possible sources of Cr in the environment include electroplating and other metallurgical industries, tanning, paints and wood preservatives. Cr(VI) is the stable dissolved inorganic form, whilst the trivalent form, Cr(III), tends to be precipitated in seawater and is rapidly scavenged by particles. Fe oxide coatings have a particularly strong affinity for Cr - hence the close correlation between Cr and Fe in Thames sediments (Figure 6). Because of it's relative insolubility, Cr(III) is considered to be less biologically available, and therefore less toxic, than Cr(VI) (Bryan and Langston, 1992).

Attempts to relate Cr body burdens in *Nereis* and *Scrobicularia* to Cr concentrations in sediments (total and 1MHCl extracts) have, in the past, been successful for multi-estuary studies where concentration ranges in sediments vary over orders of magnitude (Bryan and Langston, 1992). However, the precise mechanism by which sediment Cr reaches tissues of these clams and worms is uncertain: uptake may take place directly from sediment, e.g. during digestion, or from interstitial water.

Within the limited range of Cr concentrations in Thames sediments (five-fold), direct proportionality with tissue burdens was not readily demonstrated and there were apparently contradictory spatial trends for Cr in some of the Thames biota (Fig. 22). However, Cr concentrations in *Scrobicularia* and *Macoma* and *Littorina* all decreased significantly in a downstream direction ($r=0.74$, $p<0.001$; $r= 0.74$, $P< 0.05$ and $r=0.86$, $P< 0.001$, respectively), in a similar pattern to that of sediments. Cr burdens in *Scrobicularia* and *Littorina* were, in fact, proportional to sediment Cr, expressed either as total ($r=0.6029$, $P<0.05$; $r=0.68$, $p<0.01$, for clams and winkles, respectively) or 1MHCl-extractable ($r=0.62$ $P<0.05$; $r=0.72$, $p<0.01$) metal. Normalisation with respect to Fe improved the r values (to 0.81 and 0.77 for HCl extracts) suggesting that higher Fe levels have a modifying influence - reducing Cr bioavailability to these species.

In contrast, Cr concentrations in the cockle *Cerastoderma edule* increased sharply, seawards, between Allhallows and Southend (Fig 22). A similar, if less pronounced, gradient was evident in *Fucus* in this region. Cr levels in *Cerastoderma* were in fact proportional to those in *Fucus* ($r = 0.89$, $P<0.05$), which in turn may be regarded as a surrogate measure of soluble metal. It would be useful in future to determine Cr distributions (and speciation) in the water column, and to establish whether trends in *Cerastoderma* and *Fucus* reflect inputs of Cr, or variations in the proportions of bioavailable forms of the metal.

Bioconcentration factors for Cr in Thames biota are shown in Figure 23 and demonstrate how accumulating abilities varied between species (lowest in *Nereis*, highest in filter-feeding bivalves, particularly *Cerastoderma*). Some of the highest Cr body burdens reported in the literature (from Sawyers Bay, New Zealand - a site subjected to contamination from tannery wastes giving rise to sediment concentrations up to 3700 μg Cr g^{-1}), were also found in cockles *Chione stutchburyi* (228 $\mu g\ g^{-1}$). This compared with levels of 32 and 46 $\mu g\ g^{-1}$ in polychaetes *Perinereis nuntia* and mud snails *Amphibola crenata*, respectively (Aislabie and Loutit, 1986). It would seem from these data that cockles are generally strong accumulators of Cr (and also Ni, see below).

Experimental evidence suggests that the bioavailability of sediment-bound Cr(III) to sediment dwelling organisms could be dependent on the partitioning of the metal on, and uptake from, coatings of extracellular polymers of bacterial origin (Bremer and Loutit, 1986) - in a manner similar to that described for Ag. Whether this is of significance in the Thames is not known, but would be interesting to test. However, none of the species in the Thames survey magnified Cr to levels higher than those found in surrounding sediments (BFs<1, Figure 23).

Chromium concentrations appeared to vary with size in two of the species from the current survey - increasing with the average dry weight of individuals in *Mytilus*, and decreasing in *Nereis*. Equations were: $Cr_{Mytilus}\ \mu g\ g^{-1} = 3.828$ dry weight + 1.8066 ($r= 0.58$, $P<0.05$) and $Cr_{Nereis}\ \mu g\ g^{-1} = -7.4965$ dry weight + 0.456 ($r =0.77$, $P<0.05$).

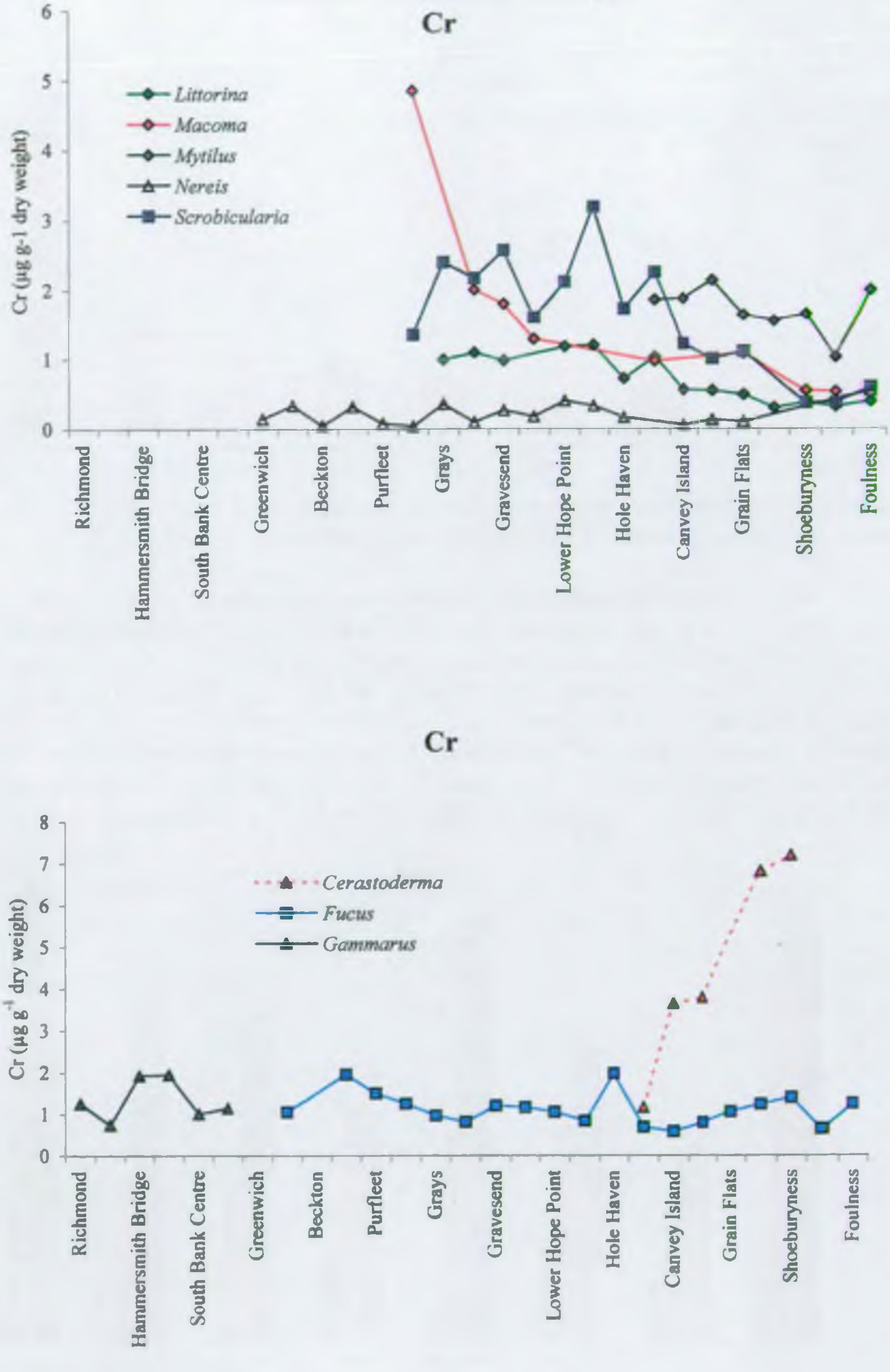


Fig 22 Chromium concentrations in organisms and sediments along the Thames Estuary (July, 1997)

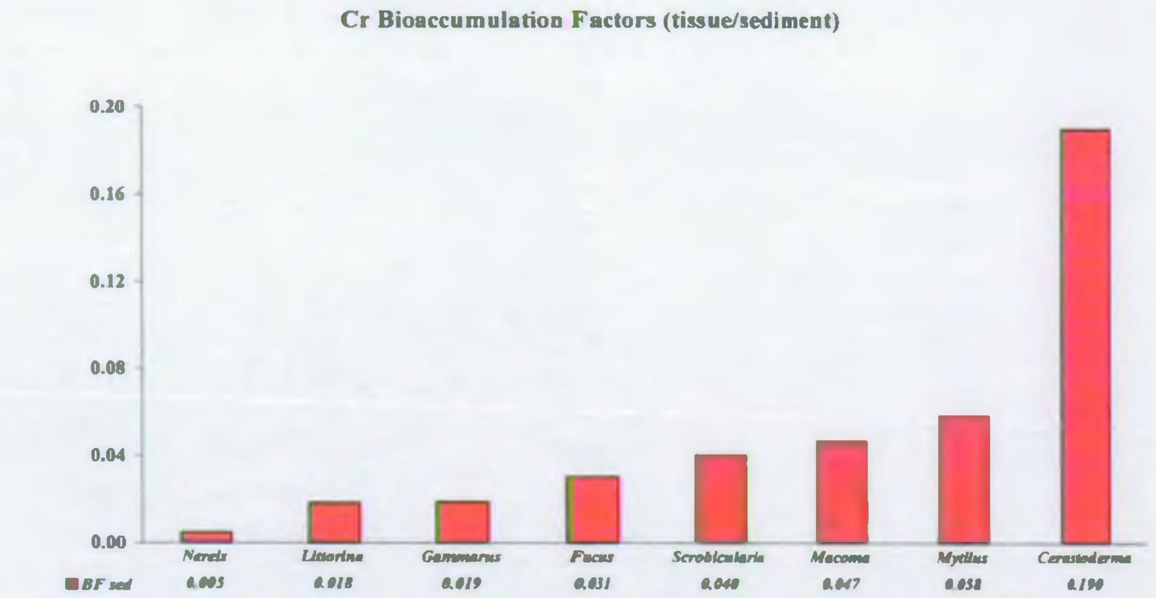


Figure. 23. Chromium Bioaccumulation Factors in Thames biota [BF = concentration in organism ÷ concentration in sediment].

Most Thames biota and sediments demonstrated enrichment in Cr, relative to background levels in UK estuaries (Fig 24). Rankings, based on mean Thames Cr concentrations, varied between species and ranged from the 23rd to the 73rd percentile (for *Fucus* and *Cerastoderma,* respectively). At the most impacted sites in the Thames, Cr values in *Cerastoderma, Macoma* and sediments were among some of the highest in national terms (>85th percentile). At the other extreme, minimum values in the Thames were below the 20th percentile for most sample types (Figure 24) and for *Nereis* and *Scobicularia* concentrations were below the 5th percentile.

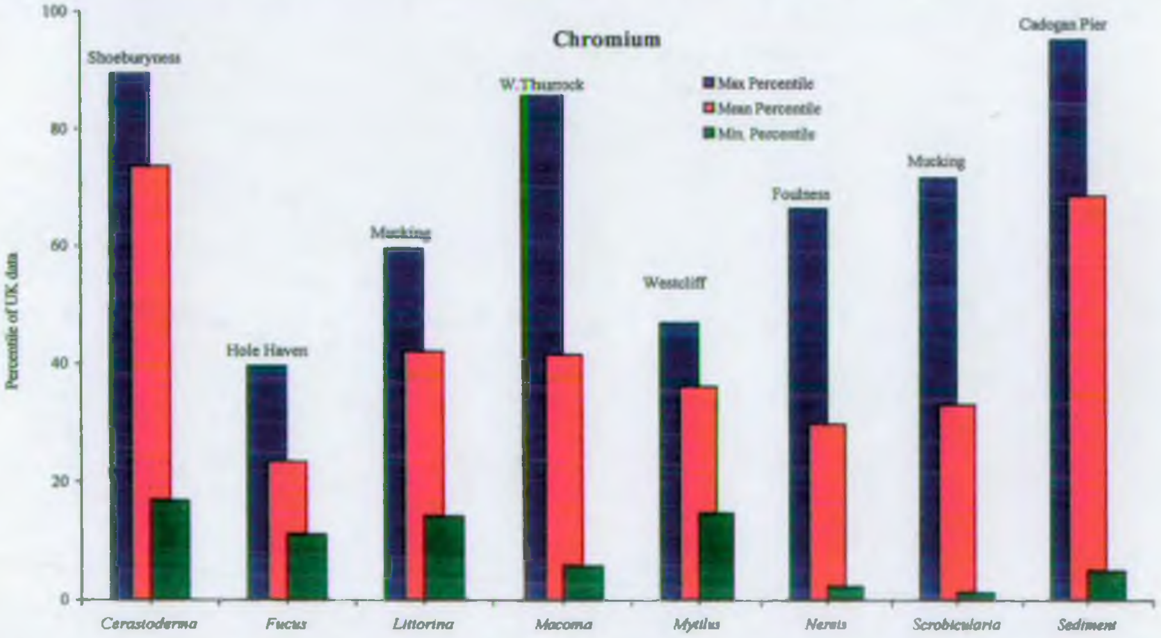


Figure 24. Chromium in Thames biota: min, max and mean values expressed as percentiles of the range in our own data-base for the UK.

The $LC_{50}120h$ for Cr in *Nereis* and *Corophium* (a crustacean which is perhaps analogous with *Gammarus* in terms of toxicity) is upwards of 1000µg l^{-1}. Tolerance is even higher in *Macoma balthica* (16000 µg l^{-1}), at least in short-term acute tests (Bryant *et al.*, 1984). Over longer periods, however, thresholds are likely to be considerably lower. Polychaetes such as *Hermione hystrix*, for example, are affected by chronic exposure to 100-500µg l^{-1} chromate (Chipman, 1966). Sublethal effects on polychaete reproduction have been detected at even lower levels, of 50-10 µg l^{-1} (Reisch, 1978), and offspring production in *Neanthes arenaceodentata* is reduced at tissue concentrations of ~50 µg g^{-1} (Oshida and Word, 1982). This body burden is two orders of magnitude higher than in Thames worms and it seems unlikely, therefore, that Cr concentrations in Thames biota are, on their own, sufficient to cause deleterious effects (though the possibility of combined effects with other contaminants in the field cannot be dismissed).

Chromium concentrations in 1M HCl sediment extracts and in *Scrobicularia* were ~50% lower in 1997 than in 1980 ($P<0.05$) at the sub-set of mid-outer estuary sites. There were no significant changes in Cr concentrations in other sample types.

Copper

Copper (Cu) is one of the most extensively used metals with applications in the electrical and water industry, in alloys, antifouling paints, wood preservatives and catalysts. Despite being designated as an essential element (present in metalloproteins such as cytochrome oxidase and the respiratory pigment haemocyanin), Cu is also one of the most toxic of metals when present in excess amounts - sometimes at concentrations only marginally above background. Like a number of non-essential metals (e.g. Ag, Hg, Cd and Pb), Cu can inhibit enzymes, by forming mercaptides with the sulphydryl groups which are responsible for catalytic activity. Tissue Cu concentrations and impact will therefore depend on essential requirements and regulatory/detoxifying abilities, together with routes of uptake and bioavailability. Relatively high Cu concentrations are inherent in many decapod crustaceans, gastropods, cephalopods and oysters.

Accordingly, Cu magnification in tissues of organisms, expressed as CF_{water} or $BF_{sediment}$ varied by as much as one order of magnitude in the bioindicators studied here (Figure 25). *Gammarus* and *Littorina* contain haemocyanin as a blood pigment (reflected in the high Cu burdens, especially in the latter), though both appear reasonable bioindicators of environmental Cu.

Bioaccumulation Factors $_{(sediment)}$ for *Nereis*, *Scrobicularia* and *Macoma* all exceeded unity suggesting that sediments could be an important contributor to body burdens in these infaunal clams and polychaetes.

The CF_{water} for Cu in *Fucus vesiculosus* (mean value = 1.7×10^3) was at the lower end of the range described by Bryan *et al.* (1985) at other field sites ($3.6 - 27 \times 10^3$). The reason for this is not known but may be due to the presence of humic acids or sewage derived organic matter in the Thames which would be expected to limit the availability of free Cu ions. Other possible causes include competitive interactions with metals, nutrients and other contaminants, together with the lack of representative (time-averaged) water samples to derive CFs.

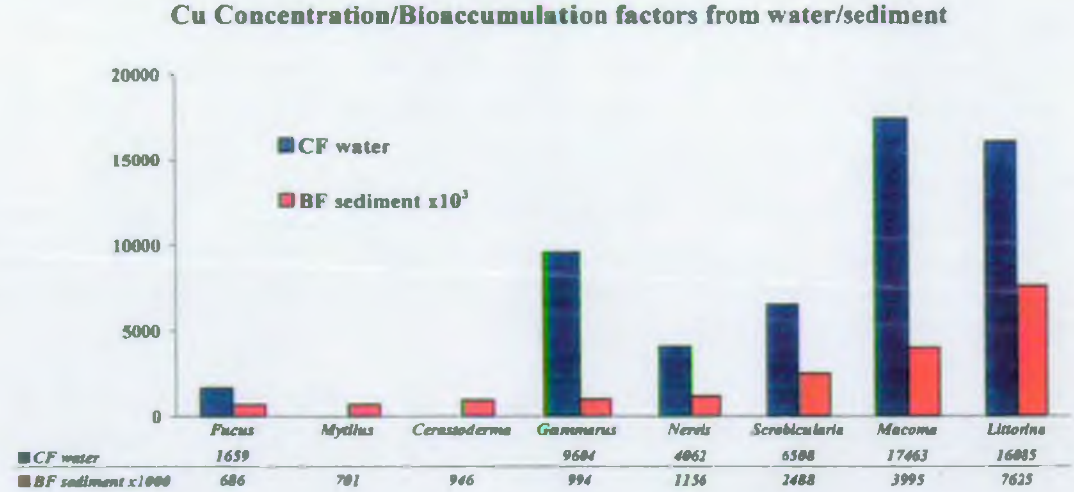


Figure. 25. Copper in Thames biota: Concentration Factors [CF = concentration in organism (µg g^{-1}) ÷ concentration in water (µg g^{-1})] and Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment]. Note BFs are multiplied by 10^3 in order to plot on same scales as CFs.

Copper concentrations in *Gammarus, Fucus, Littorina* and *Macoma* all decreased significantly in a seaward direction ($P<0.05$), as did concentrations in sediments (Fig 26). Rates of Cu absorption by estuarine biota are likely to be highest at reduced salinities which could influence these profiles, although Cu contamination levels would be expected to be the prime characteristic which determines body burdens. Not surprisingly, there were a number of correlations between Cu levels in sediments and tissues. The best-fit relationships for *Gammarus* ($r=0.79$, $P=0.06$), *Fucus* ($r=0.6843$, $P<0.001$), and *Littorina* ($r=0.7114$) were with Cu levels in 1M HCl extracts, normalised with respect to Fe. This implies that Fe has a modifying influence on Cu bioavailability in a number of estuarine species, as observed for As and Cr earlier. Copper bioavailability in freshwater bivalves also appears to be best defined as a function of Cu/Fe ratios in 1M HCl sediment extracts (Tessier *et al.*, 1984).

Such relationships do not necessarily mean that particles themselves are the direct vector for uptake (though this is probably true for some of the deposit feeding clams used here). It is likely that sediments, particularly metal-binding substrates such as Fe (oxyhydroxides), control solute metal concentrations via partitioning behaviour: therefore the ratio Cu/Fe (in 1MHCl) sediment extracts is likely to be directly proportional to dissolved Cu in surrounding water. This could account, for example, for the significant correlation between the Cu/Fe ratio in sediments and Cu concentration in *Fucus*. Masking the distinction between uptake routes still further, Cu (like Ag and Zn) has a strong affinity for algal polyphenols (Luoma *et al.*,1982): if this affinity exceeds the strength of binding to particles, direct scavenging of Cu from sediments could occur where algal tissues are in contact with sediments, hence contributing to the apparently anomalous correlations between *Fucus* and particulate Cu.

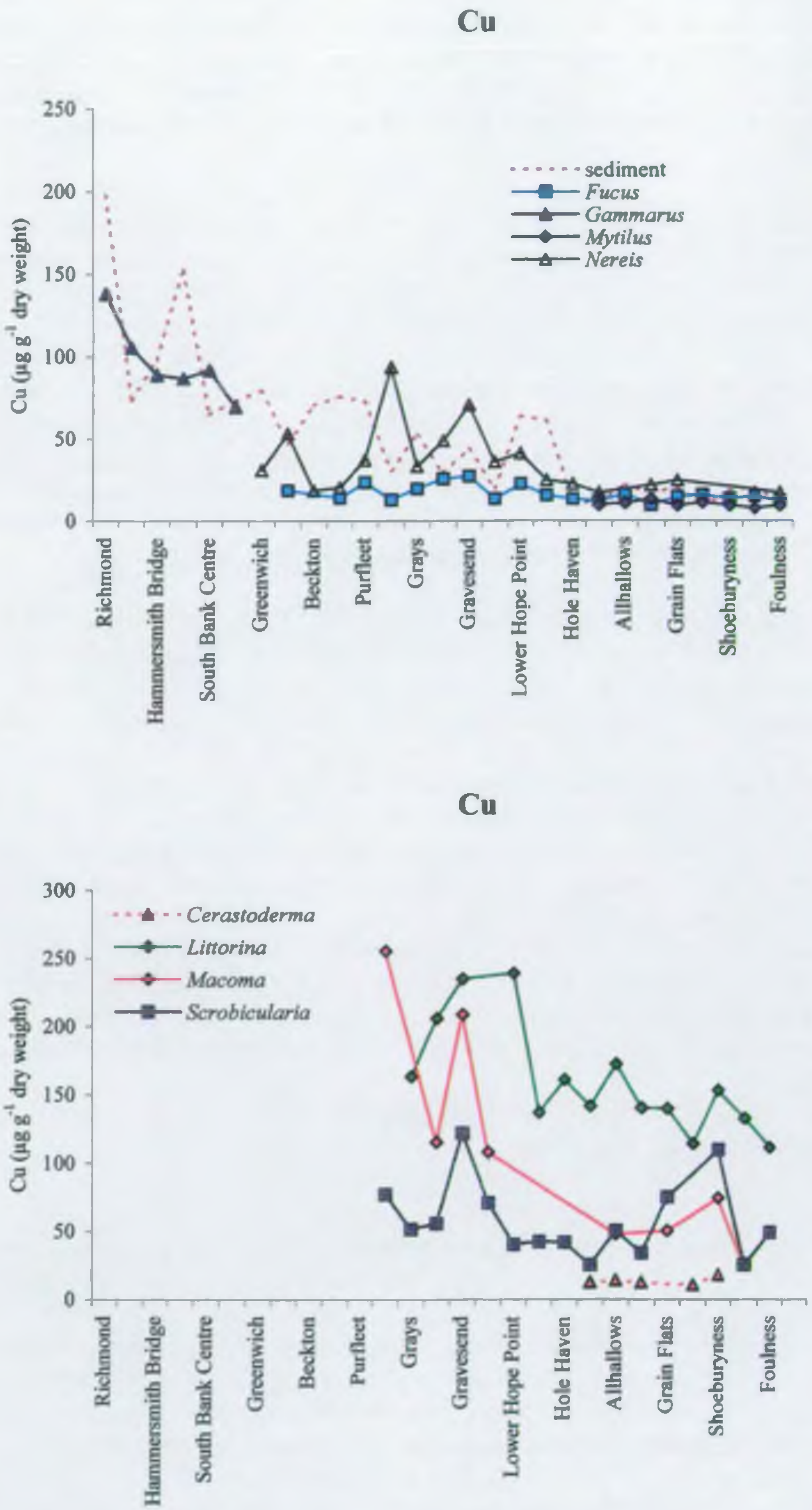


Fig 26 Copper concentrations in organisms and sediments along the Thames Estuary (July, 1997).

Cu concentrations in *Mytilus* and *Cerastoderma* did not vary greatly, between sites, in the outer Thames. This is consistent with observations that these bivalves are able to regulate, partially, their Cu burdens and are likely, therefore, to underestimate environmental Cu contamination. In contrast, most of the other organisms described here do not appear to regulate Cu, at least not in the concentration range present in the Thames Estuary.

Copper concentrations in *Macoma balthica* were significantly related to total Cu in sediments ($r=0.7568$, $p<0.03$). A similar relationship between Cu content in *M.balthica* and sediments was described in a study in San Francisco Bay (Cain and Luoma, 1990), though consistent and predictable models for Cu have been almost impossible to establish in these clams. The same is true of the related species *Scrobicularia plana*. In the current survey, body burdens in *S.plana* were not related to total Cu in sediment ($r=0.07$), nor to 1M HCl-extractable Cu ($r=0.007$), confirming results from more extensive observations in a range of estuaries (Bryan and Langston, 1992). It is thought that redox conditions are be important in modifying bioavailability of sediment Cu to bivalves: unusually high Cu levels are sometimes present in clams from sediments subjected to anoxia, even where sediment Cu is low.

A similar redox-related phenomenon could be responsible for the absence of any correlation between Cu levels in sediments and concentrations in *Nereis* (which were highest in mid-estuary, notably at West Thurrock and Purfleet). However, this seems unlikely since, typically, relationships between Cu in *Nereis* and sediments are highly significant in multi-estuary studies (Bryan and Langston, 1992). An alternative explanation for the apparent absence of correlation between Cu in Thames sediments and *Nereis* is that Cu bioavailability, particularly upstream, may be modified by complexation with organics - either natural (eg humics) or anthropogenic (from sewage treatment). Thus, normalising sediment Cu with respect to organic matter improves correlations, increasing the r value from 0.019 to 0.34 (though this still remain non-significant, statistically). Size was not an important variable affecting Cu in *Nereis* (or any of the other indicators used in the present study). Clearly, the processes of Cu accumulation are complex, and for some organisms, including worms and clams, bioavailable Cu species have still to be accurately defined in the Thames.

There were significant correlations ($P<0.001$) between Cu levels in *Littorina* and *Fucus*, *Macoma* and *Nereis*. Relationships between Cu in *Nereis* and *Scrobicularia* were also significant.

Most of the Thames biota and sediments demonstrated enrichment in Cu, relative to background levels in UK estuaries (Fig 27). Rankings, based on mean Thames Cu concentrations, varied between species, and ranged from the 41st (*Fucus*) to the 75th percentile (*Macoma*, *Scrobicularia* and *Cerastoderma*). At the most impacted Thames sites, Cu values in *Macoma* and *Scrobicularia* were among some of the highest in national terms (>90th percentile). At the other extreme, a number of sample types, including sediments, exhibited minimum values which were in the lower quartile (below the 25th percentile) (Figure 27). The exceptions were *Scrobicularia* (33rd percentile) and *Mytilus* and *Cerastoderma* (both partial regulators and restricted mainly to the mouths of estuaries).

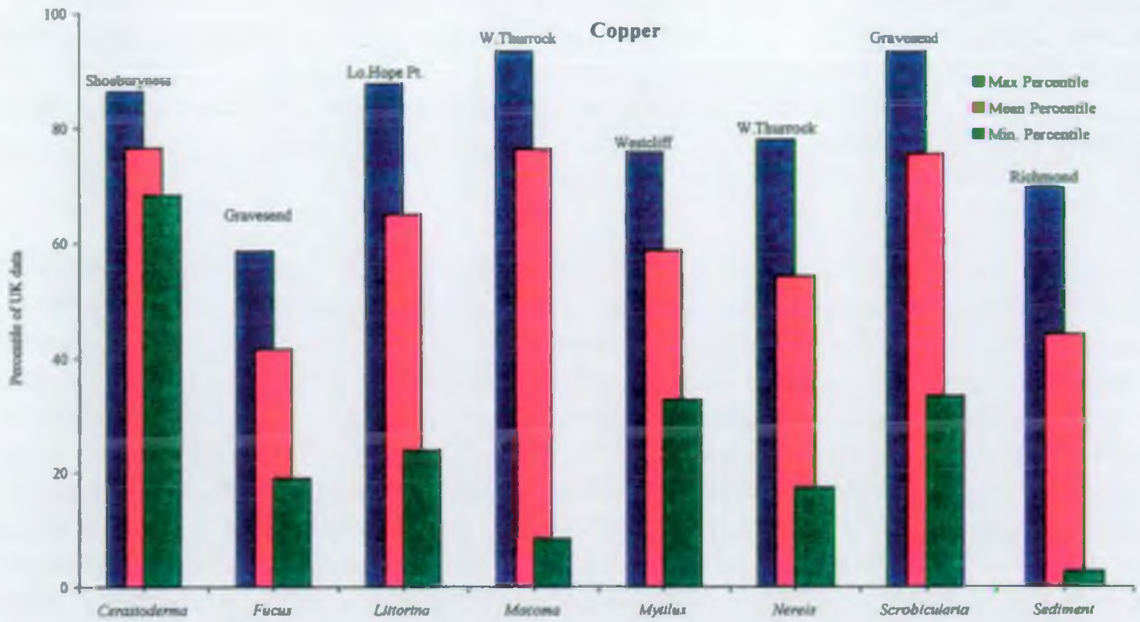


Figure 27. Copper in Thames biota: min, max and mean values expressed as percentiles of the range in our own data-base for the UK.

To many aquatic organisms, Cu is among the most toxic of metals. The LC_{50} (192h) for *Nereis diversicolor* is 270µg l^{-1} and is of a similar order, or lower, in a number of molluscan species, but may be higher for Cu regulators such as certain crustaceans and fish (Bryan, 1976; 1984). Lethal body burdens in *Nereis* were ~290 µg g^{-1} - approximately three-fold higher than in worms from the most impacted Thames sites. Acute toxicity in bivalves such as mussels may occur at concentrations of 20 µg l^{-1} or at critical body burdens of 60 µg g^{-1}- some four-five fold higher than in the outer Thames.

Such tests are generally too short to determine concentrations that are harmful in nature. Longer-term sublethal effects are more relevant: these include reduction of growth in macroalgae, fish (10 µg l^{-1}) and bivalve molluscs (3-33 µg l^{-1}); larval abnormalities (5-10 µg l^{-1}); and reduced reproductive success in a range of polychaetes, molluscs, crustaceans, echinoderms and fish (5-100 µg l^{-1}). It has even been suggested that Cu at background concentrations would, if uncomplexed, be toxic to phytoplankton (for review see Bryan, 1984; Langston, 1990). Perhaps more pertinent, at the community level, sediment concentrations above 200 µg Cu g^{-1} (the upper limit in the Thames) have been linked with a reduction in diversity - with molluscs and other sensitive species being replaced by more tolerant polychaetes (Rygg, 1985).

Although these observations indicate that Cu toxicity might be expected in the Thames, many species can develop tolerance over time - e.g. through induction of metallothionein, granule production, reduced permeability and regulation - and may not necessarily succumb to contamination in nature. There can be no doubt however that Cu poses concerns for the Thames Estuary. Future requirements should include the detection of any effects specifically attributable to Cu.

Copper concentrations in 1M HCl sediment extracts have decreased by approximately 40% since 1980 ($P<0.05$) in the mid-outer estuary sites. There have been small reductions in Cu concentrations in most of the bioindicators sampled, with the exception of *Mytilus* and *Cerastoderma*, though none of the comparisons were statistically significant.

Iron

Iron is a major element and is utilised by organisms for essential purposes including enzymes (e.g. cytochrome oxidase) and oxygen carrying proteins (e.g. haemoglobin). Because of its common geological occurrence, Fe is usually present in percent quantities in aquatic sediments. Principal anthropogenic releases are from mining, iron and steel manufacture, extraction and refining of other metals (e.g. aluminium), and the chemical industry. In oxidised form, in seawater, $Fe^{(3+)}$ is relatively insoluble and is usually deposited as solid-phase oxyhydroxide coatings in estuarine sediments. Even much of the so-called dissolved fraction passing through a 0.45µm filter is probably in colloidal form. Metal profiles in the water column, described in a previous section of this report, indicate some evidence of Fe inputs in the mid-upper Thames Estuary. These may be associated with direct discharges (including treated sewage) or, alternatively, may arise as a result of secondary remobilisation from sediments (following resuspension and diagenetic processes).

Iron appears to be regulated to some extent by most marine organisms, because of its abundance and essential usage. Concentration/Bioaccumulation Factors, and the ability to accumulate Fe, vary according to Fe requirements, though, for the majority of species studied here, the range was relatively narrow (Figure 28). Calculated values for CF ranged from 13 $x10^3$ in *Gammarus* to 50 $x10^3$ in *Fucus* and *Scrobicularia*. (Note, however, that there was insufficient data for dissolved iron to calculate CFs for cockles and mussels). Fe concentrations were not significantly influenced by size in any of the Thames biota.

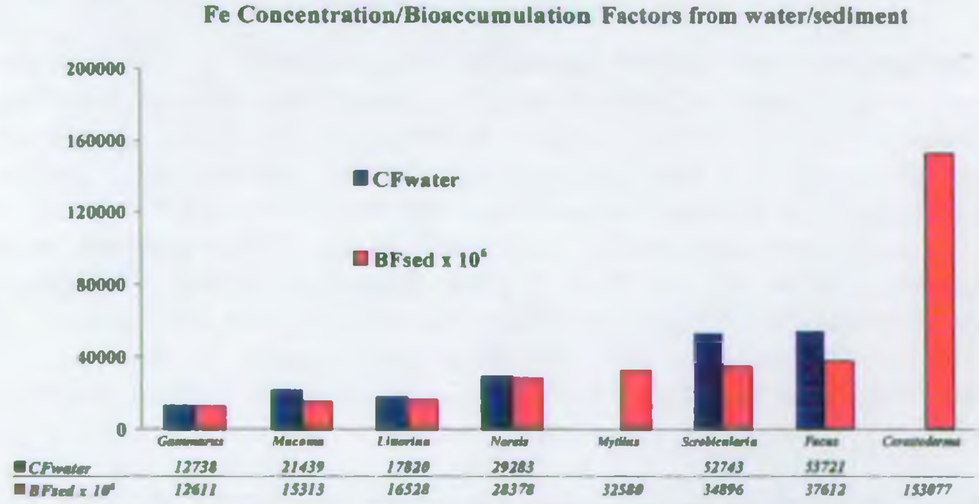


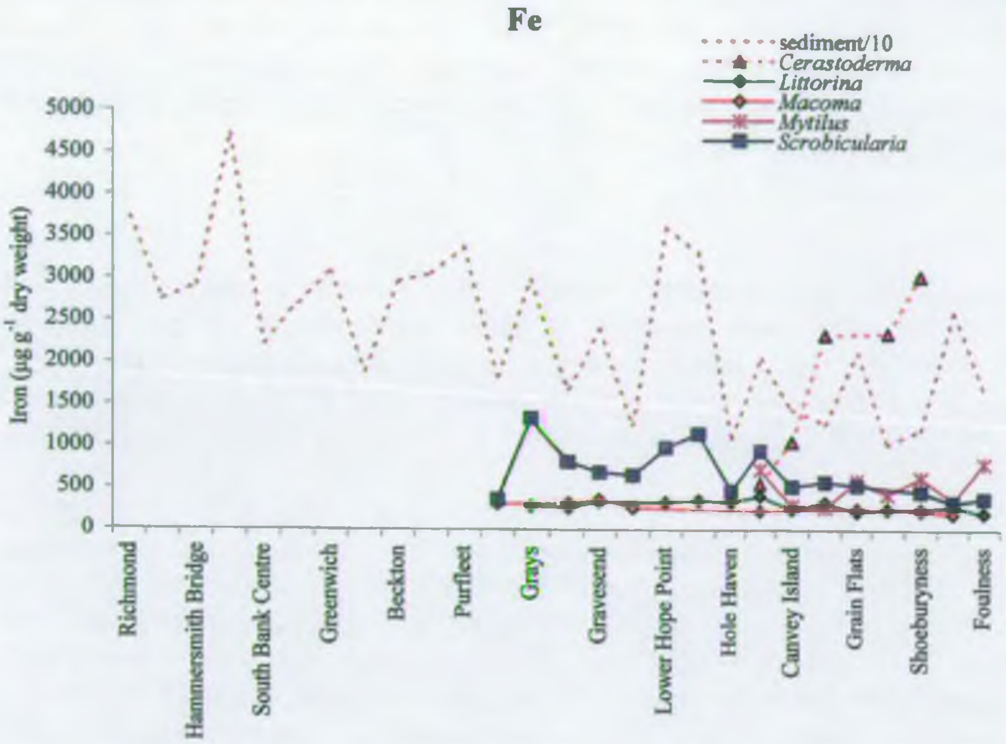
Fig. 28. Iron in Thames biota: Concentration Factors [CF = concentration in organism (µg g^{-1}) ÷ concentration in water (µg g^{-1})] and Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment]. Note BFs are multiplied by 10^6 in order to plot on same scales as CFs.

Bioaccumulation Factors ($BF_{sediment}$) for Fe ranged from 0.012 in *Gammarus* to 0.15 in *Cerastoderma* (all values in Figure 28 have been multiplied by 10^6 for scaling purposes). Thus, none of the organisms magnified Fe with respect to sediment loadings, and tissue concentrations in most species were considerably lower than in surrounding silts.

The essential role of Fe, and regulated nature of body burdens, was reflected by the absence of any specific spatial trend in Fe bioaccumulation in shrimp *Gammarus zaddachi* from the freshwater section of the waterway (above London Bridge), and in *Mytilus* and *Littorina* in the lower estuary (Figure, 29). In most other species Fe concentrations generally decreased seawards ($P<0.05$), in line with sediment loadings.

However, there were some anomalies. Despite being restricted to the outer estuary, Fe concentrations in *Cerastoderma edule* increased sharply, seawards, across this small number of sites (Fig. 29) - contrary to the Fe gradients in sediments and water. It may be that the profile of Fe in *Cerastoderma* depicted a source of bioavailable, suspended particulate Fe in the outer estuary (there is, for example, an input of sewage effluent in the area, at Southend). Alternatively, it is possible that this pattern for Fe in cockles was an artifact due to 'contamination' of some samples from particulates remaining trapped in digestive system or the mantle cavity (Cr, another particle-dominated metal, displays identical profiles to Fe in *Cerastoderma*). Nevertheless, the latter explanation is considered unlikely, since all animals were purged of sediment 'contamination' in clean sea water, before analysis, and some of the highest Fe burdens were found in cockles from the coarsest, least contaminated, sediments (e.g. Thorpe Bay). Perhaps a contributory factor in the unexpected distribution of Fe stems from the fact that cockles are relatively mobile bivalves - displaced from superficial sediment by the action of waves during storms or dredging activities. It is possible that some of the cockle populations which were sampled originated from other sites (allochthonous) - and reflected their previous contamination history - rather than truly representing native (autochthonous) populations. This issue will only be resolved after repeated surveys in the area.

Perhaps a more significant 'anomaly' was the peak in iron values in *Nereis* and *Fucus* from the mid-upper estuary - at Beckton and Crossness, respectively. Unfortunately, these were the only two bioindicators present here: comparable data was not available for other species. Clearly, however, there was an unusually high level of bioavailable Fe in this region which was not reflected in the total Fe concentration in sediment or the water column. It is assumed that the form of Fe present in this part of the Thames Estuary (possibly colloidal in nature) is accumulated disproportionately to other forms. The source of this Fe is not yet known but warrants investigation; the treatment works at Beckton and Crossness would seem to be the most obvious candidates.



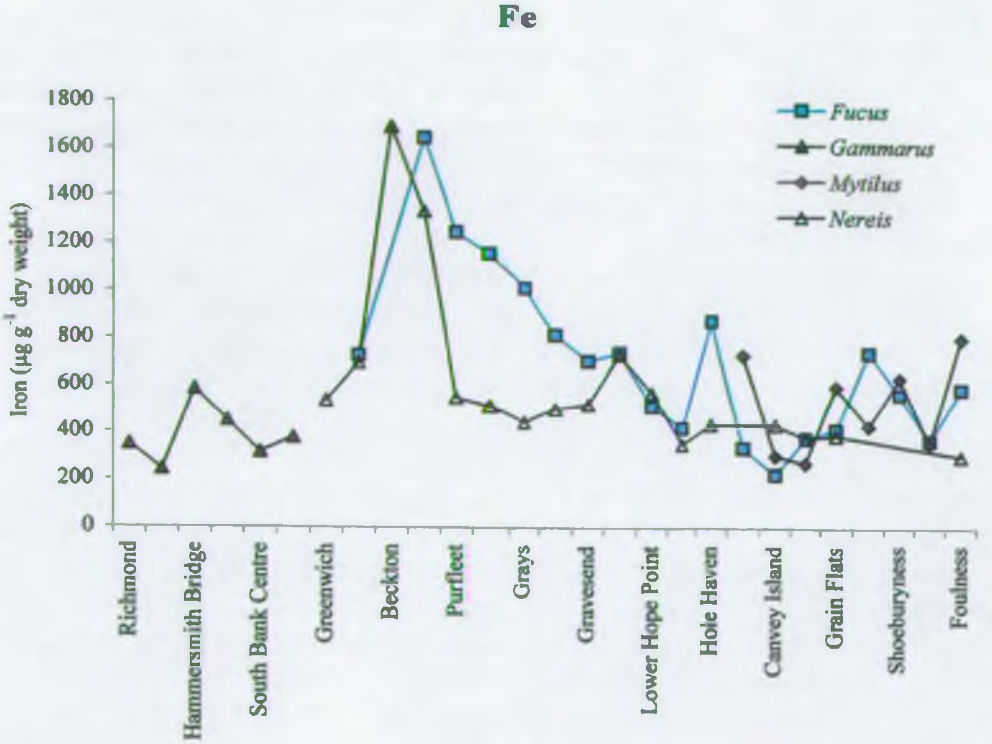


Figure 29 Iron concentrations in organisms and sediments along the Thames Estuary (July, 1997). Note Sediment values in upper figure are divided by 10 to fit scale.

There were few direct relationships between body burdens and environmental levels of Fe, probably because of the atypically high Fe bioavailability at some sites and a degree of Fe regulation elsewhere. Only in *Scrobicularia* were Fe concentrations in tissues correlated with sediment Fe ($r= 0.65$, $P =0.01$; $r= 0.52, P<0.05$ for total and 1MHCl extracts respectively). Fe concentrations in *Littorina* were correlated with those of 'dissolved Fe' ($r=0.99$, $P<0.05$)

The Thames data illustrate that the range of Fe body burdens in most species tends to be limited, across different sites, compared with most non-essential metals. Nevertherless, based on comparisons with other UK estuaries (Fig 30), the mean Fe concentrations in the Thames were higher than normal for most species (with the exception perhaps of *Macoma*). Thus, mean values for Fe in *Fucus*, *Littorina* and *Scrobicularia* were around the 30th - 40th percentile of the UK range, whilst those in *Nereis*, *Mytilus* and *Cerastoderma* were considerably higher (80-90th percentile). At the most impacted Thames sites, Fe concentrations in worms, mussels and cockles include some of the highest values in the UK (>90th percentile). For these three species the availability of Fe in the Thames is clearly exceptional.

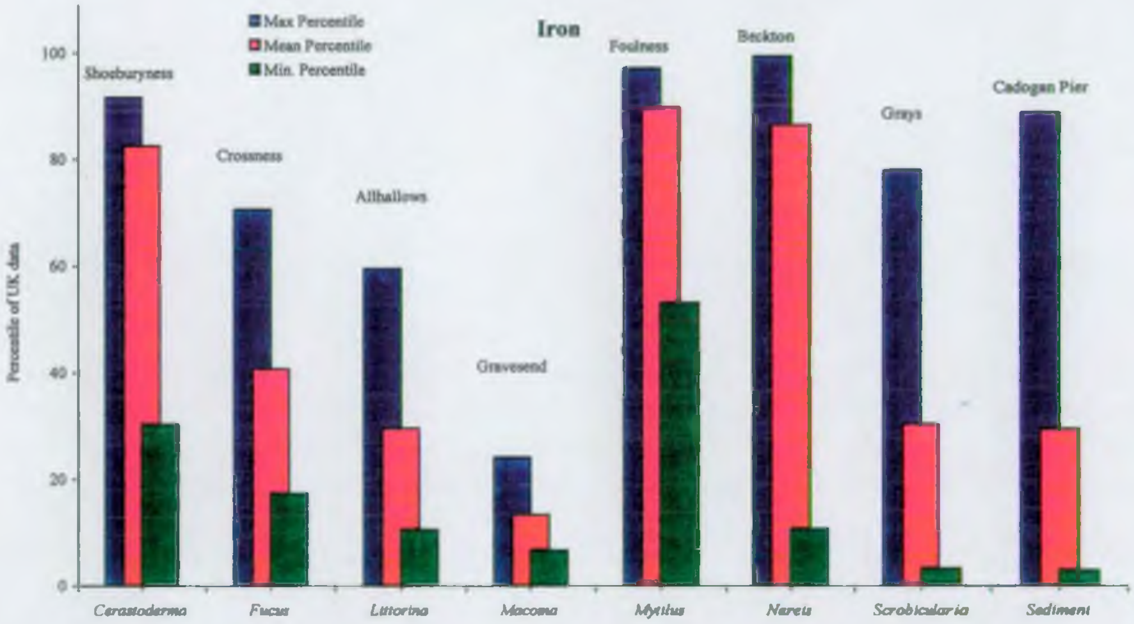


Figure 30. Iron in Thames biota: min, max and mean values expressed as percentile of the range in our own data-base for the UK.

Fe is considered to be one of the least toxic metals. Probably the most serious threat comes from physical damage to the gills of filter-feeders, from flocculating Fe particles. These arise, for example, from the disposal to the sea of bi-products from the production of titanium dioxide pigments (including ferrous sulphate). The condition of bivalves may be impaired by the diversion of energy into production of pseudofaeces - in an effort to remove excess precipitated Fe-rich particles - rather than as a result of direct toxicity (Winter, 1972). Experiments with mussels have illustrated that an increase of suspended Fe hydroxide flakes in the concentration range 0.4 - 4 mg Fe/L leads to a dose-dependent effect on filter-feeding behaviour and, ultimately, mortality (Winter, 1972). Thus, although there are few known acute (short-term) effects attributable to iron, long-term exposure to iron flocs may result in such a loss in condition that mortalities may ensue.

Winter (1972) also found correlations between the speed of mortality and amounts of FeOH passing through the gut and, hence, bioaccumulated: exposure to 0.4, 1, 2 and 4 mg Fe/L lead to 2-, 3-, 4 and 9-fold increases in Fe concentration, respectively. Since, in the current study, estimates of particulate suspended Fe in the Thames (e.g. 2.8mg/L at Crossness) were similar in range to concentrations used in the above mussel experiments, it is possible that this parameter may have contributed to the exclusion of filter-feeders from the upper/mid part of the estuary and to a reduction in their condition downstream.

There was no evidence of significant change in Fe concentrations since 1980, based on samples from the sub-set of mid-outer estuary sites.

Mercury

Mercury (Hg) has no known essential function and is regarded as among the most toxic of metals, having caused the Minamata incident in Japan during the 1950s and 1960s. It is of low natural abundance in UK geological deposits apart from a small degree of enrichment in old base-metal mining areas. Estuarine inputs of Hg have largely been through usage in chlor-alkali production, electrical applications, biocidal coatings (pesticides, fungicides and antifouling) and pharmaceuticals. Significant inputs have also been attributed in the past to domestic waste, as well as industrial disposal activities. Estimated figures for the concentrations and quantities of Hg disposed in the outer Thames have been reported at regular intervals in the MAFF (CEFAS) aquatic monitoring series.

Following recognition of it's rapid bioaccumulation and toxicity, the use of Hg - and it's subsequent release to the environment - has been falling in response to rigorous control measures imposed on the major users. Nevertheless, because it's distribution and concentration in estuaries is dominated by adsorption onto particulates, Hg has become widespread in the sediments of industrial estuaries. Once bound to sediments it may persist for considerable lengths of time as a result of a strong affinity for organic matter and insolubility as sulphides. Thus, sediments probably represent the primary source of Hg for many benthic invertebrates, despite the relatively high bioavailability of dissolved forms (see Bryan and Langston, 1992 for review).

Mercury Bioaccumulation Factors$_{(sediment)}$ in the Thames Estuary varied by more than an order of magnitude between different species (Fig 31). Highest values occurred in molluscs; notably, body burdens in the suspension feeders *Mytilus* and *Cerastoderma* exceeded Hg concentrations in sediments by a factor of two. However, cockles and mussels were restricted to the outer estuary and *Macoma* and *Scrobicularia* were the more widespread bioindicators of sediment Hg in the estuary (Fig 32). In the upstream fresh/brackish zone *Gammarus* was, potentially, a suitable equivalent. Concentrations of Hg in *Fucus* and *Nereis* were comparatively low and spatial trends relatively indistinct (Fig 32).

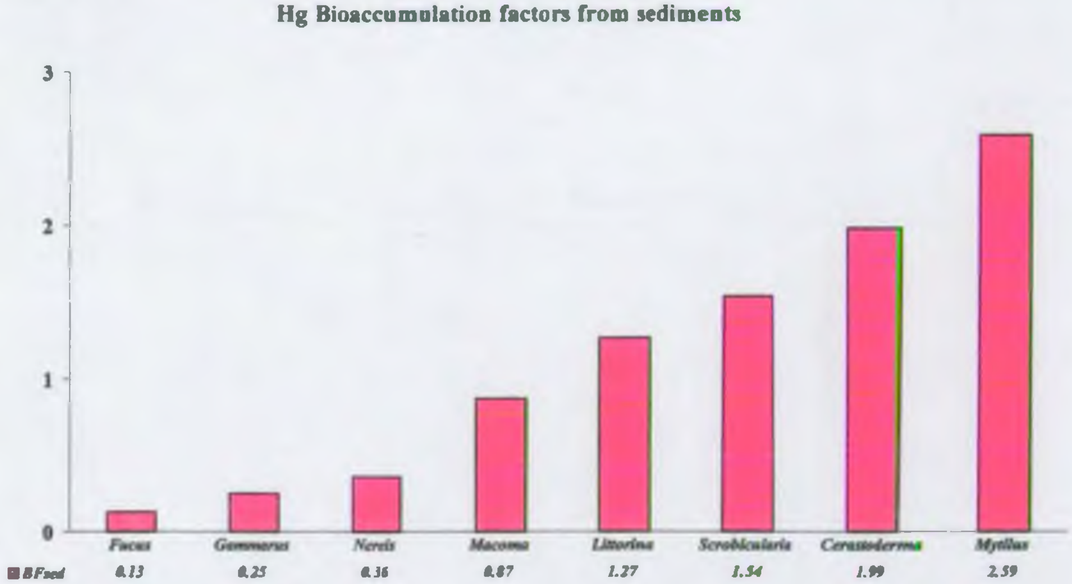


Figure. 31. Mercury in Thames biota: Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment].

Mercury concentrations in Thames sediments decreased with distance down the estuary (r 0.67, p<0.001, Fig. 32). The distribution was significantly correlated with organic content, for which Hg has a high affinity (r=0.8, P<0.001).

Hg concentrations in most of the estuarine species also tended to decrease seawards (Fig. 32), significantly so for *Macoma* and *Scrobicularia* (r = 0.97, p<0.001 and r =0.66, p<0.01 respectively). However, this overall trend in Hg contamination was disrupted at several sites in some bioindicators (e.g. relatively high Hg values in *Mytilus* and *Scrobicularia* at Foulness, and in *Littorina* from Lower Hope Point). Based on the results of a single survey it is not yet possible to establish whether these reflect consistent localised sources of Hg, or some other feature which may enhance bioavailability (e.g. methylation, mobilisation from sediment). Growth rates did not appear to be a determining variable in any of the organisms, since Hg concentrations were not affected by differences in the mean size of individuals collected from different sites.

There were a number of correlations between Hg burdens in different species, the most significant being *Macoma vs Mytilus* (r=0.99, P<0.001) and *Macoma vs Scrobicularia* (r=0.87. P<0.005).

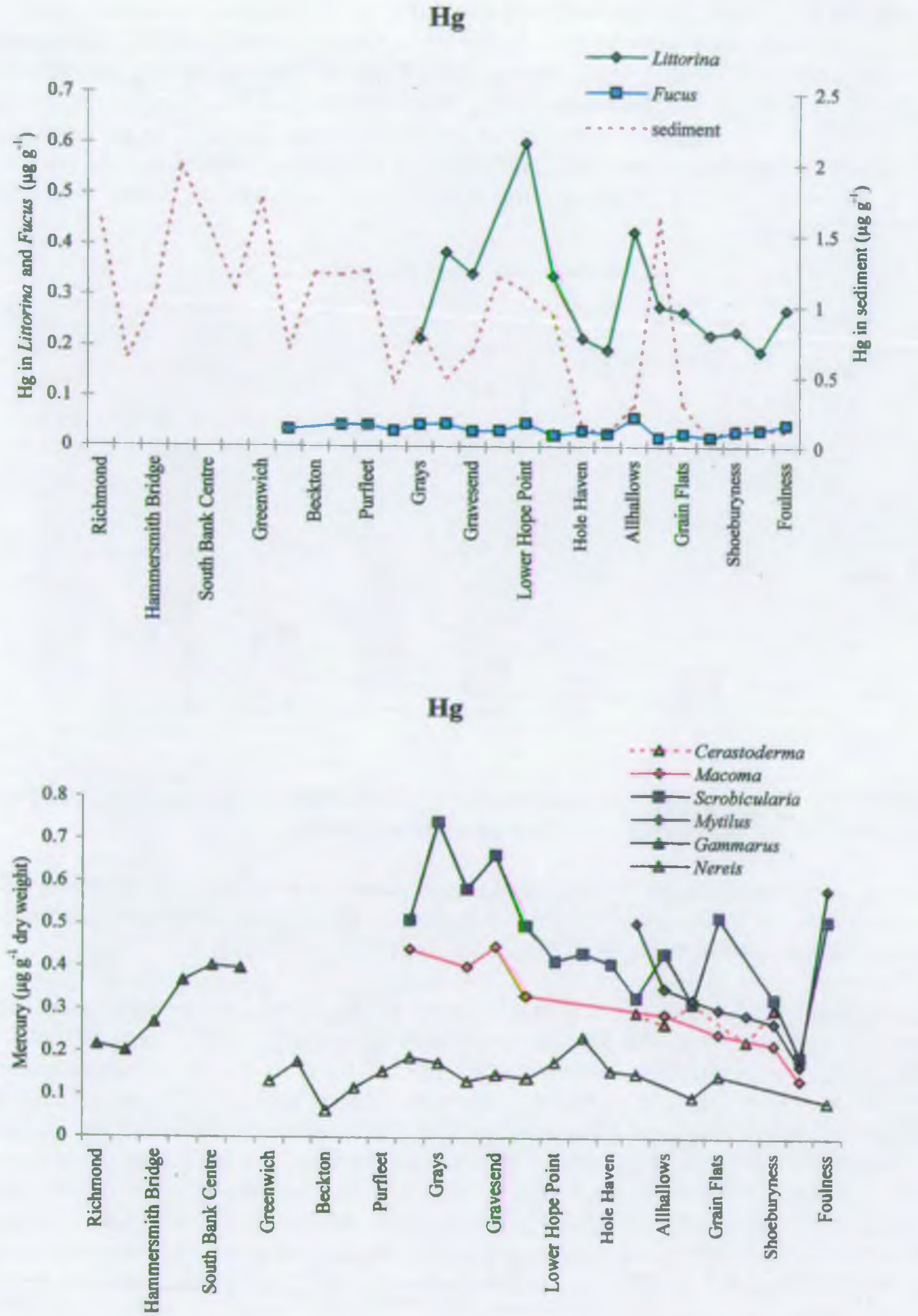


Fig 32. Mercury concentrations in organisms and sediments along the Thames Estuary (July, 1997)

There were no direct relationships between concentrations of Hg in tissues and sediment, though in most species correlations were improved by normalising sediment concentrations with respect to organic content. In the deposit feeding bivalves *Scrobicularia* and *Macoma*, r values increased from 0.15 to 0.45, and from 0.53 to 0.81 ($P<0.05$), respectively. This implies that complexation with organics modifies (reduces) Hg bioaccumulation from sediments. A similar phenomenon has been observed in multi-estuary comparisons of Hg bioavailability (Langston, 1982).

The trend in bioaccumulation in the inner estuary, as reflected by Hg concentrations in *Gammarus*, was reversed, in that bioavailability decreased significantly ($P=0.01$) upstream, towards the freshwater end-member (Fig 32). Once again relationships with sediment Hg were improved by normalisation to organic content; a high sediment organic content, such as that at the head of the estuary at Richmond, appears to reduce Hg uptake. Another factor influencing the pattern of Hg burdens observed in *Gammarus* may be the salinity gradient; although the release of Hg from oxidised sediment to the water column is generally slight, this might be accelerated by higher salinities, compared with freshwater (Frenet-Robin and Ottman, 1978). Other factors which may temporarily increase Hg mobility (and subsequent bioavailability) are dredging and the high sulphide content of anoxic sediments (Lu *et al.*, 1986).

Based on comparisons with other UK estuaries, the mean sediment Hg concentrations measured in the current survey indicate that the Thames was relatively contaminated compared to background levels (Fig 33). Comparative body burden data for Hg in *Scrobicularia*, *Mytilus* and *Littorina* confirm this assessment (mean values between 42nd and 56th percentile of the UK data range, increasing to 70-80th at the most impacted Thames sites). In other species, (e.g. *Fucus* and *Macoma*), values never exceeded the 50th percentile, and minimum values were in the lowest 10% (Figure 33). Variation in the status of Hg bioavailability in Thames biota is not fully understood but may be related to the inconsistent influence of Hg-organic complexation. The nature of this association may lower bioavailability to some organisms more than others.

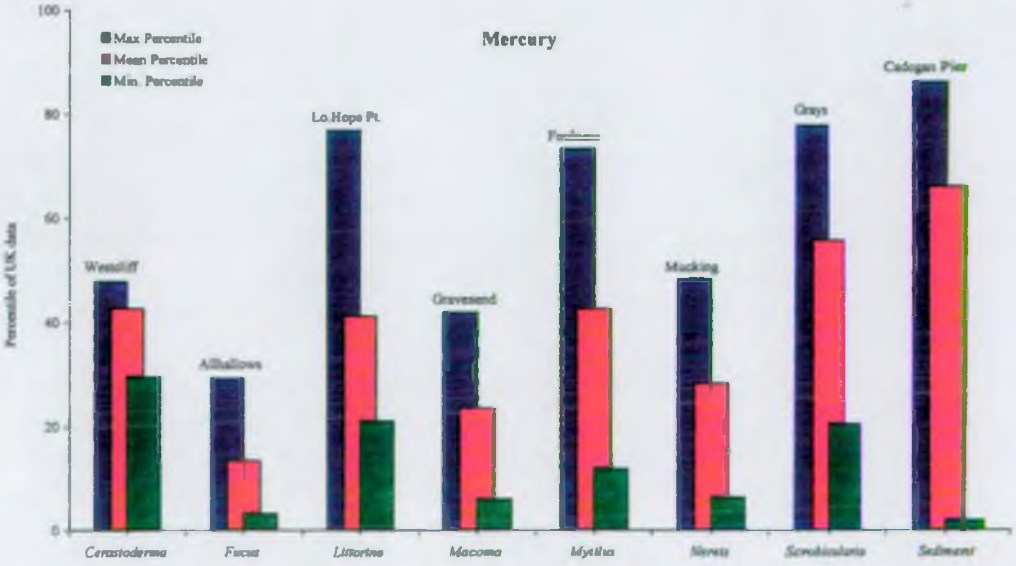


Figure 33. Hg in Thames biota: min, max and mean values expressed as percentile of the range in our own data-base for the UK.

Acute toxicity of Hg can be demonstrated at concentrations of a few µg l^{-1}, whilst sublethal effects occur at levels at least an order of magnitude lower. Invariably, when ranked alongside other metals in comparable tests, Hg is among the most toxic (see reviews by Bryan 1976, Langston, 1990). Yet, unequivocal demonstrations of mercury toxicity in the field are difficult to establish. Even where high levels occur in sediments, and are a probable cause of elimination of sensitive species, other contaminants are usually present and probably contribute to deleterious effects (Bryan and Langston, 1992). Areas exhibiting acute Hg toxicity to marine life are unlikely to be extensive nowadays. Lethal body burdens of methylmercury in fish from Minamata, for example, were of the order of 20 µg g^{-1} wet weight - considerably higher than values expected in the UK, even at the most contaminated sites. Nevertheless, concerns over food chain magnification of Hg have not subsided - especially in light of recent suspicions that placental transfer is more significant than was originally thought.

An upper guideline value of 1 µg g^{-1} (dry weight) is suggested for molluscs by the Oslo and Paris Commisions. This compares with an upper limit of around 0.8 µg g^{-1} in Thames shellfish measured in the present survey. Maximum permitted Hg levels in fish are 0.5µg g^{-1} wet weight, or 1µg g^{-1} wet weight for 'natural accumulators' such as eels and some elasmobranchs . This latter value does not appear to be exceeded in eels from the Thames (Metals in Thames Fish, *in prep*).

It is the presence of the methylated form of Hg which causes most concern. The proportion of methyl mercury in estuarine sediments is generally thought to be rather small (<1% of the total Hg is in the organic form in sediments from the Mersey, for example). However, the relative proportion of methyl mercury becomes enriched in benthic organisms (passing through membranes more readily than inorganic Hg) and may exceed 70% of the total Hg in mussels; methyl mercury bioaccumulation factors (relative to sediment) for Mersey biota range from 95 in *Macoma* to 150 in *Nereis* (Langston, 1982; Langston, *et al.*, 1995). As a result mercury is one of the few metals which is consistently magnified along marine food chains. Accumulation in top predators also increases with size (age) in almost all fish species.

Currently, there is little information on methyl mercury concentrations in the Thames and no guidance as to which species are the best bioindicators for methyl mercury. These are gaps in our knowledge of the system which need to be filled. Bacterial processes are likely to control overall methylation rates in the estuarine environment and hence the overall capacity for trophic transfer of methyl mercury: in view of the major sewage treatment outfalls along the Thames Estuary, assessment of their potential influence on mercury speciation and bioavailability is a further requirement.

Comparisons between 1980 data and the present results indicate that there have been reductions in Hg concentrations in *Fucus*, *Nereis* ($P<0.01$) and *Scrobicularia* ($P<0.05$) - of the order of 74, 64 and 43% respectively. It is possible therefore that the threat from Hg is receding. However, sediment concentrations have not fallen during this period, and the reservoir of particulate Hg could sustain current levels of contamination for a considerable period of time. Similarly, 'steady-state' conditions have been observed at other Hg contaminated sites in recent years (e.g. the Mersey Estuary) following rapid improvements during the late 1970's and early 1980's.

Manganese

Manganese (Mn) is a nutritionally-significant element and Mn concentrations in the majority of marine macrofauna are likely to be regulated to a degree. Mn may also be linked, passively, with Ca metabolism, explaining the exceptional accumulation seen in some organisms and tissues. For example, Mn can substitute for Ca in the calcite lattice of lobster shells, in $CaCO_3$ spicules in certain ascidians, and is some times present in granular form in the kidneys of bivalves such as scallops (reviewed by Bryan, 1976).

Manganese is an abundant metal and the weathering of minerals constitutes a major natural source for most estuaries. Anthropogenic uses, which include the production of steel alloys, chemicals, glass and ceramics, may add to this relatively high background.

Some secondary redistribution of Mn in estuarine sediments may occur as a result of redox changes: evidence of such a source of Mn - in sediments from the Purfleet reaches - was described in an earlier section. Nevertheless, overall, Mn concentrations in Thames Estuary waters and sediments decreased in a seaward direction, as riverine sources were diluted with low-Mn marine waters and particulates (Fig 34). The departure from linearity in the relationship between dissolved Mn and salinity signified that there was, in fact, a degree of Mn removal to sediments during estuarine mixing (Fig 4). Unfortunately, being based on a single set of results, it is impossible to deduce whether or not the trend depicted represents a consistent picture for the Thames Estuary: seasonal/climatic changes may be important in determining the mobility and fluxes of this redox-sensitive element. Furthermore, localised conditions are capable of modifying the behaviour of Mn considerably - more so than the majority of metals. However, for now it is assumed that the gradient for Mn concentrations in sediment, shown in Fig 34 (upper), is a reasonably representative Thames profile.

Manganese burdens in several species also decreased seaward, generally, along the Thames Estuary (Fig 34, upper), resembling the trends for water and sediment - though in fact (negative) correlations with distance were only significant for *Nereis* (r=0.61, P=0.01). In contrast, Mn concentrations in *Cerastoderma* were *positively* correlated with distance (r= 0.96, P= 0.01), following a pattern similar to that of Fe and Cr. The distribution of Mn concentrations in *Scrobicularia* and *Mytilus* sampled along the estuary also resembled the 'reverse gradient' described for cockles (Fig 34, lower), although relationships with distance were not statistically significant for these two bivalves. Mn bioavailability was clearly variable among different groups of organisms in the Thames.

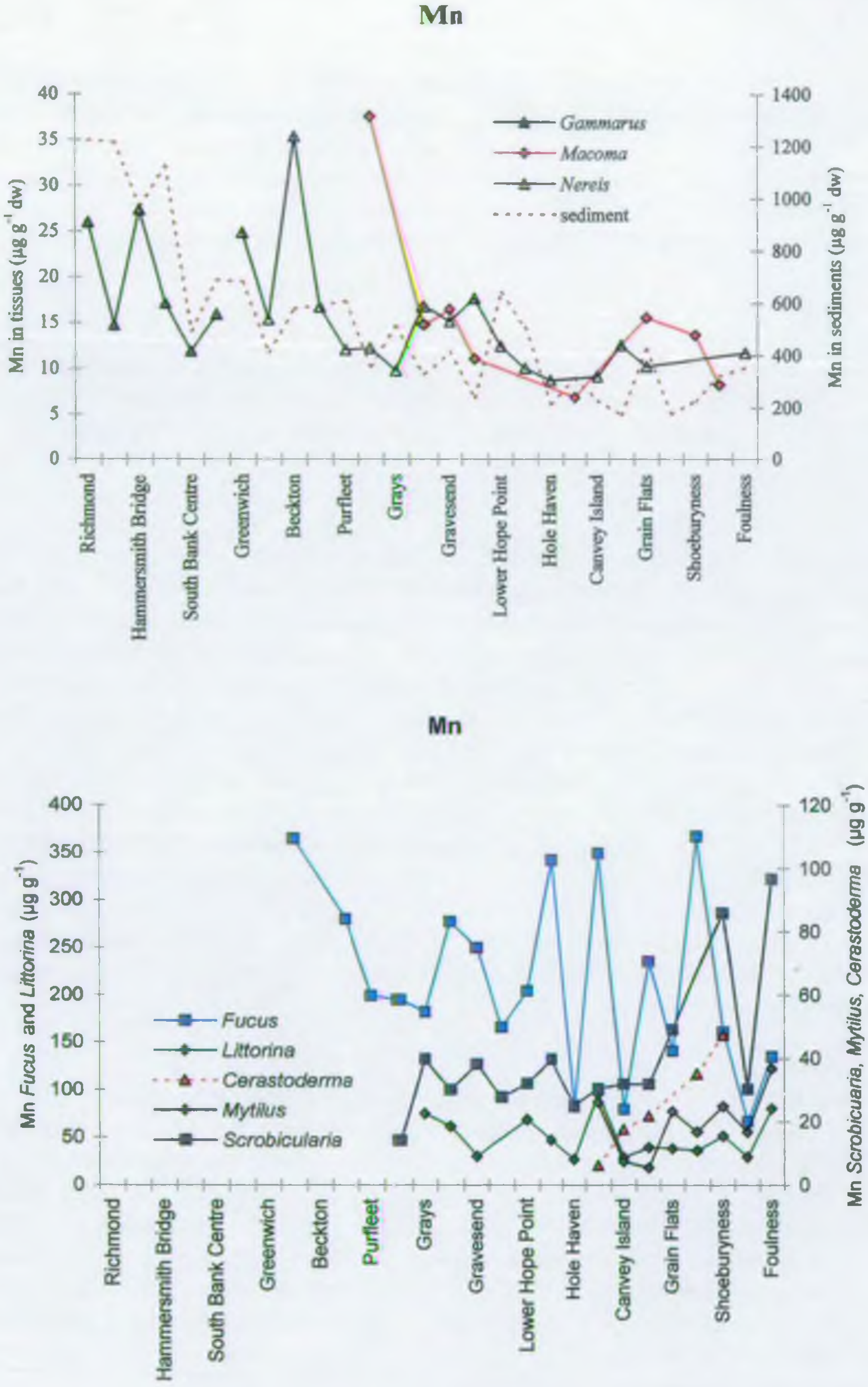


Fig 34. Manganese concentrations in organisms and sediments along the Thames Estuary (July, 1997).

Correspondingly, the ranking of Concentration Factors for Mn was unusual in that CFs were highest in the seaweed *Fucus vesiculosus* (Fig 35). Presumably this is because, in contrast to the majority of macrofauna, uptake of Mn in the macroalga is not regulated. Lowest CFs were those in *Gammarus* (mean value 1 x 10^3). Manganese Bioaccumulation Factors $_{(sediment)}$, displayed comparable variability, but were less than unity in all species (Fig 35).

Previous laboratory work has shown that Mn concentrations in *Fucus* reflect dissolved Mn concentrations, at all but the highest levels of contamination (implying some departure from direct proportionality). Concentration Factors, determined in the field, are also known to be variable, ranging from 5 x 10^3 -220 x 10^3, and tend to be lowest where Mn levels in water are high, or where the presence of other metals (particularly Zn) may result in competition for uptake (Bryan *et al.*, 1985). The large range of CFs calculated for current *Fucus* samples (16 x 10^3 -459 x 10^3) suggests the possible influence of these factors at certain Thames sites. This may explain why Mn levels in *Fucus* were not significantly related to those in water samples in the present survey.

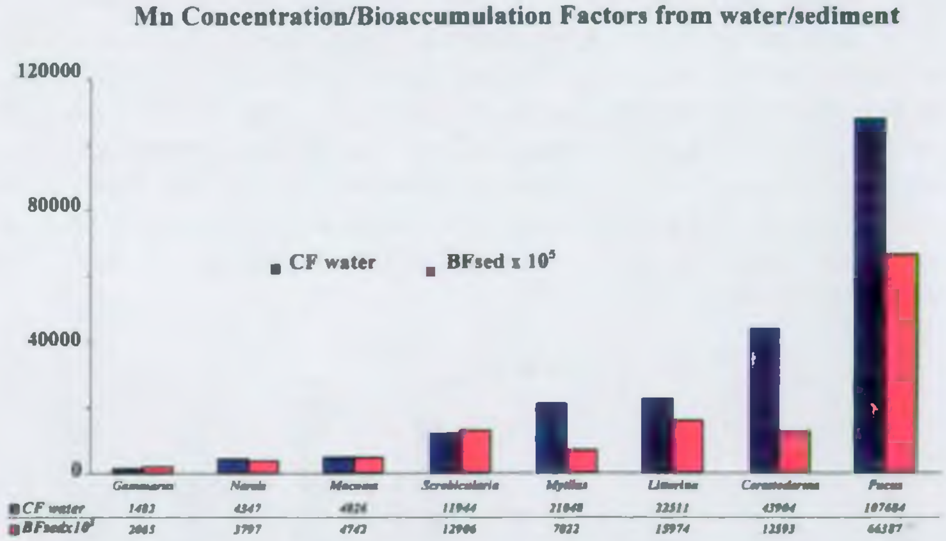


Fig. 35. Manganese in Thames biota: Concentration Factors [CF = concentration in organism (μg g^{-1}) ÷ concentration in water (μg g^{-1})] and Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment]. Note BFs are multiplied by 10^5 in order to plot on same scales as CFs.

Mn concentrations in winkles *Littorina littorea* were significantly correlated with water (r= 0.81, P=0.05). The only other species to exhibit a relationship between Mn body burdens and dissolved Mn was *Macoma* (r=0.97, P<0.05).

Dissolution of solid phase manganese oxide coatings, under reducing conditions, will tend to enrich interstitial waters considerably, so that benthic fauna may experience relatively high levels of bioavailable Mn, even in uncontaminated areas. This Mn may also diffuse out and influence epibenthic species. The dependency of such behaviour on localised conditions will obviously tend to mask any simple linkage between sediment and tissue loadings, making it difficult to relate body burdens directly to contamination levels. Consequently, r values (sediment Mn *vs* tissue Mn) were not statistically significant in most invertebrates (r=0.63, 0.56, 0.48, 0.44 for 1MHCl-extractable Mn *vs* Mn in *Gammarus, Macoma, Mytilus* and *Nereis,* respectively). Normalisation techniques were only effective for *Mytilus*: the r value increased to 0.77 ($P<0.05$) when sediment Mn was modified with respect to Fe content.

Because Mn bioavailability is subject to varied biotic influences, as well as site conditions, it is not surprising that simple, uniform trends are difficult to characterise *within* a single estuary. Comparisions *between* estuaries tend to be more forthcoming about which species are able to reflect Mn contamination, at least on a superficial basis. For example, body burdens of Mn in *Scrobicularia plana* vary by more than an order of magnitude across UK estuaries, according to environmental levels (highest concentrations are usually found in estuaries associated with metal mining and processing). In contrast *Nereis diversicolor* is known to be an efficient regulator of Mn; body burdens in these worms are less dependent on levels of contamination.

Despite their variable responses, the majority of bioindicators depicted a range of Mn bioavailability across different sites in the Thames estuary. Rankings were comparable, in national terms, to those derived from sediment contamination data (Figure 36). Minimum Mn values in Thames biota invariably fell below the 20th percentile and included the lowest recorded value in *Macoma*. At the other extreme maximum concentrations ranged between 64th percentile for *Macoma* and the 96th percentile for *Nereis* and *Mytilus* (i.e. some of the highest in the UK). Mean values in sediments, *Scrobicularia, Nereis Cerastoderma, Fucus* and *Mytilus* were at or above the 50th percentile, implying fairly widespread Mn enrichment in the Thames, compared with baseline levels.

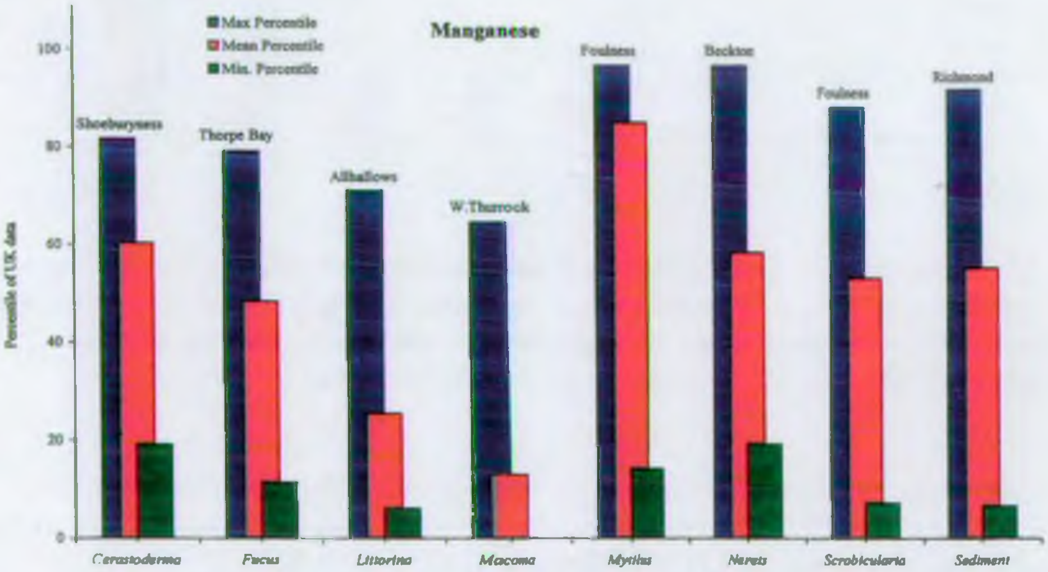


Figure 36. Manganese in Thames biota: min, max and mean values expressed as percentile of the range in our own data-base for the UK.

Manganese is not usually considered a problem in terms of acute toxicity. The 48 hr LC50 for oyster embryos of 16 mg l^{-1} (Calabrese *et al.,* 1973) compares with a maximum of 30 $\mu g\ l^{-1}$ in the Thames surface waters. However, high Mn concentrations generated near the sediment-water interface could affect sensitive species; levels of ~5-10 mg l^{-1} dissolved Mn^{2+} have been shown to reduce muscle power in the burrowing lobster *Nephrops* (Holmes *et al.*, 1998). This level of Mn enrichment is not unrealistic in pore waters. Extrapolating to oyster embryo bioassays (Calabrese *et al.*, 1973), it is also conceivable that settlement and of some bivalve larvae could also be compromised under such conditions. It is therefore important to continue surveillance of this metal in the Thames in view of its potential presence in high concentrations in interstitial water and, upstream, in overlying water.

Based on comparisons with 1980 data, there have been reductions in 'total' and 1MHCL-extractable Mn concentrations in sediments of the order of 40 and 50%, respectively ($P<0.05$). These reductions were not reflected by declining levels in biota.

Nickel

Nickel is one of a number of metals considered to be essential in small amounts but it may be toxic when concentrations are elevated. Its main uses are metallurgical (in the production of steel and other alloys), electroplating, and as a catalyst. It is also found in significant quantities in oil and is released to the environment upon combustion.

There was little indication that uptake of this metal was regulated in Thames biota and a number of the species analysed here were reasonable bioindicators of Ni. There were, however, large differences in amounts of Ni accumulated, as demonstrated by comparisons of CF_{water} and $BF_{sediment}$ in different species (Fig 37). *Cerastoderma edule*, in particular, was an exceptional accumulator of Ni, a feature which has been observed previously (Bryan *et al.*, 1985). The fact that the CF for *Fucus* was relatively high suggests that dissolved and labile forms of Ni may be much more important, in terms of bioavailability, than sediment Ni. The low CFs for other species also indicates that Ni is taken up slowly, relative to most other metals.

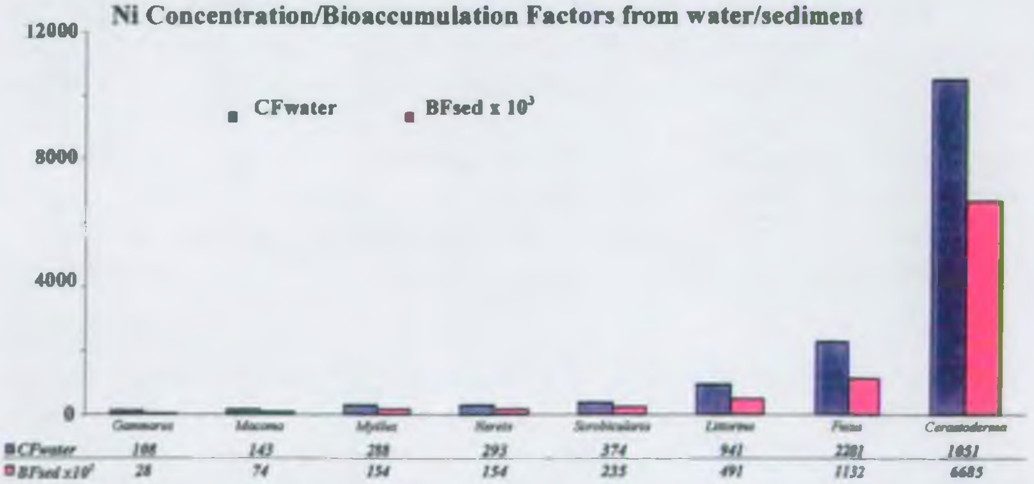


Fig 37. Nickel in Thames biota: Concentration Factors [CF = concentration in organism (µg g^{-1}) ÷ concentration in water (µg g^{-1})] and Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment]. Note BFs are multiplied by 10^3 in order to plot on same scales as CFs.

With the exception of *Cerastoderma* (BF_{sed} = 6.7), none of the benthic invertebrates accumulated Ni to concentrations above those found in sediments.

The spatial distribution of total Ni in the environment (decreasing with distance seaward) was reflected in trends for Ni in tissues of *Cerastodema. Fucus. Littorina*, and *Mytilus* ($P<0.05$; Fig 38, upper). Correlations with distance were not significance in *Macoma, Scrobicularia* and *Nereis* and it is possible that sediment characteristics modify bioavailability of Ni in these infaunal clams and polychaetes. Similarly, there was no clear spatial trend for Ni in *Gammarus* from the inner estuary (Fig 38).

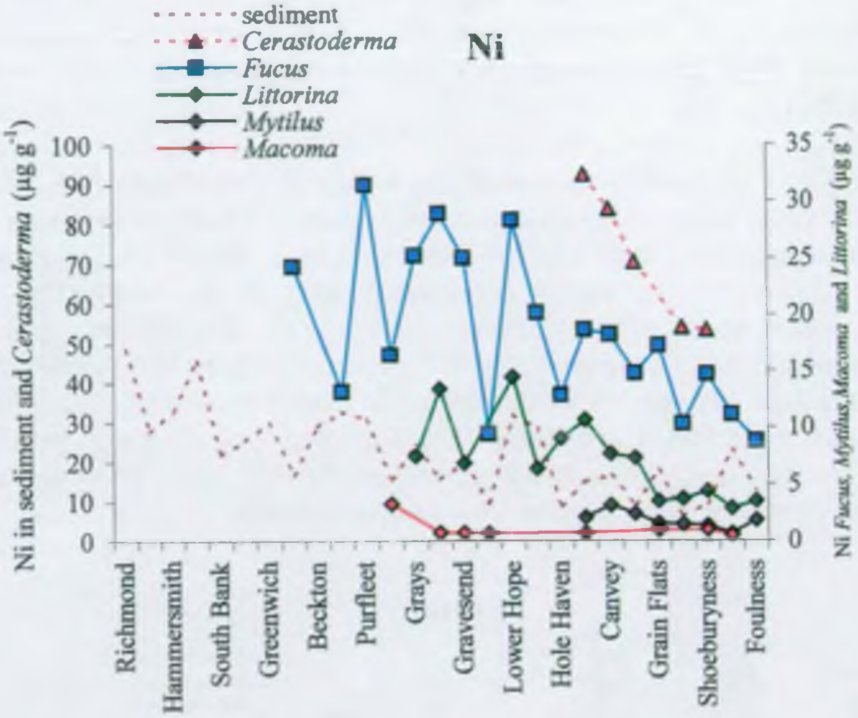
Effects of body size on the Ni profiles in biota shown in Figure 38, were negligible, with the exception of *Nereis*. Ni concentrations in worms were, like Cd, negatively correlated with average weight; the extremely small size of *Nereis* from Foulness was probably responsible for their elevated Ni (and Cd) content.

In the current Thames survey, Ni concentrations in *Fucus* were significantly correlated with levels of dissolved Ni ($r= 0.6166$, $p<0.05$). Indications are that *Fucus vesiculosus* is a reasonable monitoring organism for soluble forms of this metal, although there are some doubts whether direct proportionality is ever achieved, and the presence of high levels of Mn and Zn may tend to suppress Ni uptake (Bryan *et al.*, 1985). Nevertheless, CFs for *Fucus* from the Thames Estuary (1-3 x 10^3) were comparable with those from other areas such as the Irish Sea (2.8-6.8 x 10^3).

Ni concentrations in *Littorina littorea* were also related to environmental levels. Direct comparisons between water and *Littorina* suggest the gastropod was responsive to dissolved Ni ($r = 0.6$), though the relatively small data set (n=6) failed to establish statistical significance. Additional confirmation may be achieved, however, by assuming *Fucus* to be a surrogate measure of dissolved Ni: concentrations in the tissues of these two species were significantly correlated ($r=0.75, p<0.01$).

Similarly, there was insufficient data to test whether Ni concentrations in *Cerastoderma* increased in direct proportion to levels in water, though the correlation between Ni in *Cerastoderma* and *Fucus* was relatively high (0.87). In contrast, the correlation between *Mytilus* and *Fucus* was less distinct ($r=0.53$). Ni concentrations in *Cerastoderma* were also correlated with total sediment Ni ($r=0.88$) and, most notably, 1M HCl-extractable Ni ($r=0.91$), whereas concentrations in mussels were not. Therefore cockles reflect environmental contamination of both dissolved and suspended particulate Ni, whilst mussels appear to be inferior indicators for this metal.

Ni concentrations in *Gammarus* were best related to 1MHCl extractable Ni ($r= 0.69$) - much more so than to 'total' sediment digests ($r=0.05$). There was also an excellent correlation between Ni in *Macoma* and 1MHCl extracts (especially when normalised to Fe; $r= 0.96$, $P<0.001$) - again much better than for total metal ($r=-0.21$). These results illustrate why it is often important to consider the association of sediment-bound metals, rather than concentrations *per se*. Levels of Ni in *Scrobicularia plana* and *Nereis diversicolor* (Fig 38) were not, however, related to any of these sediment measures (nor to dissolved Ni). Based on this evidence *Macoma* was the best indicator of sediment Ni bioavailability.



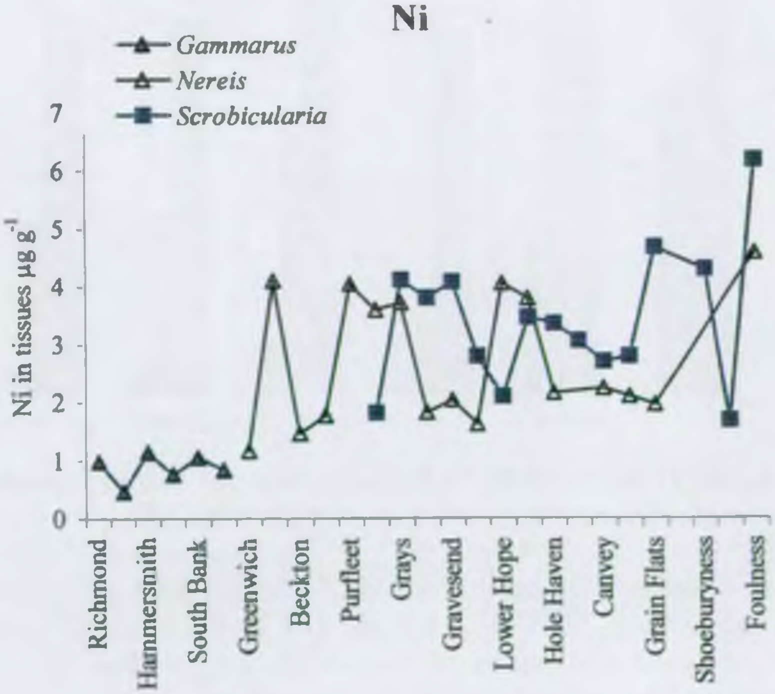


Figure 38 Nickel concentrations in organisms and sediments along the Thames Estuary (July, 1997). Note: *Cerastoderma* and sediments (upper figure) are plotted on different scales to other sample types.

Estuaries with the highest levels of Ni contamination in the UK are those associated with base-metal mining and processing, or with major chemical industries. Whilst *average* Ni values in sediments from the Thames were not outstanding (30th percentile), the most contaminated sites in the estuary ranked highly in UK terms (94th percentile).

Body burden data for Ni display similar variability to that observed in sediments. In most organisms the range of Ni concentrations found in UK estuaries spans more than an order of magnitude, according to environmental levels: Ni concentrations in Thames biota generally covered a considerable part of this range (Fig 39). Thus, minimum values in Thames *Macoma, Nereis* and *Scrobicularia* (all sediment dwellers), and *Mytilus*, were below the 10th percentile of the UK distribution. At the most contaminated Thames sites this ranking increased to between the 67th and 87th percentiles. In *Littorina, Fucus* and *Cerastoderma*, upper values were all >90th percentile, and even average values were around the 85th percentile, implying that Ni in the Thames was especially bioavailable to these species.

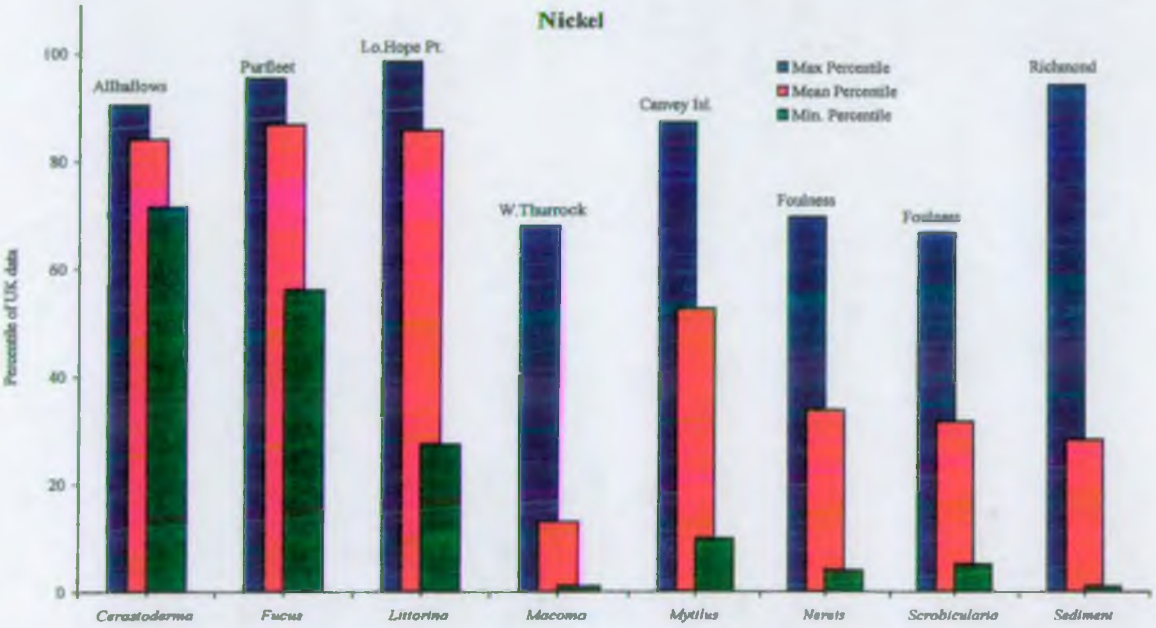


Figure. 39. Nickel in Thames biota: min, max and mean values expressed as percentile of the range in our own data-base for the UK.

Acute Ni toxicity is unlikely to occur in the field. The 48 hr LC_{50} for oyster embryos of 1.19 mg l^{-1} (Calabrese *et al.*, 1973) and the 192 hr LC_{50} for *Nereis* of >5 mg l^{-1} (Bryan, 1976) are some two orders of magnitude higher than concentrations in Thames surface waters. Lethal body burdens of Ni in *Nereis* exceed tissue residues in the Thames ragworm to a similar degree.

Sublethal effects from dissolved Ni would not be anticipated at the levels measured in Thames and comparisons with published data suggest a safety margin of one order of magnitude. It would seem that Ni in surface waters poses little threat for Thames biota. However, it is not known whether levels in sediments and pore waters could adversely affect sensitive species.

Since 1980 there have been reductions in total- and 1M HCl-extractable Ni of the order of 30 and 50 %, respectively, in sediments from the mid-outer Thames ($P<0.05$). This was reflected by comparable reductions in Ni burdens in most biota, though differences between years were only significant for *Fucus, Scrobicularia* ($P<0.05$) and *Nereis* ($P<0.01$).

Lead

There are no known essential roles for lead (Pb), which is considered to be among the most toxic of metals. Its past and present uses include paints, pigments, batteries, solder, pipes, ammunition and wire covering, although its use as an additive in petrol has, until recently, provided a major source in estuaries (through run-off and also via atmospheric deposition).

Concentration Factors for Pb in *Fucus vesiculosus* varied between 4×10^3 - 15×10^3 in the Thames Estuary (Fig 40) - within the range of 2×10^3 - 26×10^3 cited for other estuaries and sea areas (Bryan *et al.*, 1985). The free ion, Pb^{2+}, is considered the most bioavailable form of dissolved inorganic Pb. However, Pb is relatively insoluble and the greatest proportion (>90 %) in Thames estuarine waters was bound to suspended solids (Table 4). Most of this sediment Pb was easily leachable (probably signifying anthropogenic origins) and was, presumably, biologically available. A comparison of Pb levels in different feeding-types supports this contention, since bioaccumulation was highest in the deposit-feeding clam *S.plana*. Generally, molluscs as a group tended to accumulate higher concentrations of Pb than most other aquatic taxa: for example, CFs in *S.plana* were an order of magnitude higher than in the crustacean *Gammarus zaddachi* and the polychaete *Nereis diversicolor* (Fig 40).

Bioaccumulation Factors$_{(sediment)}$ indicate that *S.plana* and *M.edulis* concentrated Pb consistently above levels found in Thames sediments (by two- to three-fold, Fig. 40).

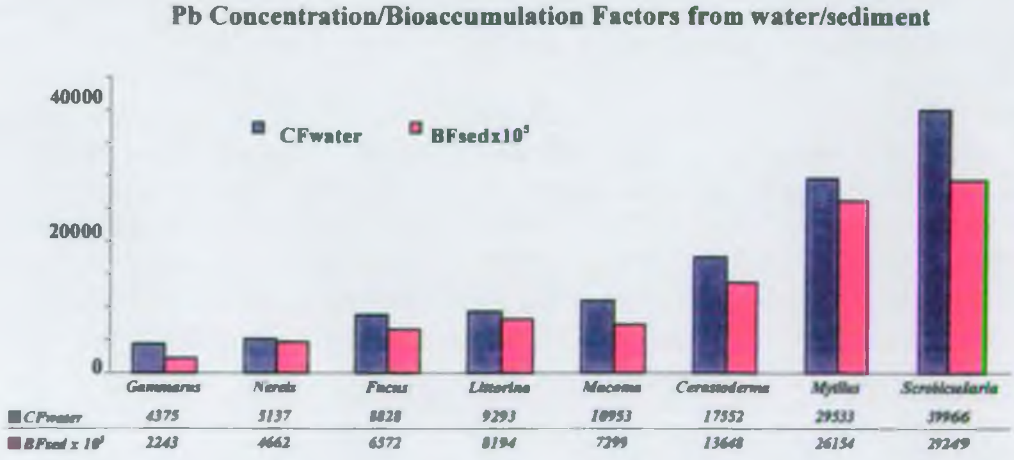


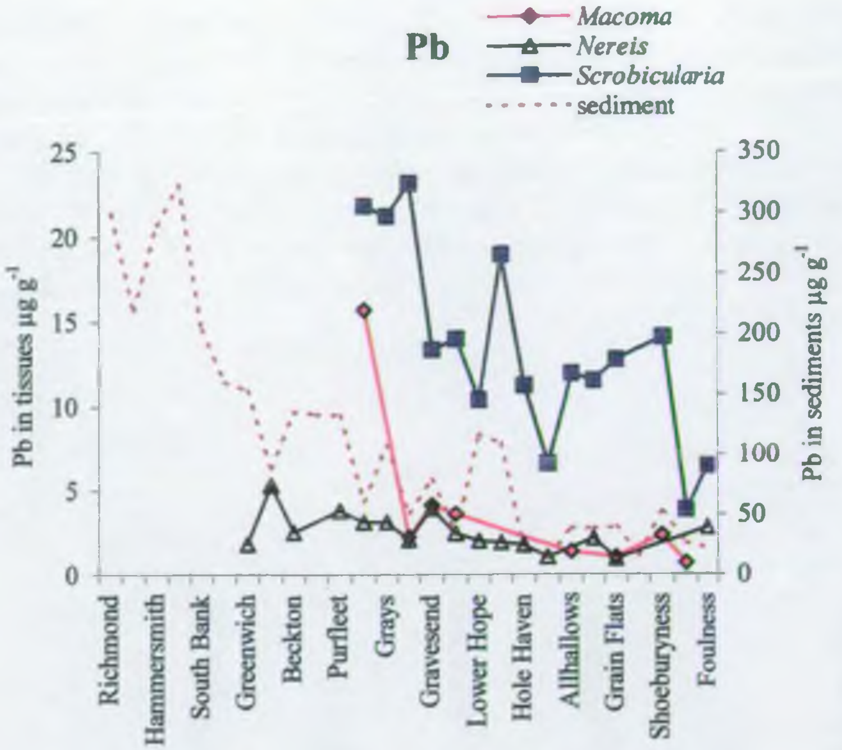
Figure 40. Lead in Thames biota: Concentration Factors [CF = concentration in organism ($\mu g\ g^{-1}$) ÷ concentration in water ($\mu g\ g^{-1}$)] and Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment]. Note BFs are multiplied by 10^5 in order to plot on same scales as CFs.

Few organisms have the ability to regulate Pb burdens which, in most species, are likely to be a function of external concentrations (water and/or sediment). In the current Thames survey, environmental Pb concentrations were highest upstream and decreased sharply, seawards (see sediments, Fig 41). This pattern was mirrored by estuarine biota to a large extent. Lead in *Scrobicularia plana* and *Fucus vesiculosus*, for example, declined as a function of distance down the estuary ($r=0.76$, $P=0.001$ and $r=0.85$, $P<0.001$, respectively), whilst levels in *Macoma* decreased sharply in the middle reaches, between West Thurrock and Tilbury (Fig 41). Trends were less obvious for cockles, mussels and winkles in the outer estuary due to the relatively small number of sites and reduced gradient in contamination (together with some anomalously high Pb levels in molluscs at Shoeburyness).

In the inner estuary, the pattern of Pb concentrations in *Gammarus* did not reveal any clear spatial trend in Pb bioavailability, nor any close relationship with Pb levels in sediments or water. In contrast, Pb concentrations in most of the estuarine biota were significantly correlated with levels in water, or on particulates, or occasionally both. For example, Pb in *Fucus* was closely related with dissolved Pb ($r= 0.83$, $P<0.01$), and also, to a lesser extent, with sediment Pb concentration. This might signify a Pb contribution to algal tissues by direct scavenging from particulates. Pb is one of several elements which has an extremely strong affinity for algal polyphenols - strong enough, perhaps, to overcome binding to certain sediment phases (Luoma *et al.*, 1982). However, the relative importance of each mode of uptake is not yet proven. Thus, the best fit between Pb concentrations in algae and sediments was that using 1M HCl extracts normalised with respect to Fe ($r=0.72$, $P<0.01$): if Fe (oxyhydroxide) is assumed to control Pb adsorption onto particles, this Pb/Fe ratio may be a surrogate measure of 'equilibrium' concentrations of dissolved Pb in surrounding water and is not, in itself, proof of a particulate route of assimilation (see also Bryan and Langston, 1992; Langston *et al.*, 1998).

Similar arguments apply to the source of Pb concentrations in *Littorina*, which were highly correlated with levels in water ($r=0.93$, $P<0.01$) and also to 1M HCl sediment extracts normalised with respect to Fe ($r=0.81$, $P<0.01$). Pb levels in *Mytilus*, *Nereis* and *Scrobicularia* were also significantly related to the Pb/Fe ratio in 1M HCl sediment extracts ($r= 0.87$, $P<0.01$; $r=0.59$,$P<0.05$; and $r=0.72$, $P<0.01$, respectively), though not with dissolved Pb, implying that particulate metals were relatively more important in these suspension and deposit-feeding species. This argument probably applies to *Cerastoderma* also ($r=0.89$, *vs* 1M HCl Pb/Fe ratio) though there were too few data points for cockles to test comparisons adequately. *Macoma* was the only species in which normalisation to Fe did not improve the relationship with sediment Pb. Invariably, however, the use of 1M HCl extracts was superior to that of total extracts in predictions of bioaccumulation.

For the majority of species the size of individuals had no obvious effects on the Pb profiles shown in Figure 41. One possible exception was the slightly elevated Pb concentrations in *Nereis* from Foulness, which may have been due to their small size (Pb concentrations in Thames worms were negatively correlated with their average weight).



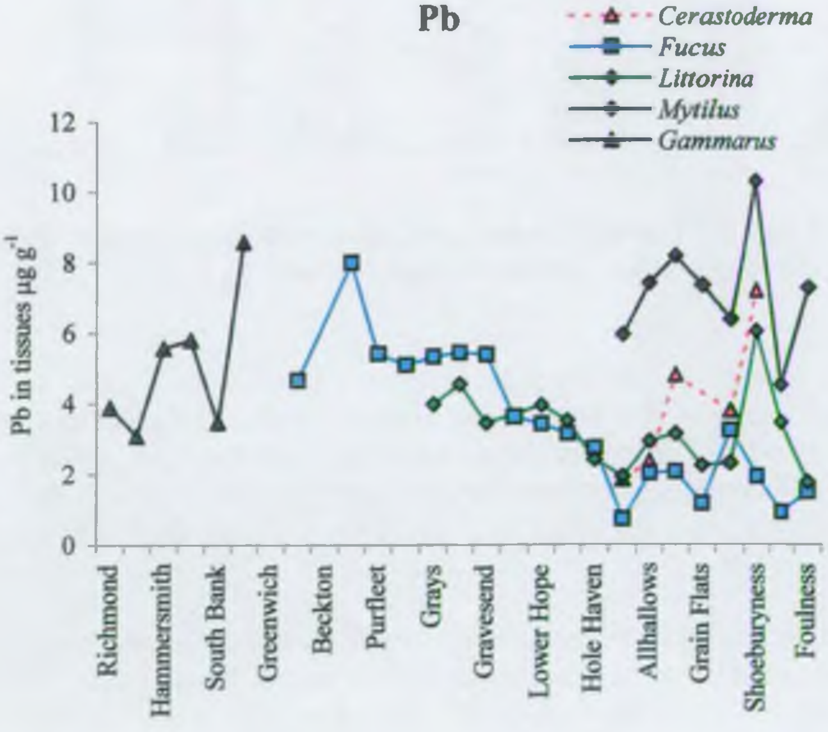


Figure 41 Lead concentrations in organisms and sediments along the Thames Estuary (July, 1997). Note: biota and sediments (upper figure) are plotted on different scales.

Pb concentrations in sediments from the Thames were an order of magnitude lower, generally, than in highly impacted estuaries such as the Gannel (sw England) which receive drainage from old lead mines. This relative level of contamination was reflected in biota, though at the most contaminated sites in the middle and upper Thames, Pb values in many organisms approached the 70th percentile in terms of records from other UK estuaries (Figure 42). At the other extreme, Pb concentrations in organisms from the least contaminated sites in the outer Thames Estuary were below the 20th percentile: for *Macoma*, *Fucus*, and *Scrobicularia* these are close baseline values in the UK.

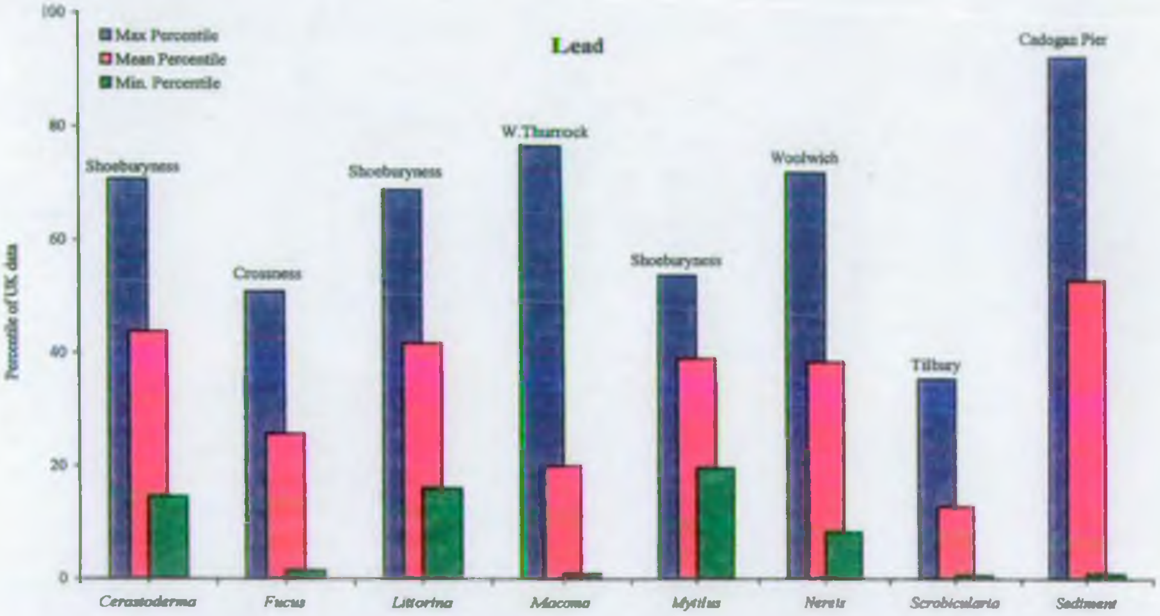


Figure. 42 . Lead in Thames biota: min, max and mean values expressed as percentile of the range in our own data-base for the UK.

Acute toxicity from Pb is unlikely to occur in the Thames Estuary. The reported 48 hr LC_{50} for oyster embryos of 2.46 mg l^{-1} (Calabrese *et al.*, 1973) and the 192 hr LC_{50} for *Nereis* of >5 mg l^{-1} (Bryan, 1976) are some three orders of magnitude higher than concentrations measured in surface waters of the Thames. Lethal body burdens in *Nereis* (>1000 µg g^{-1}) exceed concentrations in worms from the Thames by a similar margin.

Sub-lethal effects arising from levels of dissolved Pb in the Thames are also unlikely. Average Pb concentrations determined in surface waters would have to be exceeded by between one and two orders of magnitude before effects on, for example, larval development in molluscs, and growth in macroalgae, are manifested (see reviews by Bryan, 1976 and Langston, 1990). However, this does not rule out the possibility that levels of Pb at the sediment-water interface (or labile particulate Pb) could adversely affect sensitive species. Pore-water from high-lead sediments in the Gannel Estuary, for example, is capable of generating potentially sub-lethal concentrations up to 168µg l^{-1}.

A general concern over the occurrence of lead in the marine environment is the potential contribution to human diets, following bioconcentration by shellfish. As a precautionary measure guidelines of 10 $\mu g\ g^{-1}$ (wet weight) in shellfish have been established in England and Wales. None of the molluscan species analysed in the Thames Estuary exceed this value (assuming a wet:dry weight ratio of five). However, a proposed EC regulation sets a limit of 2 $\mu g\ g^{-1}$ ww (equivalent to approximately 10 $\mu g\ g^{-1}$ dw) which is similar to levels in cockles and mussels from the outer Thames, and is exceeded by two-fold in clams from further upstream (though the latter are not directly consumed by humans).

Comparisons with 1980 data indicate that there have been reductions in Pb concentrations of the order of 40 % in 1M HCl sediment-extracts ($P<0.05$) and also in soft tissues of *Scrobicularia plana* ($P<0.001$).

Selenium

Selenium (Se) behaves as a sulphur analogue. Sulphide deposits may contain substantial amounts of Se, though in the UK there is no evidence of outstanding geological enrichment. Fluvial action is most important in terms of Se mobilisation and transport in estuaries, whilst, locally, anthropogenic sources (including fossil fuel burning, fly-ash disposal, fertilisers, glass manufacture, the semi-conductor and electronic industry, and use in photocopying and photographic toners) may result in enrichment.

The estuarine chemistry of Se is poorly understood at present. The bulk of Se occurs as particulate elemental and selenide forms. Determinations of dissolved Se were not included in this survey, though work in other estuaries demonstrates complex speciation behaviour. Total dissolved Se (composed of Se^{4+}, Se^{6+} and possibly some organoselenides) appears to be largely conservative in terms of mixing behaviour. Although Se^{4+} tends to be scavenged by Fe oxyhydroxides, $Se6^{+}$ is less easily removed; furthermore, much of the Se in estuaries may be organically bound. Most invertebrates and algae accumulate Se in the lower oxidation state, preferentially. However, Se Concentration Factors, relative to water, tend to be low and, whilst plants and microbes are able to fix inorganic Se along S/Se pathways (to synthesise Se analogues of the sulphur amino acids) 'higher' organisms cannot: uptake from dietary/sediment sources are likely to be of greater importance to aquatic fauna. Sorensen *et al.*, (1982) showed, for example, that Se levels in fresh water organisms were correlated with Se concentrations in sediments.

Indeed, of the elements determined, Se was unusual in that tissue burdens were invariably concentrated to levels higher than those in sediments (Fig 43). This was most significant in molluscs where BF_{sed} ranged between 169 (*Cerastoderma*) and 544 (*Littorina*). Relatively low BF_{sed} in *Fucus* and *Gammarus* presumably reflected the limited influence of sediment-bound Se on uptake in these species.

Most of the Se in organisms is bound to amino acids and proteins, leading to an assumption that all the Se is present as essential enzymes and peptides (e.g. glutathione peroxidase) and that excess Se is excreted. This now seems unlikely to be the case and when organisms are faced with excess Se (e.g. in areas laden with Se containing wastes, such as fly ash and phosphorites), bioaccumulation would be expected.

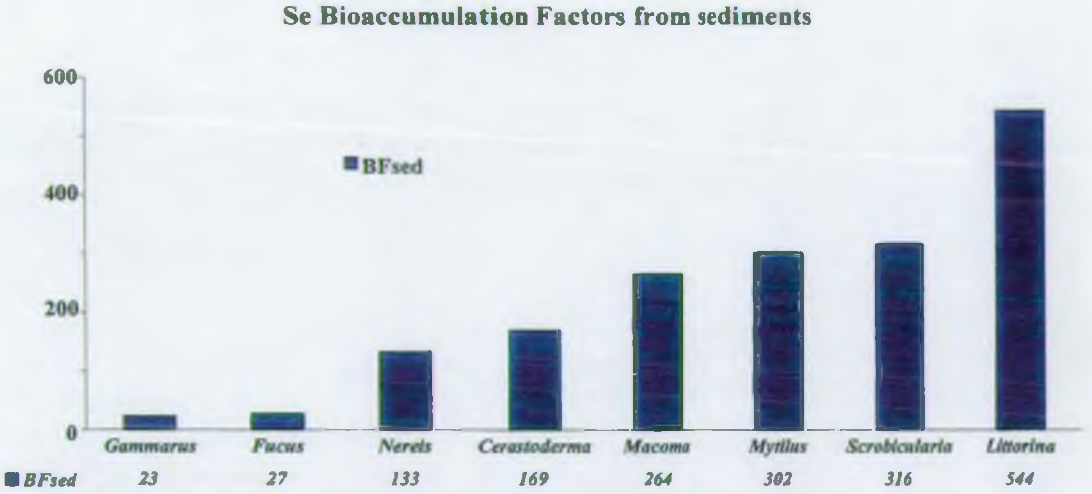


Figure 43. Selenium in Thames biota: Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment].

The patterns of Se distribution in Thames biota confirmed that body burdens in most species respond to environmental concentrations, as represented by sediment concentrations (Figure 44). There was an extremely sharp downstream decrease in particulate Se in the upper estuary, which was mirrored by concentrations in *Gammarus* (Figure 44). Below Greenwich, the gradient was less marked but Se concentrations in most species decreased with distance (seaward), significantly so in *Mytilus* ($r = 0.71$, $P<0.05$), *Nereis* ($r=0.68$, $P<0.01$) and *Littorina* ($r = 0.63$, $P<0.05$).

Direct relationships between Se concentrations in sediments and tissues were reasonably strong for *Gammarus*, *Macoma*, *Mytilus*, *Cerastoderma* and, to a lesser extent, *Nereis* (r = 0.88, 0.78,0.76, 0.72 and 0.4) - those for the first three species being statistically significant. Correlation coefficients for *Gammarus* and *Cerastoderma* were improved slightly by normalising the Se content of sediment with respect to Fe (r = 0.89 and 0.78, respectively).

Selenium concentrations in *Fucus*, *Littorina* and *Scrobicularia* were not closely correlated with sediments. Presumably, levels in the seaweed were related more closely to dissolved species than to sediments, though this was not tested here. Likewise, it is not known whether dissolved Se was a factor determining Se bioavailability in the two molluscs. The relationship between Se in sediments and *Littorina* may be obscured by unusually high (and as yet unexplained) Se body burdens at Tilbury and Lower Hope.

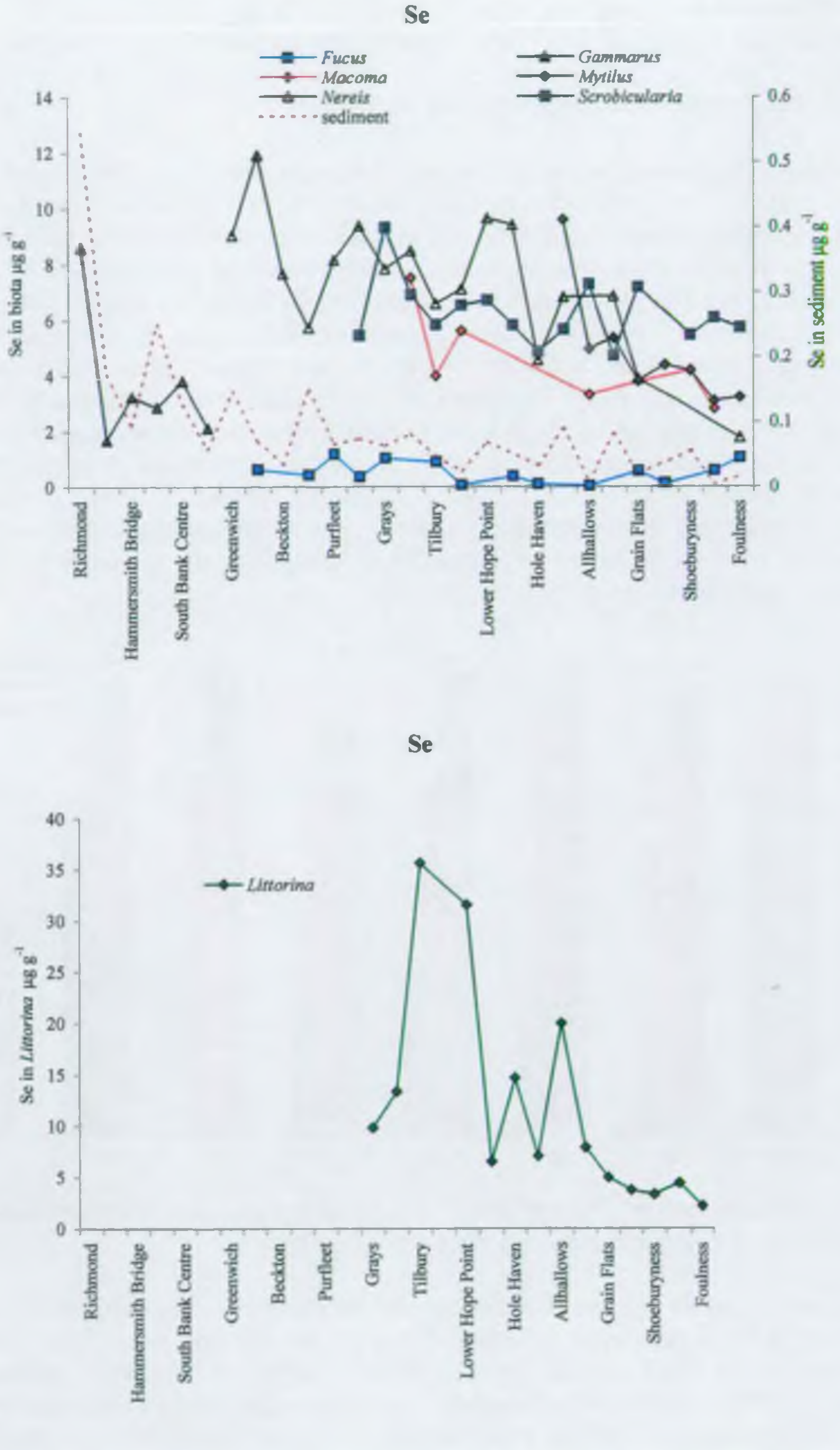


Figure 44. Selenium concentrations in organisms and sediments along the Thames Estuary (July, 1997).

Selenium has not been measured as extensively in UK estuaries as most of the other metals discussed here, and this may well have a bearing on the comparisons made with other sites in England and Wales. Even so, the number of records examined was substantial (from 68 for *Cerastoderma* to 460 for sediments) and was probably representative of the range encountered in the UK.

The average Se concentration in Thames sediments was at the lower end of the national scale (4th percentile), and included the lowest recorded value in our data-base. Even the most Se-contaminated sediment, at Richmond, was below the 50th percentile (Figure 45). It is intriguing, therefore, that Se concentrations were consistently high in virtually all of the Thames biota, with mean values for individual species ranked from 68th (*Mytilus*) to 88th (*Cerastoderma*) percentiles. Worst-case Se concentrations in Thames biota were all above the 90th percentile, with the exception of *Mytilus* (82nd percentile). Even some of the minimum Thames values were considerably elevated compared to background levels (n.b. in *Cerastoderma* and *Scrobicularia*). It would seem from these results that Se bioavailability in the Thames was disproportionately high, with respect to Se concentrations in sediments. The cause of this is unknown, though, as with Ag, one possible explanation may be the anthropogenic origin and form of the element in the estuary, modified, perhaps, by the influence of sewage-treatment by-products and bacterial exudates.

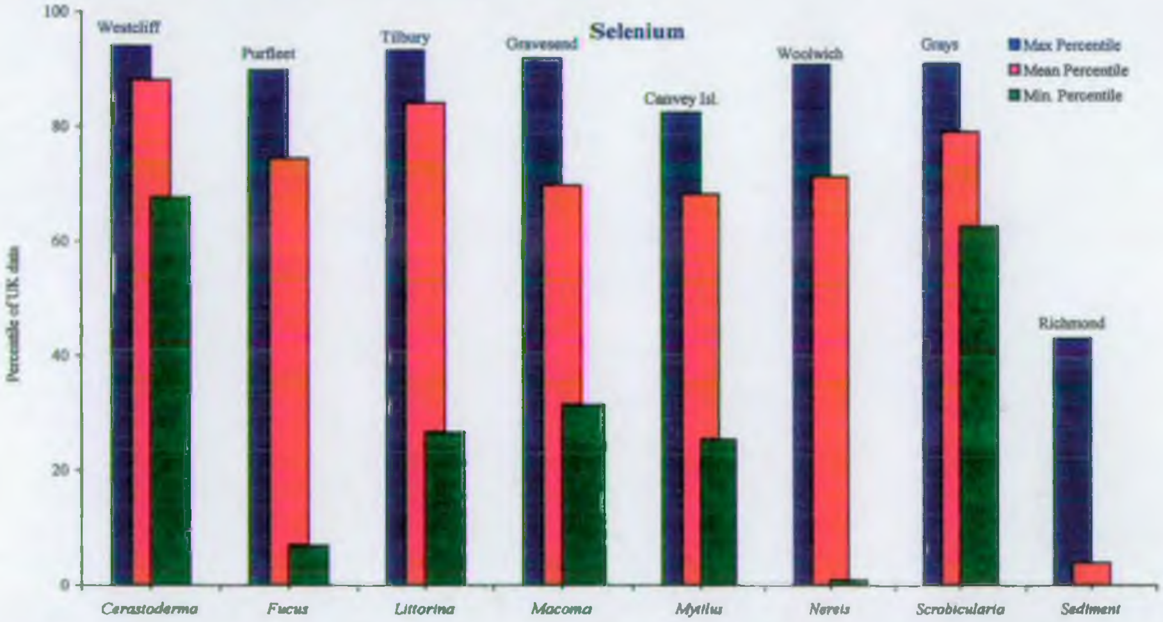


Figure. 45. Selenium in Thames biota: min, max and mean values expressed as percentile of the range in our own data-base for the UK.

The toxicology of Se is unusual since, despite being an essential element, it has been associated with significant ecological effects at Se-enriched sites. Thus, although short-term acute tests suggest Se is relatively harmless in marine invertebrates (typically ~ 5000 μg l^{-1} is lethal to small crustaceans and bivalves and 100,000 μg l^{-1} to *Nereis*), sublethal effects take place at concentrations between one and three orders magnitude lower (see Bryan, 1984, Ahsanullah and Palmer, 1980, and review by Bryan and Langston, 1992). More significant, however, are reports of effects in higher organisms, especially birds, where there may be a fine-line between dietary levels considered as essential (1 µg g^{-1}) and those regarded as potentially hazardous (> 5 µg g^{-1}). Consumption of invertebrate prey containing >20 µg g^{-1} Se has been linked with reproductive abnormalities in waterfowl in Se contaminated ponds in California (Ohlendorf *et al.*, 1986). Similar enrichment may be observed near oil refineries and outfalls in estuarine environments. Thus, although concentrations in biota from the mouth of Thames generally contained < 6 µg g^{-1} Se, this increased upstream to 10-12 µg g^{-1} Se in clams and worms and 35 µg g^{-1} in winkles.

Perplexingly, Se is reported to play a detoxifying role in some organisms - having an antagonistic action upon Hg and Cd uptake and toxicity (reviewed in Bryan and Langston, 1992). This phenomenon may even contribute to the high Se burdens in Thames biota. The chemistry and ecotoxicology of Se in UK estuaries would seem to be an important area for future work in view of it's complex and variable properties.

Whilst Se concentrations in sediment of the mid-outer Thames Estuary appear to have declined by 80% since 1980 ($P<0.05$), this was not matched by lower Se burdens in organisms. If anything, bioaccumulation in several species seems to show the reverse trend (though increases are not statistically significant). This supports the hypothesis that Se bioavailability in the Thames is anomalously high, compared with sediments. Such anomalies highlight the importance of establishing the form of each element in the environment, as well as concentration.

Tin

Inorganic tin (Sn) is relatively insoluble and distributions in estuaries are likely to be determined by particulate forms. In south west England the mineralised component (mainly cassiterite, SnO_2) is high in estuaries influenced by past metal-mining activities and sediments may contain in excess of 1000µg g^{-1} Sn. This form is largely inert and unlikely to be bioavailable. The use of tin in tinplate and other metallurgical applications, and tanning, results in the presence of more reactive forms in estuarine sediments: relationships have been established between Sn levels in biota and easily extractable Sn in sediments (Langston *et al.*, 1990). However, the lability / ease of removal of inorganic Sn from sediments, and hence it's bioavailability, is low in comparison with many metals, due to the formation of relatively insoluble and inert hydroxide species.

Of more concern in recent years has been the disproportionately high bioavailability (and toxicity) of organotins, notably tributyl tin (TBT) which has been used extensively in antifouling preparations and wood preservatives. A concurrent survey has specifically addressed the of issues of TBT distribution, impact and persistence in the Thames Estuary and adjacent coastlines (Langston *et al.*, 2000a). Since legislation was introduced in 1987, to limit the use TBT-containing paints to vessels >25m, there has been some evidence of recovery from TBT pollution, based on imposex levels and distributions of dogwhelk (*Nucella lapillus*) populations along the north Kent coast. Nevertheless, even after the ten-year partial ban, TBT concentrations in upper Thames Estuary waters often exceeded the EQS of 2ng l^{-1}, sometimes by up to an order of magnitude. There was also widespread distribution of TBT in the sediments and biota of the estuary. It is unlikely that these levels are acutely toxic, though some impact on the condition of estuarine molluscs, if not their distribution, cannot be ruled out and the contaminant still remains a cause for concern in the Thames Estuary.

The results described below largely refer to 'total' Sn (in sediments and biota) and some qualification of what is being measured is needed. Firstly, most particulate Sn is inorganic: organotins in sediments constitute only a small fraction of the 'total' acid-extractable tin (average <0.2%) and are eventually degraded to inorganic tin. Secondly, the use of HNO_3 as a measure of 'total' tin in sediments is strictly operationally defined (as is 1M HCl, a measure of easily-extractable Sn): these mineral acids do not extract tin oxides (e.g. cassiterite), quantitatively. However, in UK estuaries, cassiterite is only of major significance in the far south west of England, and for Thames sediments HNO_3 digests approximate to a true measure of total Sn. Thirdly, the proportion of total tin present as organotin is invariably higher in biota than in sediments because it is considerably more bioavailable than inorganic Sn. Most organisms are capable of metabolism of TBT through stepwise debutylation to dibutyltin (DBT), monobutyltin (MBT) and eventually inorganic Sn. The digestion and analytical procedures for total tin in biota used here quantitatively recover each of these chemical forms and therefore represent true 'total' Sn levels.

The proportion of total Sn in Thames biota present as organotin (defined here as ΣTBT+DBT measured in hexane extracts) varied according to species. Average values were: *Fucus*-13%, *Gammarus* -27%, *Nereis* -34%, *Littorina*- 45%, *Mytilus* -56%, *Scrobicularia* -72%, *Cerastoderma* -80% and *Macoma* -92%. This demonstrates that, whilst inorganic Sn predominated in sediments, total Sn levels in bivalve molluscs in particular (and probably other invertebrates) were likely to be determined by levels of organotin contamination. BF_{sed} values for Sn were also highest in bivalves (Fig 46), largely as a result of their capacity for organotin bioaccumulation. However, because most of the tin in sediments was inorganic, and of limited bioavailability, all of the BF values were below unity (0.1-0.25).

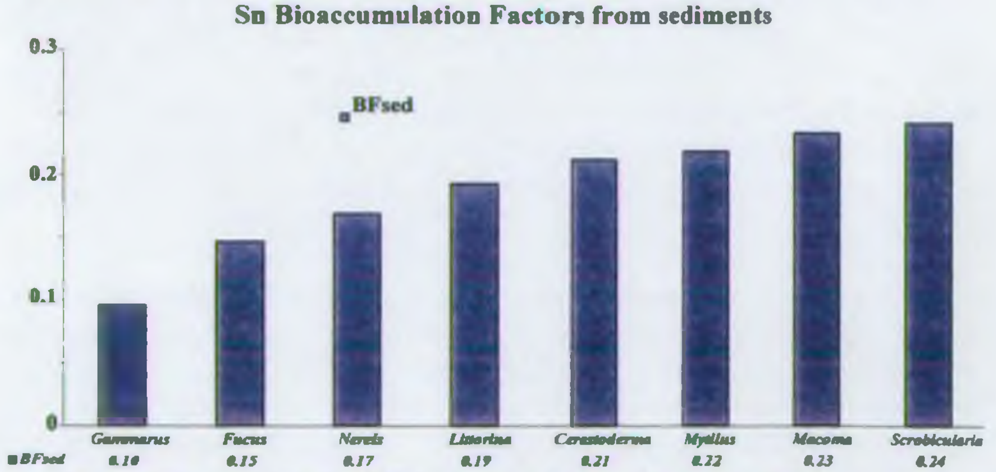


Fig 46. Tin in Thames biota: Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment]

Tin concentrations in sediments decreased significantly ($P<0.001$) with distance seawards, a trend mirrored in most biota except *Gammarus* (Figure 47). Best-fit correlations were with 1MHCl sediment extracts, notably for *Fucus* ($r=0.69$, $P<0.001$), *Littorina* ($r=0.8547$, $P=0.001$), *Nereis* ($r=0.592$, $p<0.05$) and *Scrobicularia* ($r=0.7095, p<0.01$). Normalisation did not improve the strength of these relationships.

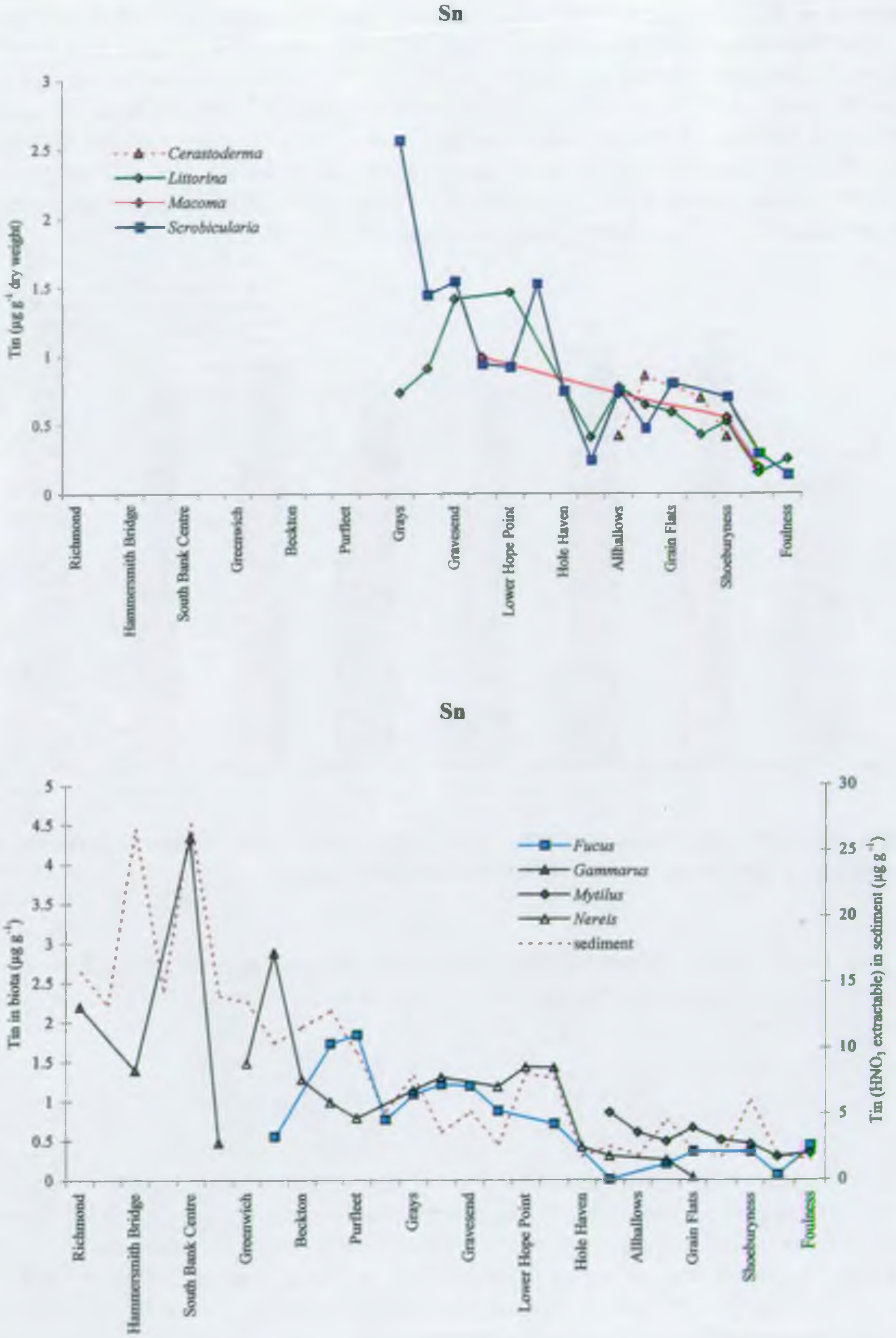


Figure 47. Tin concentrations in organisms and sediments along the Thames Estuary (July, 1997).

Bearing in mind the dominance of organotins as bioavailable species, levels of TBT could be of concern to molluscs, as suggested above, though inorganic tin is unlikely to be toxic at the concentrations found in the Thames because of its limited solubility and bioavailability. Comparisons of total Sn with other UK estuaries generally confirmed moderate levels in Thames biota. Mean values for individual species ranged from the 42nd percentile in *Scrobicularia* to the 60th percentile in *Littorina*, *Mytilus* and *Nereis*. Maximum Sn values in Thames biota (usually towards upstream limits of the organism's distribution) were mainly at, or below, the 80th percentile, whilst minimum values ranged from the 42nd percentile (*Mytilus*) down to virtually baseline values for *Fucus*, *Nereis* and *Scrobicularia* (Figure 48).

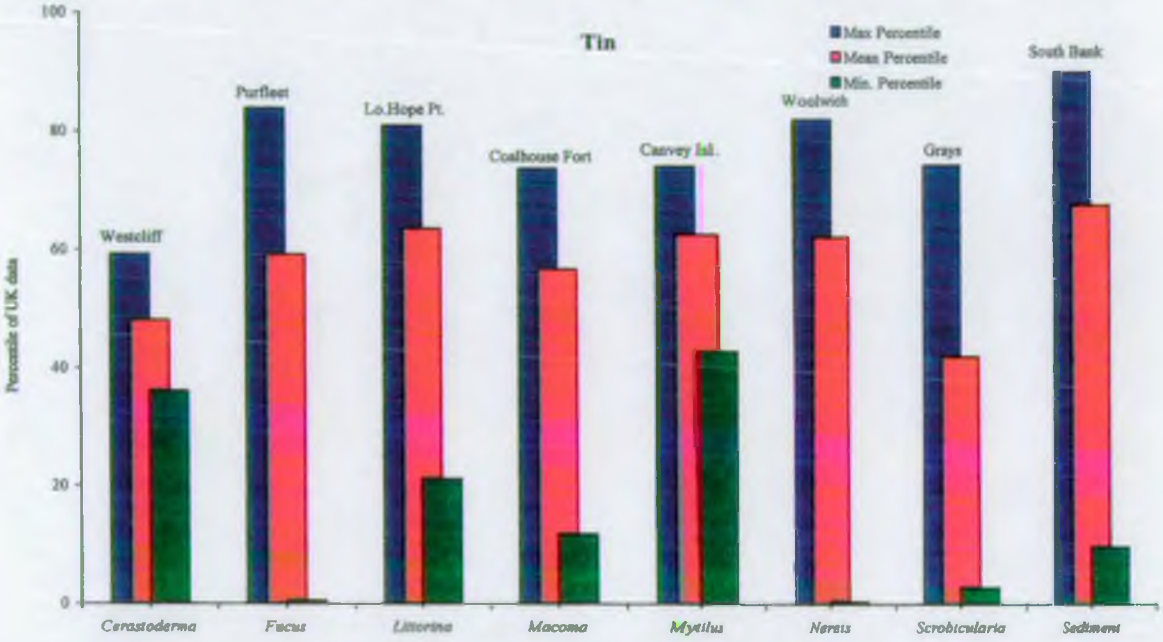


Figure 48. Tin in Thames biota: min, max and mean values expressed as percentiles of the range in our own data-base for the UK.

Between 1980 and the present survey there were reductions in Sn concentrations in sediments (1M HCl-extractable), *Scrobicularia* and *Nereis*. These were of the order of 40 % - 60% ($P<0.05$).

Zinc

The abundance of Zn in nature has lead to widespread biological utilisation e.g. in a number of enzymes such as carbonic anhydrase, carboxypeptidase and several dehydrogenases; as a gene regulating element; and for some unusual structural purposes - as in the jaws of various polychaetes, including *Nereis*. Because Zn is not usually limiting in the aquatic environment, most organisms contain considerably more Zn in tissues than their estimated requirements.

Industrially, zinc is a widely used metal (i.e. in galvanising processes) and is a component of alloys such as brass and bronze. It is also used in paints, batteries and in the production of rubber. Hotspots in the UK include areas involved with mining and smelting of Zn and, to a lesser extent, sewage disposal areas. Consequently, there is considerable scope for anthropogenic loading and increased bioavailability as a result of zinc's extensive mobilisation.

To counteract excess Zn, there is evidence that a large number of species can regulate their body burdens, at least partially. In many crustaceans, polychaetes and some molluscs, for example, Zn accumulation does not appear to change proportionately in response to environmental contamination, except perhaps at extremely high levels (Bryan *et al.*, 1985). Body burdens in these organisms tend to underestimate Zn pollution. In contrast species such as *Scrobicularia* and *Fucus* are less efficient Zn regulators and, hence, are more valuable bioindicators. It is important to be aware of these biological variables when monitoring Zn contamination

Accordingly, Zn magnification in tissues of organisms from the Thames, expressed as CF_{water} or $BF_{sediment}$, varied by more than one order of magnitude (according to behaviour and physiology) and were highest in tellinid clams *Scrobicularia* and *Macoma* (Figure 49). Lowest values were those for *Gammarus*.

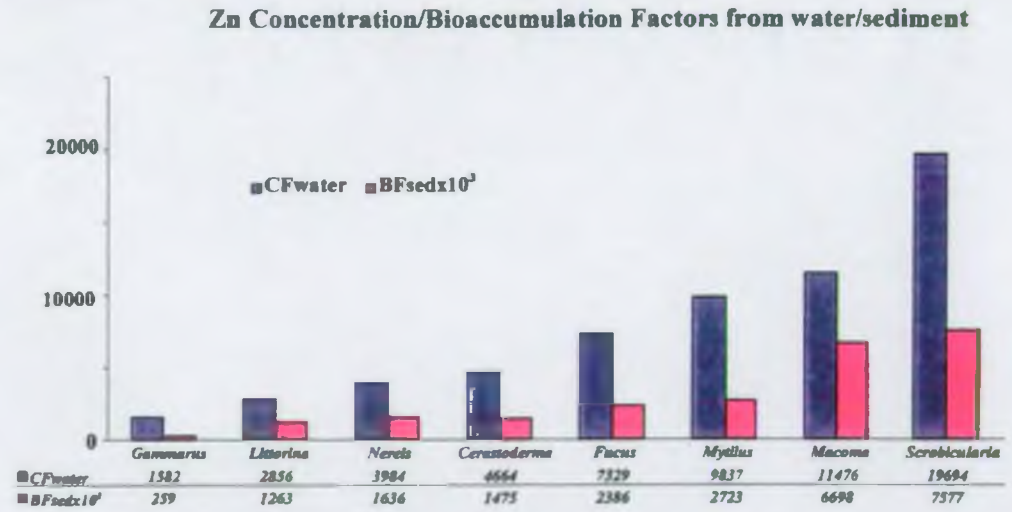


Figure 49. Zinc in Thames biota: Concentration Factors [CF = concentration in organism (μg g^{-1}) ÷ concentration in water (μg g^{-1})] and Bioaccumulation Factors [BF = concentration in organism ÷ concentration in sediment]. Note BFs are multiplied by 10^3 in order to plot on same scales as CFs.

The calculated mean CF_{water} for Zn in *Fucus vesiculosus* (7.3 x 10^3) was at the lower end of the range described in by Bryan *et al.* (1985) for other field sites (7.1 -64 x 10^3). The explanation for low Zn CF values in Thames *Fucus* is not known but, as indicated for Cu earlier, may be due to the presence of organic matter or other complexing agents (which would be expected to limit the availability of free ions), or possibly competition for uptake sites from other contaminants.

Zinc Bioaccumulation Factors $_{(sediment)}$ exceeded unity in all species, with the exception of *Gammarus*, and were highest in *Scrobicularia* and *Macoma* (Fig. 49), perhaps reflecting an important contribution from sediments in these infaunal clams.

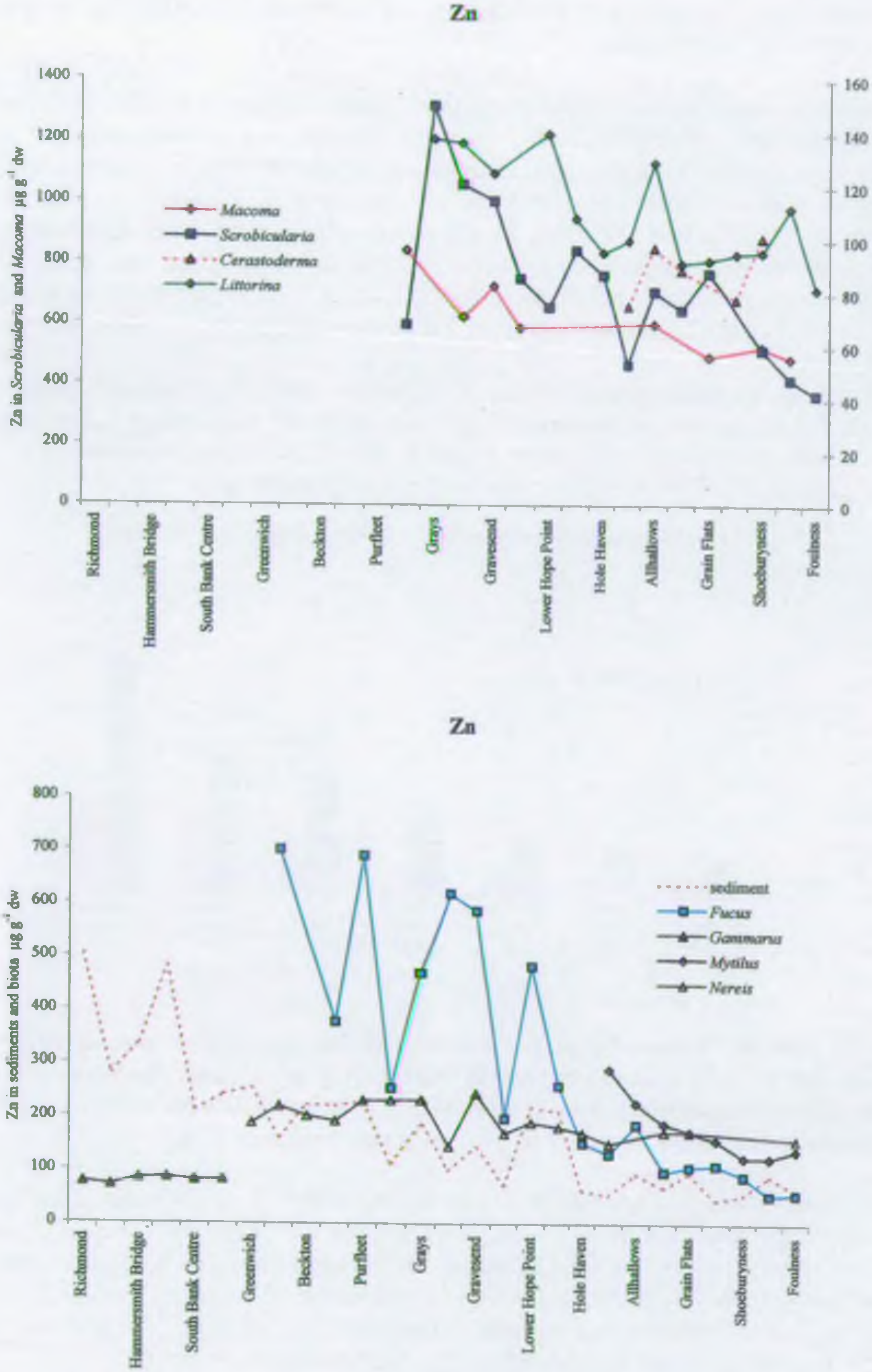


Figure 50 Zinc concentrations in organisms and sediments along the Thames Estuary (July, 1997).

Zinc concentrations in sediments decreased significantly ($P<0.001$) with distance seawards, a trend mirrored in most biota (Figure 50). The only exceptions were for *Gammarus* and *Cerastoderma* ($P>0.05$) perhaps because of regulation, partly, but also because of their relatively restricted distributions in the inner and outer estuary, respectively. Consequently, Zn in these two species was not significantly related to environmental levels. For other species, some of the best-fit correlations between tissue and sediment Zn (1M HCl extracts) were improved by normalising the latter with respect to Fe, e.g. *Fucus* ($r=0.78$, $P<0.001$), *Littorina* ($r=0.63$, $P<0.001$), *Mytilus* ($r=0.94$, $p=0.001$), *Nereis* ($r=0.5$, $p<0.05$) and *Scrobicularia* ($r=0.65, p<0.01$). This suggests that Fe may modify Zn bioavailability to some estuarine biota, as has been reported for Zn in freshwater bivalves (Tessier *et al.*, 1984). Normalisation did not improve the strength of the relationship for *Macoma* ($r=0.83$, $p<0.05$).

The only species whose Zn concentrations were correlated with levels of dissolved Zn was *Littorina* ($r=0.833$, $p<0.05$). This paucity in relationships with dissolved Zn, as with other metals, may be due to the transient nature of water samples. It seems likely that Zn in most organisms may originate from a mixture of sources, including both pore-waters and the overlying water column, together with readily-extractable sediment Zn.

Comparison with other UK estuaries indicates moderate levels of Zn bioavailability in the Thames: mean Zn values for biota in the estuary ranged from the 29th percentile in *Scrobicularia* to just over 50th percentile in *Fucus*, *Littorina*, *Mytilus* and *Nereis*. Maximum Zn body burdens (usually at sites near the upstream limits of the organism's distribution in the Thames) were at or just below the 80th percentile and were generally of significance, in a national context. Minimum Zn concentrations ranged from the 28th percentile (*Mytilus*) down to virtually baseline values (*Fucus*) at the mouth of the estuary (Figure 51).

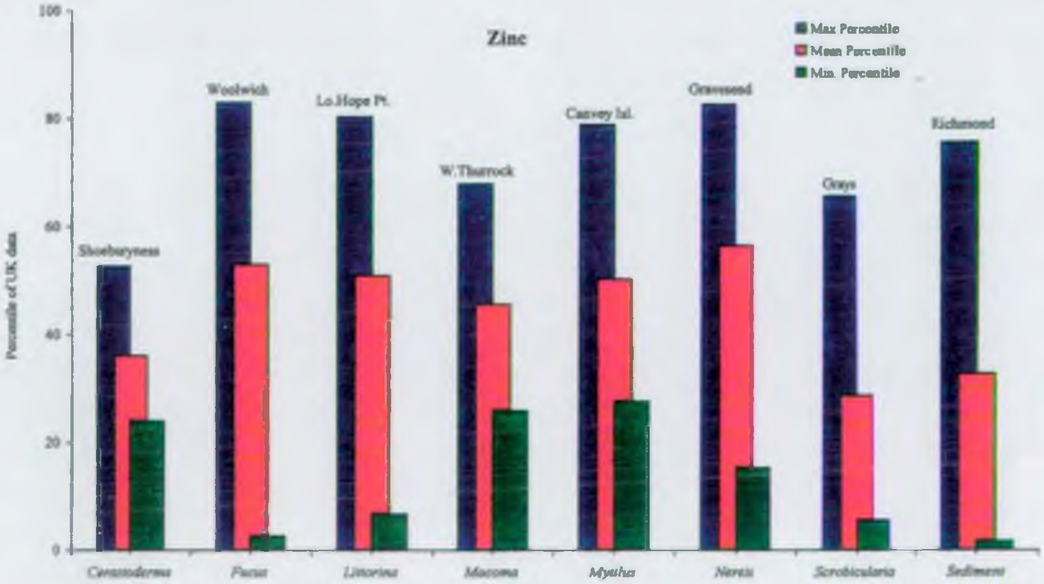


Figure 51. Zinc in Thames biota: min, max and mean values expressed as percentiles of the range in our own data-base for the UK.

The ability of many organisms to adapt to moderate concentrations of this essential element - by regulating body-burdens - may help to reduce the threat of acute Zn toxicity. The 192hr LC_{50} for *Nereis*, for example, is of the order of 30 µg Zn ml^{-1}, and the lethal body burden 2930µg Zn g^{-1} (Bryan, 1984) - both considerably higher than Zn levels in the Thames estuary. However, although Zn is not regarded as being especially toxic, the widespread nature of elevated Zn concentrations in the environment should be of concern. Concentrations of dissolved zinc in the Thames exceeded the current EQS value of 40 µg l^{-1} (possibly to be revised down to 10 µg l^{-1}) in a number of samples, and were consistently elevated compared to background. These values are at the thresholds of various sublethal indices of stress, including morphology, development and reproduction, and are of the order of 10 µg l^{-1} in the most sensitive species (see Langston, 1990 for review).

Comparisons between 1980 values and the present data, for mid-outer estuary sites, suggest there have been reductions in concentrations of sediment Zn (1M HCl-extractable) of the order of 60 % ($P<0.05$). Similar reductions were observed for Zn in *Scrobicularia* ($P<0.01$) and *Fucus* ($P<0.05$).

DISCUSSION AND CONCLUSIONS

There are few published records concerning metals and other persistent contaminants in the Thames Estuary, which is extraordinary considering the importance of the waterway. Consequently there are only limited baseline data-sets against which improvement or deterioration in environmental quality might be accurately judged.

In this study, biological and chemical data has been assembled for up to 14 metals at a series of 27 sites along the estuary, in order to determine their occurrence and potential impact, and to provide a means of assessing future change. The approaches and information on metal distribution and behaviour in water, sediments and selected bioindicators may also be useful in a wider context - enabling more extensive geographical comparisons to be made.

Dissolved metals

Water analyses represent a 'snapshot' of metal concentrations at the time of sampling, yet, despite this limitation, interesting features were revealed. Concentrations of most metals were elevated at inner- and mid-estuarine sites, though only Cu and Zn consistently exceeded Environmental Quality Standard values (5 and 40 µg l^{-1}, respectively). Even in the outer estuary, concentrations of several metals (Cd, Cu, Ni, Pb and Zn) were markedly higher than typical background values for the North Sea. Anthropogenic enrichment in the Thames was similar to that in other heavily industrialised European estuaries. Sources of contaminants to the estuary include the River Thames, sewage treatment plants, storm water run-off, and various industries along the water course (including metal refineries, dockyards and marinas). Prior to cessation of sewage dumping in 1998, the outer estuary also received large quantities of sludge and dredge spoils.

The profiles for dissolved metals gave some insight into estuarine behaviour. There was net removal of Mn to sediments in the estuary particularly at low salinities with, perhaps, a small degree of redox cycling in the middle reaches. Dissolved Pb concentrations increased between Teddington and Kew, thereafter concentrations declined seawards with little evidence of reactivity (similar behaviour was also observed for Co). Arsenic, zinc and, to a lesser extent, nickel profiles were characterised by an extensive mid-estuarine augmentation in concentrations, suggestive of diffuse inputs to the estuary, probably from sediments (pore waters). For Ag and Cu, peaks in concentrations occurred at one or more sites, suggesting that localised inputs could be important in influencing their distributions. The profile for dissolved Cd was unusual in that concentrations increased in a seaward direction (opposite to the trend for Cd in sediments and biota). The disposal grounds in the outer estuary are one possible reason for this gradient; in addition, there is a tendency for Cd to form highly stable, soluble chloro-complexes in seawater .

It would be valuable to assess in more detail the significance of the current major inputs to the estuary (natural and anthropogenic), and to evaluate both the spatial and temporal variability in metal concentrations and behaviour in the water column, particularly with respect to tidal conditions and river flow. This would help to prioritise future management options. The application of model simulations might also be considered with a view to explaining how cyclical extremes in effluent composition and quantity, e.g. from the major treatment plants, influence metal profiles and water quality in the estuary.

Sediment metals

Sediment metal-contamination patterns were fairly uniform, with concentrations decreasing, generally, in a downstream direction. The gradient was particularly marked for Ag, Cd, Pb, Se and Zn. These results imply that the influence of inputs was greatest towards the upper tidal limits. However, the significant co-variance between the majority of metals shows that their distributions may be determined to an extent by shared granulometric and geochemical factors, most important of which were the metal binding substrates that coat the surface of particulates, such as organic matter, and Fe oxyhydroxides. By performing geochemical 'normalisation' procedures to (e.g. relating metals to Fe and organics) it was possible to explain much of the residual variation in Thames sediments. In future, it would be useful to normalise sediment metals with respect to the appropriate metal-binding components, and to a geogenic component such as Al or Li, in order to determine which procedure provides the best indicator of anthropogenic influence and the best comparisons of sediment contamination between sites or different sea areas.

Sediments, particularly those in the inner Thames, were significantly enriched in metals compared with deposits from the central North Sea, or from an 'unpolluted' reference estuary (Tweed). This was most obvious for Ag (concentration in Thames sediments 50 fold higher, on average, than those at reference sites), Cu, Hg (8 fold), Sn, Cd, Pb, Zn and Co (3-5 fold). Arsenic was the only element whose concentrations were not markedly higher. For most metals, the levels of contamination in sediments from the inner Thames were comparable to those of other industrialised estuaries bordering the North Sea (including the Humber, Tees, Tyne and Wear), whilst levels of Ag and Sn in the Thames were higher. Since sewage treatment is one of the major vectors of contamination in the Thames, it may be that Ag and Sn act as tracers for this form of impact. This possibility should be investigated further.

Extensive sediment-metal comparisons with other estuaries, countrywide, indicate that the mean value for Ag concentrations in Thames sediments was equivalent to the 97th percentile of the UK range (percentile = position within the normal distribution of sediment values in the PML data base, expressed as a percentage). Thames sediment loadings ('total' - concentrated HNO_3-extractable - metal) were also important for Cr, Sn, Hg, Cd, Mn, Co and Pb (>50th percentile), whilst Cu, Zn Fe and Ni ranged between the 25th and 50th percentiles. As and Se concentrations were relatively low by comparison (< 25th percentile).

In addition to 'total' digests, sediments were extracted with 1M HCl as a measure of non-refractory metal (and a possible surrogate for the 'bioavailable' sediment fraction). Almost all of the Pb in Thames sediments was extractable in 1MHCl, suggesting a high proportion was of anthropogenic origin - e.g. from urban run-off. Other metals with a high proportion in readily-extractable form (50-80%) were Cd, Mn, Zn, Sn, Cu and Co. At the other extreme, the value for Cr (16%) indicates that most of this metal was refractory in nature. The variability of these sediment associations influences the reactivity and bioavailability of metals in the estuary.

Bioaccumulation

A biomonitoring strategy which encompasses the whole tidal Thames was developed. By adopting a multi-species approach, it was possible to provide at least some measure of bioaccumulation throughout all the sites, using one or more indicator organism.

In the estuary proper, distribution ranges of biomonitoring organisms (seaweed *Fucus vesiculosus*; ragworm *Nereis diversicolor*; winkles *Littorina littorea*; clams *Scrobicularia plana* and *Macoma balthica*; cockles *Cerastoderma edule*; mussels *Mytilus edulis*) often overlapped and therefore provided corroboration of trends in bioavailability.

Gammarus zaddachi was the only practical option for study in the inner, 'fresh water' section of the tideway; first impressions are that it may be a valuable bioindicator for several metals including Ag, As, Co, Cu, Hg, Se and Sn. It would be useful to exploit these properties further and to investigate in more detail the responses of *Gammarus zaddachi* to metals. The only paper found in the literature describing metals in *G. zaddachi* also suggests it responds to environmental levels of Cd, Pb and to a lesser extent Cu, but regulates Zn (Amiard *et al.*, 1987). If *Gammarus* is to be used more extensively as a bioindicator in the difficult, often highly contaminated environment of the fresh-brackish zone, it would also be valuable to determine how bioaccumulation varies with respect to salinity, season, biological parameters (e.g. size and moulting), and in relation to responses in other organisms (n.b. *Nereis*).

Patterns in bioavailability along the estuary were broadly comparable between metals, with impact *usually* increasing upstream, resembling trends in contamination in sediments (n.b. Ag, Cd, Cr, Cu, Pb, Se, Sn) and, sometimes, water (n.b. Co, Ni, Pb). In certain organisms bioaccumulation of, for example, Ag, Cd and Pb, increased disproportionately upstream, in relation to sediment contamination (notably between the outer- and mid-reaches), suggesting that bioavailability was promoted by conditions in the estuary.

There were other examples of apparently anomalous trends in body burdens, demonstrating how environmental and biotic factors influence metal accumulation. Physicochemical properties and sediment metal-binding characteristics were particularly important; hence, 1M HCl extracts were, frequently, more appropriate measures of bioavailable sediment-metal than total digests (e.g. for As, Pb, Sn, Zn). Arsenic concentrations in 1M HCl extracts and most biota were, in fact, characterised by a 'reverse gradient' (higher concentrations in a seaward direction) - in direct contrast to total sediment As. Other factors suspected of affecting bioavailability included levels of sediment Fe (reduced bioaccumulation of As, Pb, Cr, Cu, Mn, Ni, Zn and Se in several species) and phosphate (competition with arsenate for uptake). Complexation with particulate organic matter may have inhibited the bioaccumulation of Hg: thus, whilst there were no significant direct relationships between Hg concentrations in tissues and sediments, correlations in most species were improved by normalising sediment Hg concentrations with respect to organic content. In the inner estuary, this modifying influence produced another example of a reverse gradient in that Hg:organic sediment ratios, and bioavailability (as reflected by Hg concentrations in *Gammarus*), *decreased* upstream - contrary to sediment Hg levels *per se*. At the mouth of the estuary a reverse gradient was also observed for Mn, Fe and Cr in *Cerastoderma*.

Varying degrees of homeostasis of the biologically-important metals Cu, Fe, Mn and Zn may have masked spatial trends in contamination to an extent, particularly in invertebrates whose concentrations are inherently high due to essential requirements. Furthermore, Cu uptake may have been enhanced by anoxia in some species (clams) but inhibited by organics in others, making it difficult to detect uniform trends in Cu bioavailability. Unusual features identified for Fe included high levels in *Nereis* (normally an Fe regulator) and *Fucus* from Crossness and Beckton, which may signify atypically high Fe bioavailability at these sites.

Another biological feature which modified bioaccumulation was the selective ability to metabolise certain metal species. Thus, the known capability of *Mytilus* and *Littorina* to synthesise the metal-binding protein metallothionein probably accounted for the their comparatively high Cd burdens. Also, the high Sn concentrations in several bivalves, relative to other taxa, may be attributed to the slow-degradation of bioavailable organotin species (notably, TBT), coupled with their filter-feeding diet. Allometric effects on metal burdens were relatively few, because of the selection of similar-sized animals for analysis. However, the unavoidably small size of *Nereis* from the Foulness site was responsible for elevated concentrations of Co and, to a lesser extent, Pb and Cr. Size effects were also observed for Cr in *Mytilus*.

It is difficult to generalise over the status of metals in biota from the estuary because of phylogenetic variables, but, by averaging percentiles across all species, simplistic rankings (for maximum, mimimum and mean values in the Thames) can be derived, in the context of UK ranges (Fig 52). The major features are:

1) At the most contaminated Thames sites, bioavailability was high, in UK terms, for the majority of metals.

2) Mean levels in Thames biota were also ranked relatively highly, confirming a

widespread degree of contamination throughout much of the estuary, though, for most metals, concentrations decreased considerably at the most seaward sites. Thus, generally, there was an extensive range of bioavailabilities along the estuary.

3) Silver bioaccumulation in the Thames was exceptional, even at the least contaminated sites near the mouth of the estuary.

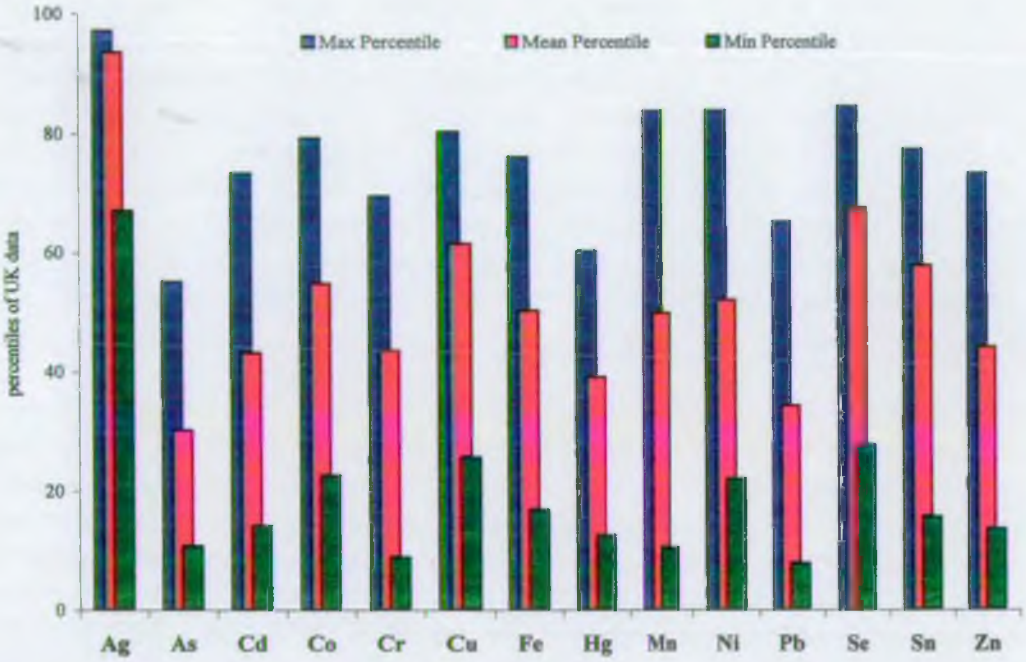


Figure 52. Metals in Thames biota. Minimum, maximum and mean values expressed as percentiles (averaged across all species) and summarised in terms of UK ranges.

Towards their upper distribution limits in the Thames, winkles *Littorina littorea* and sediment-dwelling clams *Scrobicularia*, and *Macoma*, contained some of the highest Ag concentrations reported for the UK: Ag bioavailability in particulate matter appears to have increased markedly upstream. Selenium bioavailability in the Thames was also disproportionately high with respect to Se concentrations in sediments (many species with values >90th percentile for UK data). Comparable spatial trends were observed for Cd, though speciation (more free ion at low salinities) may have been an important factor in promoting Cd bioavailability at upstream sites. The scale of Cd contamination in biota was moderate to high (upper values between 50th and 90th percentiles).

Concentrations of Ni, Mn, Cu, Co, Sn, Fe, Zn, Pb and Hg in biota from the most contaminated Thames sites also ranked highly, in national terms (60th- 80th percentile, based on average values across all species). At the least contaminated outer estuary sites rankings were considerably lower (all metals < 27th percentile, except Ag).

Evidence presented here suggests that the bioavailability of certain metals is modified by the large proportions of sewage effluent discharged to the estuary. Ag, Cd, Pb and Se bioaccumulation from sediments may be enhanced, whilst uptake of As may be suppressed, by the presence of other agents. This hypothesis should be tested further by, for example, looking at distributions and sources of bacteria, phosphate and detergents, and investigating their influence on metal bioavailability and toxicity.

Food Chains and Toxicity

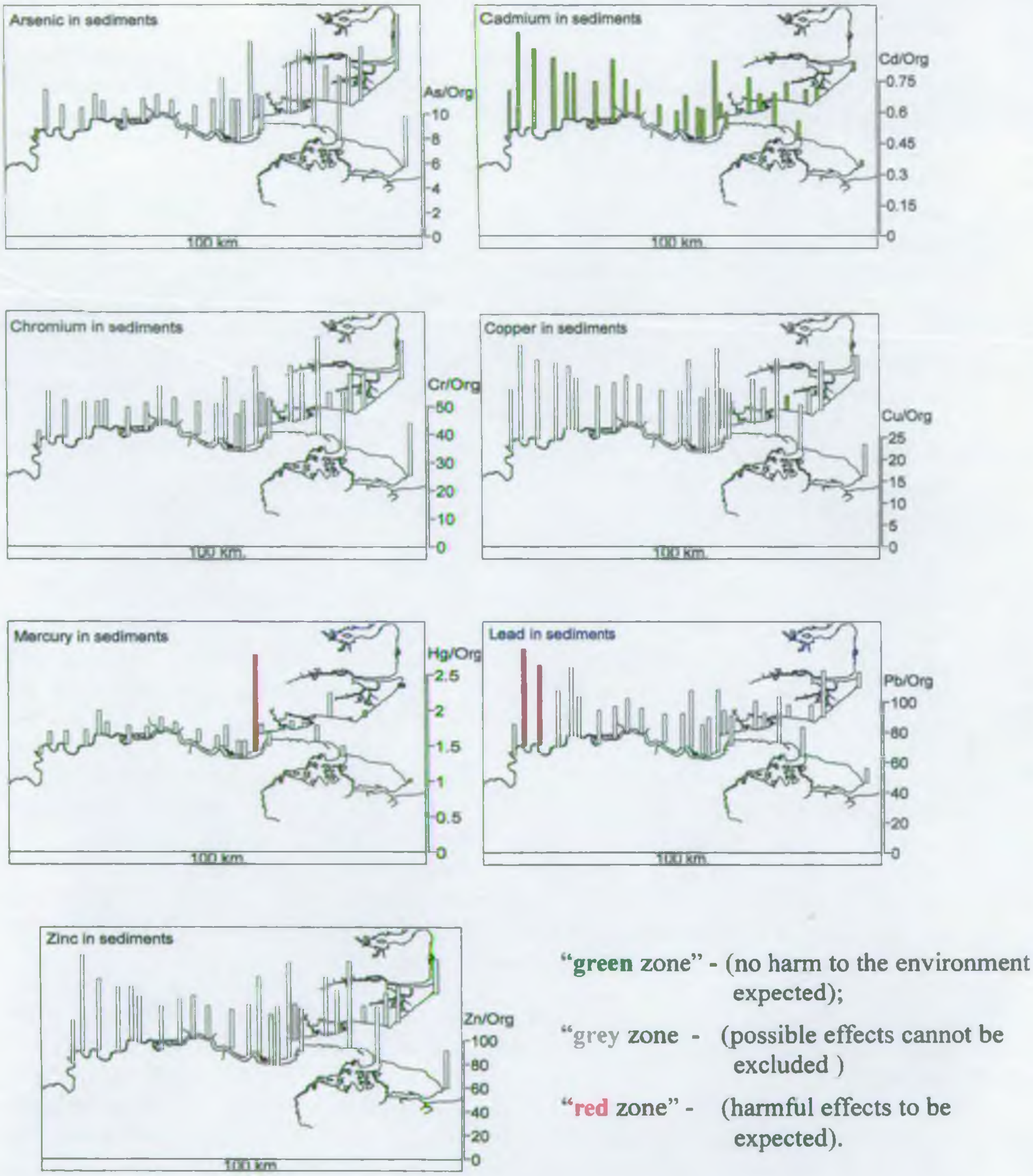
Concerns over food chain magnification of toxic metals in Thames biota are equivocal. Mercury is the element usually singled out as being most important in terms of bio-magnification, and advisory limits exist for Hg in fish and shellfish. The upper guideline value for Hg of 1 μg g^{-1} (dry weight), suggested for molluscs by the Oslo and Paris Commissions, compares with an upper limit of around 0.8 μg g^{-1} in Thames shellfish. Thus, invertebrate samples from the current survey are within public health guidelines, but considering that top predators such as fish, birds and mammals are capable of further magnification of Hg residues, the margin of safety is not large. Toxicologically, methylmercury is the most important Hg species in marine organisms and an evaluation of the distribution organomercury:total Hg in sediments and biota from the Thames would help to improve the assessment of risk and identify conditions favouring methylation.

Lead levels in Thames biota did not exceed current UK guidelines for food. However, a proposed EC regulation sets a limit of 2 μg g^{-1} ww (equivalent to approximately 10 μg g^{-1} dw) - similar to levels in cockles and mussels from the outer estuary, and exceeded by two-fold in clams from further upstream (though the latter are not directly consumed by humans). The proposed threshold for Cd of 1.5 μg g^{-1} wet weight (equivalent to approximately 7.5 μg g^{-1} dw) was not exceeded: highest values were found in winkles and mussels - up to 50% of the limit. Incongruously, all shellfish samples in the Thames surpassed the UK guideline for arsenic in food of 1 μg g^{-1} wet wt (5 μg g^{-1} dw equivalent). However, this limit does not apply when contamination is deemed to come from 'natural sources'. It would be difficult to exclude the possibility of a contribution from industrial origin to the As burden of Thames biota, though present indications suggest this is likely to be minimal; in either case the limit value for As would appear to be set too low.

In higher organisms, especially birds, there may be a fine-line between dietary levels of Se considered as essential (1 μg g^{-1}) and those regarded as potentially hazardous (> 5 μg g^{-1}), though there are no official limit values. Clams and worms from the inner Thames contained up to 10 μg g^{-1} Se, and winkles up to 35 μg g^{-1}, implying possible adverse effects, though the actual consequences for wading birds and other top consumers in the estuary are unknown. This topic merits further attention.

Possible adverse effects in Thames biota

Reports in the last three decades have indicated that the diversity and numbers of biota in the Thames Estuary are increasing as a result of waste treatment and water quality improvements (e.g. Andrews and Rickard, 1980; Andrews, 1984). Environmental levels and body burdens of individual metals encountered in the 1997 survey were almost certainly below levels considered to be acutely toxic. Nevertheless, the EQS was exceeded for Cu, Zn (and TBT), and other metals were sufficiently elevated in the Thames to raise the issue of possible sub-lethal impact on



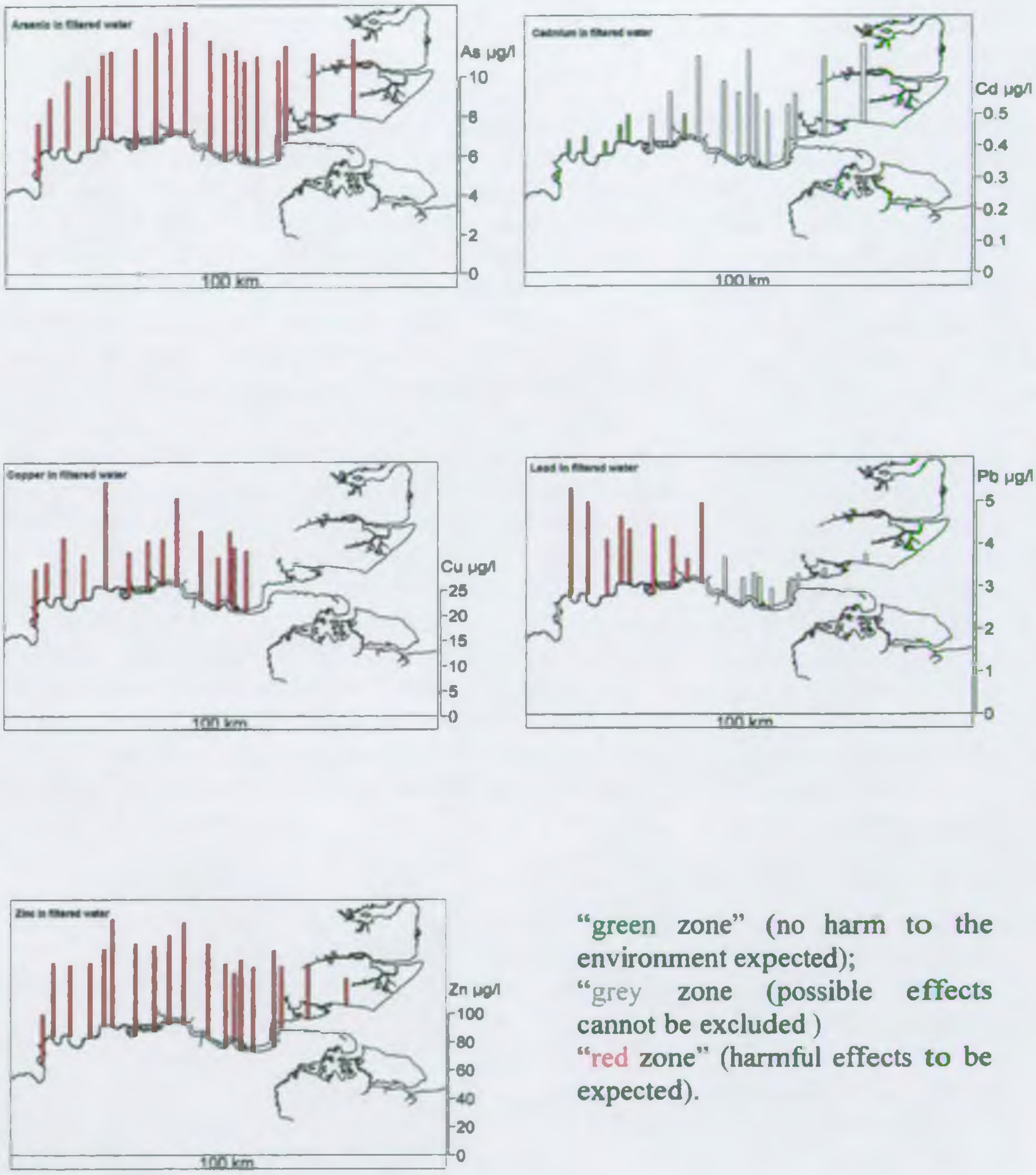
"**green** zone" - (no harm to the environment expected);

"grey zone - (possible effects cannot be excluded)

"**red** zone" - (harmful effects to be expected).

Figure 53. Classification of the Thames Estuary into zones based on OSPARCOM ecotoxicological assessment guidelines for sediment.

Note: OSPARCOM guidelines refer to sediment metals normalised to 1% organic carbon whereas Thames values are normalised to 1% organic matter (this would tend to reduce the apparent risk from Thames sediments by a factor of ~2, since approximately 50% of the total organic matter is organic carbon).



"green zone" (no harm to the environment expected);
"grey zone (possible effects cannot be excluded)
"red zone" (harmful effects to be expected).

Figure 54. Classification of the Thames Estuary into zones based on OSPARCOM ecotoxicological assessment guidelines for water.

reproduction, recruitment and development. The risk of biological effects is increased because of the wide spectrum of metals present (raising the likelihood of additivity) and because of interactions with other physiological and chemical stressors - including reduced oxygen tension, salinity, nutrients and organic contaminants. Enhanced metal levels in pore waters and labile sediment phases represent an additional risk factor.

Establishing biological effects is not a major objective of the present study and therefore the evidence on which to assess impact is largely circumstantial and subjective - based on comparisons of metal concentrations in the Thames with published sub-lethal toxicity values for aquatic organisms. On this basis Ag, Cd, Cu and Hg and Zn are *potentially* significant, with, perhaps, Mn, Ni and Pb posing a lesser toxic threat. Although there are few reported direct effects attributable to Fe, estimates of particulate suspended Fe in the estuary were similar to concentrations alleged to reduce the nutritional status of filter feeding molluscs (Winter, 1972) and may have been a contributory factor affecting the condition of Thames shellfish.

Generic recommendations and guidelines on safe levels of metals in water, sediments and some fish and shellfish tissues may be found in the literature. OSPARCOM, for example, is in the process of developing a series of ecotoxicological assessment citeria, arising from concensus values. Whilst acknowledging the limitations in extrapolating to case-specific studies, it is interesting to compare 'predicted risks' for the Thames, based on current sediment and water data. Of the 7 metals for which sediment guidelines are available, concentrations of As, Cr, Cu, Hg, Pb and Zn (but not Cd) at some Thames sites were within concentration ranges where, according to OSPARCOM, "adverse biological effects could not be excluded" (mapped in Fig 52). Equivalent comparisons for water characterised the concentrations of As, Cd, Cu, Pb, and Zn at a number of Thames sites as within the range where "adverse effects would be expected" (mapped in Fig 53).

With the possibility of biological effects in mind, we have examined relationships between mollusc condition and body burden of metals in *Scrobicularia plana* from the Thames. Condition index (CI), an estimate of flesh content in relation to shell size, was determined from the equation:

$$CI = 100 \times \{\text{dry flesh weight (g)} \div \text{internal cavity volume (ml)}^{*}\}$$

Significant negative correlations were obtained for a number of metals, including Ag, Cd, Co, Cr, Hg, Pb, Sn (and TBT) and Zn (Figure 55), suggesting that these metals *could* be associated with poor performance along the estuary, and possibly poor recruitment at upstream sites. The most statistically important relationships were for Ag, Zn and Cr ($P<0.01$). It is stressed that these observations are only correlations and are not, as yet, proof of cause and effect. It would be useful to continue CI measurements in future surveys as an indication of trends in clam condition and to confirm links with metal burdens.

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[*] (see Appendix 12 for details)

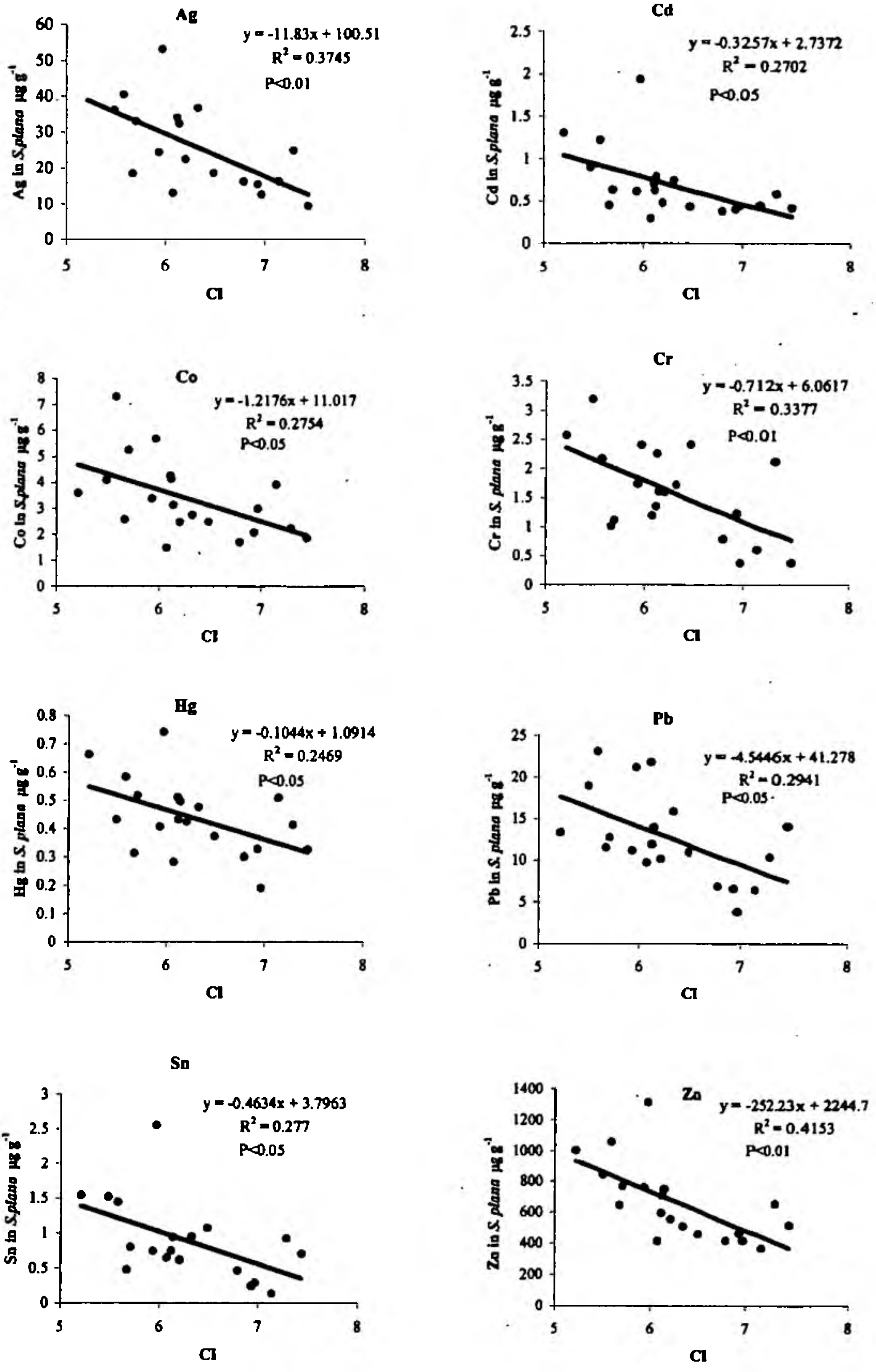

Figure. 55. ***Scrobicularia plana.*** **Relationships between condition index (CI) and metals, Thames Estuary, July 1997.**

Therefore, the balance of evidence supports the notion that several of the metals present in the Thames Estuary could contribute, jointly, to adverse effects in sensitive species and life stages. Since Ag bioaccumulation in Thames molluscs was outstanding (Fig 52) it is worth focussing on this metal. Remarkably little is known about the impact of Ag in estuaries despite the fact that, in dissolved form at least, it is one of the most toxic of metals. Growth and development of embryonic stages of bivalves, for example, are affected by concentrations between 2 and 25 µg l^{-1} (reviewed in Bryan and Langston, 1992; Langston, 1990) and possibly even lower (Conrad, 1988). Measured concentrations in the Thames water samples were below these thresholds but not always by a substantial amount.

Silver concentrations in deposit feeding clams certainly provide cause for concern, with tissue residues of 100-200µg g^{-1} (100-200 x background) expected to result in deleterious effects, based on data for *Macoma* populations in other Ag impacted estuarine environments. For example, in parts of San Francisco Bay, where sediment Ag concentrations are sometimes in excess of 10 µg g^{-1}, there are clear indications of sublethal metal-induced stress and, periodically, populations of *Macoma* disappear following the build up of high tissue concentrations of Ag and Cu (Johansson *et al.*, 1986; Luoma and Phillips, 1988). Comparable trends have been observed in *Macoma* and *Scrobicularia* populations at sites in the Mersey estuary (Langston *et al.*, 1994c). Given the high Ag body burdens (up to 80 µg g^{-1}) in Thames clams, and substantial sediment loadings upstream (up to 40 µg g^{-1}), further toxicological evaluation of Ag is important.

There are obvious shortcomings in the methods and data with which to evaluate the 'health' of the Thames Estuary and its biota. The same conclusion applies to the majority of UK estuaries. As in most environmental impact assessments, uncertainties arise because evidence of effects is seldom unequivocal. The main problem lies in the ability to detect effects against the background variation and to attribute them to specific causes.

To address these limitations, various biochemical and physiological indices of 'stress' and 'condition' are being developed and applied in Thames biota. Reports of these studies will be added to the 'Thames Estuary Environmental Quality Series'. When coupled with residue analysis, these should enable classification of impacted locations and detection of the most important stressors. Some of the preliminary work (e.g. on TBT impact in molluscs; metallothionein induction in eels in response to metals) has been undertaken in parallel with the present work. The findings generally affirm the concerns reported here over sub-lethal effects of metal and organomental contaminants in the Thames Estuary (Langston *et al.*, 2000a,b). The sensitive metallothionein assay would, when combined with studies on condition, be particularly useful to apply to mollusc populations in future surveys, to answer the question as to whether organisms are successfully adapting to metal stress. Knowledge acquired from this integrated chemical and biological approach should assist in environmental management decisions, not only in the Thames Region, but over much wider spatial and temporal scales. It may eventually help to deliver a sounder basis for the setting of environmental standards.

Temporal trends

Biological recovery of the Thames Estuary has been highly publicised in recent years. As yet there is not sufficient data to establish whether trends in metal contamination are part of this recovery, but some contribution is likely. Based on comparisons with a limited set of data for the mid-outer estuary from 1980, there appear to have been reductions in concentrations of As, Cd, Cr, Cu, Pb, Mn, Se, Sn and Zn in sediment, ranging from 30% to 80% (examples, Fig 56 and summary, Table 11).

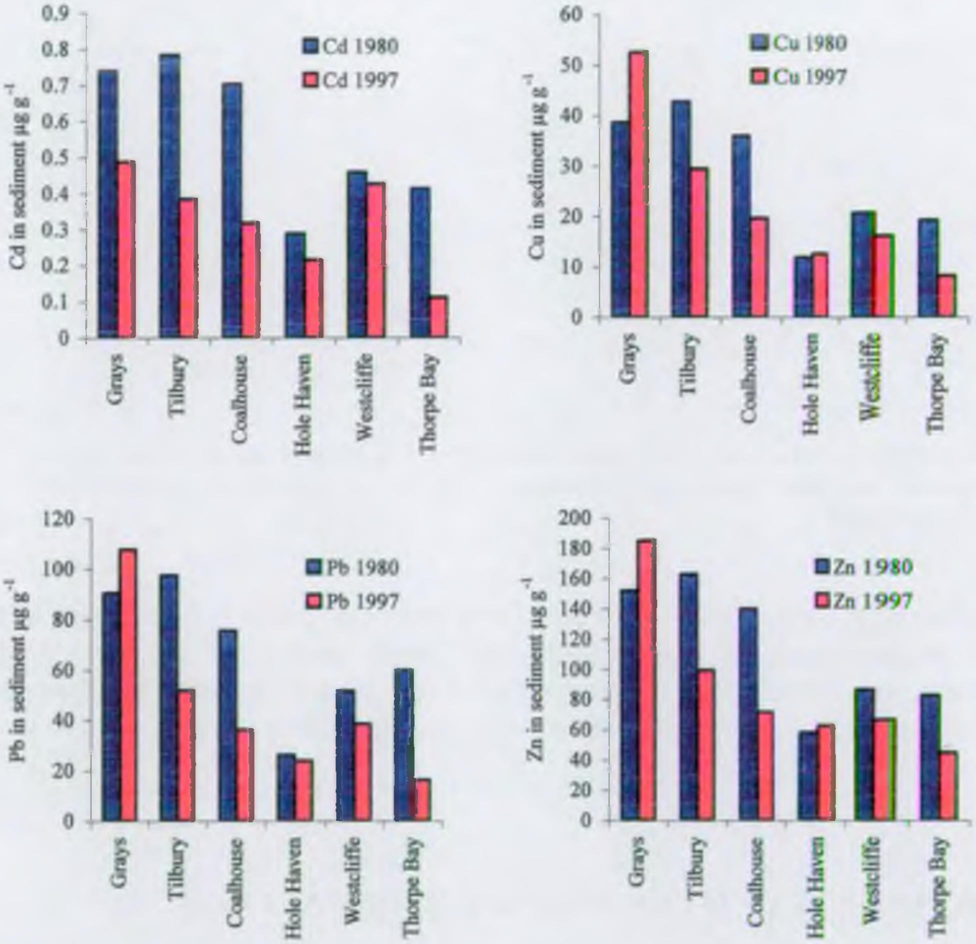

Figure 56. Comparisons of metal concentrations in a subset of Thames sediment samples, 1980 vs 1997 (HNO_3 digests).

In biota (*Fucus, Nereis, Littorina* and *Scrobicularia*), reductions were observed for As, Cd, Co, Cr, Hg, Ni, Pb and Zn in at least one species - coincidentally upto 80% - although the scale of change was not always directly linked to that in sediments (Table 11). Concentrations of other metals, notably Ag, have not changed significantly in this part of the estuary.

Table 11. Metal contamination trends in sediments and biota from the outer Thames, 1980 vs 1997. ↘ depicts significant reduction ($P<0.05$).

	Sediment Total	Sedment HCl	*Fucus*	*Nereis*	*Littorina*	*Scrobicularia*
Ag						
As	↘	↘	↘	↘		↘
Cd	↘	↘	↘		↘	↘
Co						↘
Cr		↘				↘
Cu		↘				
Fe						
Hg			↘	↘		↘
Mn	↘	↘				
Ni	↘	↘	↘	↘		↘
Pb		↘				↘
Se	↘					
Sn		↘		↘		↘
Zn		↘	↘			↘

Note : Data refer to six sites in the outer estuary (see Fig 56). Comparable data upstream of Grays, and for *Gammarus*, *Macoma*, *Mytilus* and *Cerastoderma*, are not yet extensive enough to provide meaningful comparisons.

These preliminary comparisons infer that there has been some improvement to the quality of the outer estuary (for metal contaminants), during the last two decades. Unfortunately, at present, there is no comparable information on temporal changes in the more contaminated inner- and mid-estuarine reaches, above Grays.

RECOMMENDATIONS FOR FUTURE WORK

The rehabilitation of the Thames Estuary over the last thirty years, particularly from the more obvious noxious effects of sewage and industry, has been widely acclaimed. Sustained recovery of Thames biota may now depend on further improvements to water (and sediment) quality: at the very least it will be necessary to ensure that estuarine quality is not allowed to deteriorate. These criteria can only be upheld by determining the distributions, bioavailability and impact of persistent chemicals such as metals.

Development of a continuing survey programme which integrates chemistry and biology, at established reference sites, is essential if the Agency is to evaluate the changing status of the Thames. Only then can decisions be made as to whether further improvements are attainable, practical or necessary (to fully comply with quality standards). This strategy of developing long-term data sets has been highly successful in discriminating trends in natural and anthropogenic chemicals in other estuarine and coastal areas, and establishing the effectiveness of clean-up measures. Use of the current data as time-zero baselines provides an excellent opportunity to evaluate, for example, future changes in the estuarine ecosystem arising from the recent cessation of sludge dumping in the outer Thames and the concomitant shift towards incineration at Crossness.

There are numerous research topics which would contribute to such a programme, including:

- Identification and quantification of metal sources
- Behaviour, fate and fluxes of metals during estuarine mixing, including temporal and spatial variation and estuarine simulations
- Sediment characterisation to distinguish anthropogenic vs natural sources of metal (geochemical fingerprinting and normalisation) and their uptake; use of Ag as a tracer of sewage influence
- More detailed validation of *Gammarus zaddachi* as a bioindicator of metals in the fresh-brackish zone
- Effects of sewage effluents, and their composition, on the bioavailability of metals in estuarine organisms
- An evaluation of the distribution of organomercury:total Hg in sediments and biota from the Thames to improve the assessment of risks from food chain transfer, and to identify conditions favouring methylation.
- Evaluation of sediment-metal toxicity to molluscs populations: measurement of critical burdens and sub-lethal measures of response (e.g. condition, production of the detoxifying protein metallothionein)

Most importantly, however, it is intended that many of the sites and sample types described here will form a reference set against which future trends in the Thames estuarine environment might be assessed. A high priority option would be to continue this chemical and biological surveillance programme, perhaps at two-yearly intervals, over at least a decade, and preferably longer. This will provide a meaningful baseline and time-series to ensure that the prognosis for the estuary remains favourable.

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Appendix 1. Metals in water samples, Thames 1997

Site	Map Ref	Distance km (Teddington)	Salinity (‰)	pH	Ag µg/L		As µg/L		Cd µg/L		Co µg/L		Cu µg/L	
					Total	Filtered	Total	Filtered	Total	Filtered	Total	Filtered	Total	Filtered
Teddington	TQ 165717	0	0.14	8.30	0.23	0.22	2.61	2.73	0.15	0.03	0.50	0.31	281	11
Kew	TQ 191779	9	0.22	8.15	0.50	0.09	3.33	2.60	1.10	0.04	2.09	0.40	204	7
Hammersmith Bridge	TQ 230780	15	0.47	8.10	0.48	0.11	4.45	3.46	3.05	0.05	2.45	0.40	191	12
Cadogan Pier	TQ 276775	22	1.16	7.90	0.43	0.04	4.53	3.86	1.00	0.04	1.18	0.29	174	9
South Bank Centre	TQ 308804	27	1.84	8.00	0.35	0.02	5.00	4.25	1.23	0.05	1.29	0.23	178	
London Bridge	TQ 327805	29	1.96	8.00	0.40	0.25	4.94	4.38	0.76	0.09	1.11	0.24	164	21
Greenwich	TQ 380781	36	4.47	7.50	0.29	0.38	5.83	5.06	0.63	0.12	1.48	0.26	199	9
Woolwich	TQ 424796	43	8.08	7.45	0.16	0.29	6.01	5.56	0.58	0.17	0.99	0.26	261	10
Beckton	TQ 457813	47	9.98	7.50	0.31	0.17	5.98	5.38	0.28	0.08	1.04	0.24	384	9
Crossness	TQ 490813	51	11.79	7.50	0.63	0.09	7.24	5.68	0.42	0.26	2.11	0.22	324	17
Purfleet	TQ 545783	58	13.95	7.55	0.44	0.04	5.98	5.44	0.41	0.22	0.95	0.11	268	13
West Thurrock	TQ 585756	62	16.49	7.60	0.30	0.09	6.24	5.40	0.47	0.22	1.02	0.10	276	10
Grays	TQ 611770	66	17.08	7.60	0.24	0.03	6.05	5.23	0.54	0.34	1.07	0.11	217	14
Tilbury	TQ 621755	68	17.17	7.60	0.14	0.23	5.93	5.00	0.42	0.22	0.78	0.13	185	12
Gravesend	TQ 649748	70	19.23	7.55	0.17	0.40	6.00	5.41	0.51	0.18	0.70	0.09	151	12
Coalhouse Fort	TQ 696758	75	21.07	7.60	0.12	0.20	5.85	4.99	0.32	0.18	0.96	0.09	111	
Mucking	TQ 713799	80	22.92	7.60	0.39	0.15	5.40	4.79	0.32	0.16	0.41	0.04	314	
Hole Haven	TQ 774821	87	28.76	7.85	0.73	0.09	4.95	3.88	0.23	0.25	0.65	0.05	257	
Southend	TQ 863852	97	31.58	8.10	0.18	0.21	4.55	3.89	0.08	0.24	0.31	0.12	220	

Site	Map Ref	Distance km (Teddington)	Salinity (‰)	pH	Fe µg/L		Mn µg/L		Ni µg/L		Pb µg/L		Zn µg/L	
					Total	Filtered	Total	Filtered	Total	Filtered	Total	Filtered	Total	Filtered
Teddington	TQ 165717	0	0.14	8.30	416	25	58	30.4	9.5	6.765	4.15	0.42	77	34
Kew	TQ 191779	9	0.22	8.15	1715	31	104	15.2	13.55	8.24	26.35	2.505	109	52
Hammersmith Bridge	TQ 230780	15	0.47	8.10	2407	37	122	12.1	13.9	8.595	31.9	2.165	110	50
Cadogan Pier	TQ 276775	22	1.16	7.90	1393	32	61	11.1	10	7.97	15.85	1.34	90	53
South Bank Centre	TQ 308804	27	1.84	8.00	1313		60	7.85	9.85	8.49	13.95	1.59	88	54
London Bridge	TQ 327805	29	1.96	8.00	1142	31	43	9.1	9.85	8.51	11.2	1.28	75	75
Greenwich	TQ 380781	36	4.47	7.50	1667	45	66	6.2	11.2	8.49	15.75	1.615	91	65
Woolwich	TQ 424796	43	8.08	7.45	1023	47	49	5.05	10.15	8.77	8.5	1.2	74	59
Beckton	TQ 457813	47	9.98	7.50	1078	40	50	5.15	8.4	7.975	9.65	0.505	88	61
Crossness	TQ 490813	51	11.79	7.50	2800	37	125	3.5	11.55	7	30.55	1.81	117	70
Purfleet	TQ 545783	58	13.95	7.55	970	19	39	12.05	7.55	9.995	10.45	0.86	65	64
West Thurrock	TQ 585756	62	16.49	7.60	1203	13	46	6.75	8.35	9.655	10	0.62	62	58
Grays	TQ 611770	66	17.08	7.60	1229	15	48	5.35	6.8	9.525	10.45	0.59	61	47
Tilbury	TQ 621755	68	17.17	7.60	765	12	20	3.8	5.6	9.225	6.1	0.645	52	61
Gravesend	TQ 649748	70	19.23	7.55	946	27	38	2.95	6.35	8.905	7.05	0.46	51	58
Coalhouse Fort	TQ 696758	75	21.07	7.60	871		29	2.6	5.7	9.335	6.95	0.6	49	67
Mucking	TQ 713799	80	22.92	7.60	497		21	1.6	4.4	8.69	3.8	0.295	59	43
Hole Haven	TQ 774821	87	28.76	7.85	757		33	1.4	3.15	7.68	4.55	0.2	47	38
Southend	TQ 863852	97	31.58	8.10	343		15	0.8	0.8	5.125	1.75	0.215	24	19

As most water samples were collected from mid-channel exact locations may differ slightly from sediment and biota sites

Appendix 2. Metals in HCl sediment extracts, Thames 1997.

				Metal ($\mu g\ g^{-1}$ dry weight)															
Site	**Mapef**	**Bank**	**Dist**	**Ag**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Mn**	**Ni**	**Pb**	**Se**	**Sn**	**Zn**	**Ca (%)**	**%Org**
Richmond Locks	TQ 168752	N	5	2.39	1.49	2.68	9.29	15.43	90.2	9,850	NA	721	12.75	210.7	NA	13.54	300	4.37	14.40
Kew Bridge	TQ 191779	N	9	1.84	1.55	0.96	8.71	6.59	39.6	6,952	NA	786	7.41	164.7	NA	14.44	181	2.72	3.44
Hammersmith Br.	TQ 230780	S	15	4.69	2.24	1.50	11.13	10.34	64.1	8,797	NA	763	10.31	283.5	NA	30.47	260	4.08	5.49
Cadogen	TQ 276775	S	22	2.85	2.00	1.64	5.34	11.78	47.5	10,393	NA	560	9.60	198.6	NA	8.75	247	4.73	8.62
South Bank	TQ 308804	S	27	2.19	2.41	0.97	6.02	7.11	48.7	9,500	NA	469	9.96	291.1	NA	17.10	223	4.76	4.53
London Bridge	TQ 327805	S	29	4.21	2.51	1.28	6.75	8.22	49.6	9,702	NA	545	8.44	161.7	NA	7.38	189	5.03	6.30
Greenwich	TQ 388783	S	37	1.49	1.43	0.68	5.25	8.64	23.8	11,074	NA	555	8.41	143.2	NA	7.43	180	5.08	6.44
Woolwich	TQ 439798	N	44	2.27	2.72	0.73	3.71	5.72	33.5	7,654	NA	332	5.61	102.8	NA	7.52	147	3.86	3.77
Beckton	TQ 456817	N	47	4.79	2.76	0.96	3.51	15.31	42.0	8,769	NA	399	8.05	121.4	NA	7.87	149	4.44	5.41
Crossness	TQ 492809	S	51	2.09	1.54	0.71	4.02	20.65	20.1	11,876	NA	513	11.39	139.4	NA	7.20	185	5.52	7.36
Purfleet	TQ 548786	N	58	3.06	3.53	0.57	4.81	16.55	42.7	9,717	NA	436	9.10	122.8	NA	8.16	152	4.75	6.79
W.Thurrock	TQ 592770	N	64	0.87	1.64	0.30	30.97	6.60	15.7	6,326	NA	277	25.63	62.0	NA	2.88	88	4.29	2.79
Grays	TQ 614774	N	66	2.04	3.02	0.35	4.13	9.54	25.3	6,648	NA	279	6.03	78.5	NA	5.10	104	3.88	2.41
Tilbury	TQ 647753	N	70	1.49	2.74	0.34	2.11	6.19	17.9	5,564	NA	245	3.87	52.3	NA	3.31	76	4.05	2.47
Gravesend	TQ 648745	S	70	1.86	2.86	0.42	2.85	8.88	25.3	7,011	NA	277	4.91	75.1	NA	4.70	99	4.35	2.85
Coalhouse	TQ 690762	N	75	0.89	2.04	0.27	1.62	3.90	11.1	3,765	NA	169	1.87	35.5	NA	2.18	52	3.29	0.88
Lo.Hope Pt.	TQ 709776	S	77	2.34	7.09	0.37	5.83	18.47	41.1	11,375	NA	452	7.29	107.4	NA	6.10	152	5.38	6.53
Mucking	TQ 699807	N	80	1.45	5.63	0.54	5.51	16.90	40.7	10,719	NA	375	7.64	108.9	NA	6.65	159	5.26	1.28
Hole Haven	TQ 774821	N	87	0.23	1.60	0.21	1.00	3.44	6.4	3,324	NA	141	1.24	24.0	NA	1.49	44	3.21	4.23
Canvey Isl	TQ 800825	N	91																
Allhallows	TQ 834789	S	91	0.47	3.89	0.16	3.15	6.99	13.3	5,741	NA	213	3.24	42.2	NA	1.98	63	4.52	1.60
Southend	TQ 863852	N	97	0.41	4.72	0.26	3.64	8.29	17.5	8,671	NA	201	3.14	59.2	NA	2.33	79	4.74	1.70
Grain	TQ 894751	S	99	0.35	3.56	0.23	2.26	7.61	11.1	6,778	NA	283	3.52	34.5	NA	1.85	59	4.65	2.15
Thorpe Bay	TQ 916844	N	102	0.18	2.06	0.10	1.11	2.66	4.3	3,240	NA	111	1.19	18.3	NA	0.81	30	2.88	5.55
Shoeburyness	TQ 947852	N	106	0.15	3.02	0.07	1.33	2.93	8.9	3,894	NA	155	1.06	50.9	NA	2.92	34	3.81	1.17
Shellness	TR 055682	S	117	0.23	3.41	0.08	6.26	7.19	8.9	6,223	NA	186	4.60	23.9	NA	1.01	46	3.11	2.01
Foulness	TR 036929	N	117	0.11	4.40	0.05	2.43	2.84	5.8	4,953	NA	269	2.85	22.1	NA	0.87	33	4.32	2.79
UK minimum *				0.00	0.60	0.003	0.10	0.54	0.9	649		7	0.05	4.5		0.20	2	0.14	0.337
UK maximum *				9.63	8,304	11.5	73.80	791	4,607	149,922		3,775	80.40	5,048		421.4	11,707	42.50	20.4

Underlined values refer to minimum and maximum values recorded in the 1997 Thames survey

* values from PML/MBA database

NA - Not analysed (below detection limit)

Appendix 3. Metals in HNO_3 sediment extracts, Thames 1997.

				Metal ($\mu g\ g^{-1}$ dry weight)															
Site	**Mapef**	**Bank**	**Dist**	**Ag**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Mn**	**Ni**	**Pb**	**Se**	**Sn**	**Zn**	**Ca (%)**	**%Org**
Richmond Locks	TQ 168752	N	5	43.52	13.1	3.41	30.92	87.6	198	37,285	1.59	1,225	48.7	299.2	0.545	NA	504	4.37	14.40
Kew Bridge	TQ 191779	N	9	7.34	11.1	1.60	24.27	56.8	74	27,465	0.63	1,217	27.7	219.4	0.173	NA	281	2.72	3.44
Hammersmith Bridge	TQ 230780	S	15	12.33	10.8	2.12	20.88	71.5	99	29,251	1.04	972	33.0	290.2	0.095	NA	335	4.08	5.49
Cadogan Pier	TQ 276775	S	22	21.33	16.2	3.02	28.75	114.9	153	47,164	1.98	1,125	45.5	322.6	0.251	NA	482	4.73	8.62
South Bank Centre	TQ 308804	S	27	6.01	9.4	1.03	13.23	42.3	65	22,330	1.56	494	21.8	203.8	0.126	NA	211	4.76	4.53
London Bridge	TQ 327805	S	29	8.62	9.2	1.40	12.91	61.3	73	27,119	1.12	689	25.4	160.5	0.059	NA	241	5.03	6.30
Greenwich	TQ 388783	S	37	6.23	10.9	1.52	16.89	70.1	80	30,866	1.75	683	29.8	152.8	0.147	NA	254	5.08	6.44
Woolwich	TQ 439798	N	44	4.80	8.0	1.26	8.61	40.8	47	19,038	0.70	413	16.7	89.0	0.072	NA	160	3.86	3.77
Beckton	TQ 456817	N	47	5.05	10.6	1.08	17.03	83.5	71	29,745	1.23	579	28.9	135.5	0.034	NA	222	4.44	5.41
Crossness	TQ 492809	S	51	6.04	11.2	1.04	12.82	77.9	76	30,696	1.22	593	32.6	133.6	0.150	NA	220	5.52	7.36
Purfleet	TQ 548786	N	58	5.23	11.9	0.71	16.99	81.2	73	33,933	1.25	608	30.7	132.8	0.066	NA	227	4.75	6.79
West Thurrock	TQ 592770	N	64	1.98	7.1	0.27	9.70	35.0	31	18,384	0.46	360	15.7	61.1	0.075	NA	111	4.29	2.79
Grays	TQ 614774	N	66	3.87	12.3	0.49	15.17	62.6	53	30,032	0.84	513	24.0	107.9	0.063	NA	185	3.88	2.41
Tilbury	TQ 647753	N	70	1.58	8.2	0.39	7.36	30.5	30	17,001	0.50	328	15.6	51.8	0.047	NA	100	4.05	2.47
Gravesend	TQ 648745	S	70	2.90	10.4	0.47	10.50	52.4	44	24,152	0.68	414	19.7	79.4	0.082	NA	144	4.35	2.85
Coalhouse Fort	TQ 690762	N	75	1.16	6.8	0.32	4.45	24.7	20	12,591	1.21	240	9.5	36.4	0.025	NA	72	3.29	0.88
Lower Hope Point	TQ 709776	S	77	3.82	16.5	0.49	13.43	86.5	64	36,401	1.10	640	31.7	117.1	0.069	NA	218	5.38	6.53
Mucking	TQ 699807	N	80	4.30	13.3	0.51	9.60	81.8	62	33,356	0.93	508	28.3	109.1	NA	NA	210	5.26	1.28
Hole Haven	TQ 774821	N	87	0.61	5.2	0.22	2.88	25.3	13	11,070	0.14	216	8.9	24.0	0.033	NA	63	3.21	4.23
Canvey Island	TQ 800825	N	91	4.97	7.2	0.12	6.15	24.2	11	14,555	0.10	229	16.5	14.2	0.091	NA	53	NA	1.44
Allhallows	TQ 834789	S	91	0.96	10.1	0.20	5.76	45.0	23	20,602	0.29	315	14.9	38.7	0.007	NA	94	4.52	1.60
Westcliff	TQ 863852	N	97	1.40	13.6	0.43	3.04	29.1	16	12,786	1.62	174	9.1	38.5	0.082	NA	67	4.74	1.70
Grain Flats	TQ 894751	S	99	1.17	10.8	0.19	9.43	41.4	21	21,307	0.29	427	17.8	39.7	0.020	NA	95	4.65	2.15
Southend (Thorpe Bay)	TQ 916844	N	102	0.24	6.1	0.11	2.61	21.9	8	10,274	0.06	176	6.1	16.3	NA	NA	45	2.88	5.55
Shoeburyness	TQ 947852	N	106	0.29	7.4	0.11	2.77	21.3	19	12,142	0.15	228	9.4	52.3	0.056	NA	54	3.81	1.17
Shell Ness	TR 055682	S	117	0.47	11.6	0.08	12.84	52.4	21	26,219	0.14	321	22.8	26.3	0.004	NA	90	3.11	2.01
Foulness	TR 036929	N	117	0.11	9.8	0.10	7.99	29.2	12	16,826	0.11	355	13.0	21.8	0.017	NA	61	4.32	2.79
UK minimum*				0.01	1.68	0.003	0.46	1.41	1	2,541	0.01	28	3.20	1.8	0.017		26	0.136	0.34
UK maximum*				28.40	4,990	27.60	68.80	826	23,201	247,100	8.94	2,897	413	9,305	27.50		25,693	42.500	20.40

Underlined values refer to minimum and maximum values recorded in the 1997 Thames survey

* values from PML/MBA database

NA - Not analysed (below detection limit)

Appendix 4. Metals in *Gammarus zaddachi*, Thames 1997.

				Metal (µg g^{-1} dry weight)													
Site	**Mapef**	**Bank**	**Dist**	**Ag**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Mn**	**Ni**	**Pb**	**Se**	**Sn**	**Zn**
Richmond Locks	TQ 168752	N	5	8.56	5.45	0.16	8.23	1.25	138	348	0.22	26.0	0.98	3.88	8.60	2.20	76.3
Kew Bridge	TQ 191779	N	9	6.69	NA	0.16	7.35	0.73	106	242	0.20	14.8	0.46	3.08	1.68	NA	70.7
Hammersmith Bridge	TQ 230780	S	15	5.27	3.24	0.17	6.39	1.92	89	583	0.27	27.3	1.14	5.57	3.24	1.39	84.3
Cadogan Pier	TQ 276775	S	22	3.44	NA	0.34	5.22	1.94	87	449	0.37	17.1	0.75	5.80	2.85	NA	85.8
South Bank Centre	TQ 308804	S	27	3.64	2.53	0.30	4.69	1.00	92	316	0.40	11.9	1.05	3.46	3.80	4.34	80.7
London Bridge	TQ 327805	S	29	2.96	2.15	0.22	5.20	1.14	70	377	0.40	15.9	0.83	8.57	2.10	0.47	81.4
Greenwich	TQ 388783	S	37														
Woolwich	TQ 439798	N	44														
Beckton	TQ 456817	N	47														
Crossness	TQ 492809	S	51														
Purfleet	TQ 548786	N	58														
West Thurrock	TQ 592770	N	64														
Grays	TQ 614774	N	66														
Tilbury	TQ 647753	N	70														
Gravesend	TQ 648745	S	70														
Coalhouse Fort	TQ 690762	N	75														
Lower Hope Point	TQ 709776	S	77														
Mucking	TQ 699807	N	80														
Hole Haven	TQ 774821	N	87														
Canvey Island	TQ 800825	N	91														
Allhallows	TQ 834789	S	91														
Westcliff	TQ 863852	N	97														
Grain Flats	TQ 894751	S	99														
Southend (Thorpe Bay)	TQ 916844	N	102														
Shoeburyness	TQ 947852	N	106														
Shell Ness	TR 055682	S	117														
Foulness	TR 036929	N	117														

Underlined values refer to minimum and maximum values recorded in the 1997 Thames survey

NA - Not analysed (below detection limit); empty rows -samples not collected at these sites.

Appendix 5. Metals in *Fucus vesiculosus*, Thames 1997.

				Metal (μg g^{-1} dry weight)													
Site	Mapef	Bank	Dist	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
Richmond Locks	TQ 168752	N	5														
Kew Bridge	TQ 191779	N	9														
Hammersmith Bridge	TQ 230780	S	15														
Cadogan Pier	TQ 276775	S	22														
South Bank Centre	TQ 308804	S	27														
London Bridge	TQ 327805	S	29														
Greenwich	TQ 388783	S	37														
Woolwich	TQ 439798	N	44	1.65	5.51	2.16	4.15	1.04	18.6	726	0.034	364.6	24.3	4.65	0.624	0.55	701
Beckton	TQ 456817	N	47														
Crossness	TQ 492809	S	51	1.14	5.13	1.10	3.44	1.95	14.1	1,648	0.043	279.7	13.2	7.99	0.430	1.72	376
Purfleet	TQ 548786	N	58	3.29	6.48	2.99	3.11	1.49	23.7	1,247	0.043	198.9	31.4	5.40	1.171	1.83	690
West Thurrock	TQ 592770	N	64	1.07	4.17	0.94	2.51	1.24	12.9	1,158	0.031	194.8	16.4	5.09	0.358	0.76	253
Grays	TQ 614774	N	66	2.18	6.30	1.32	2.69	0.95	19.7	1,012	0.044	182.0	25.2	5.32	1.033	1.08	469
Tilbury	TQ 647753	N	70	3.30	8.96	2.26	3.99	0.80	25.7	813	0.046	277.2	28.9	5.43	0.900	1.20	619
Gravesend	TQ 648745	S	70	4.39	9.54	1.82	3.16	1.19	27.3	704	0.030	249.6	25.0	5.37	NA	1.19	586
Coalhouse Fort	TQ 690762	N	75	1.03	7.04	0.73	2.80	1.15	13.3	739	0.032	165.7	9.4	3.61	0.061	0.87	197
Lower Hope Point	TQ 709776	S	77	3.24	8.27	1.76	3.10	1.03	22.6	510	0.047	204.0	28.3	3.40	NA	NA	482
Mucking	TQ 699807	N	80	1.09	8.28	0.90	4.74	0.82	15.6	419	0.023	342.2	20.2	3.13	0.380	0.71	258
Hole Haven	TQ 774821	N	87	1.44	6.13	0.87	1.26	1.96	13.4	875	0.032	82.4	12.8	2.73	0.105	NA	151
Canvey Island	TQ 800825	N	91	1.14	7.81	0.65	2.01	0.57	12.4	223	0.026	79.6	18.3	0.71	NA	0.01	130
Allhallows	TQ 834789	S	91	1.85	13.55	1.05	3.44	0.68	16.4	334	0.058	349.2	18.7	2.01	0.041	NA	185
Westcliff	TQ 863852	N	97	0.57	9.68	0.62	3.73	0.79	9.7	377	0.018	235.3	14.8	2.04	NA	0.20	97
Grain Flats	TQ 894751	S	99	1.13	9.62	0.51	3.31	1.04	14.8	413	0.026	141.0	17.3	1.15	0.564	0.36	106
Southend (Thorpe Bay)	TQ 916844	N	102	1.53	18.64	0.99	4.13	1.22	16.0	740	0.019	367.3	10.3	3.21	0.126	NA	109
Shoeburyness	TQ 947852	N	106	1.05	9.76	0.55	2.11	1.38	13.6	565	0.031	161.1	14.7	1.91	NA	0.35	89
Shell Ness	TR 055682	S	117	2.34	11.49	0.98	2.60	0.64	14.8	369	0.034	67.0	11.2	0.91	0.586	0.06	53
Foulness	TR 036929	N	117	1.37	16.73	0.33	2.29	1.23	12.4	589	0.045	135.1	8.8	1.48	1.045	0.43	56
UK minimum*				0.02	4.20	0.01	0.04	0.02	0.88	4	0.006	9.2	0.59	0.20	0.01	0.001	27.8
UK maximum*				7.40	2,530	58.20	66.70	53.50	3,476	118,018	50.50	3,912	57.80	610	21.40	11.80	10,908

Underlined values refer to minimum and maximum values recorded in the 1997 Thames survey

* values from PML/MBA database

NA - Not analysed (below detection limit); empty rows -samples not collected at these sites.

Appendix 6. Metals in *Littorina littorea*, Thames 1997.

				Metal ($\mu g\ g^{-1}$ dry weight)													
Site	**Mapef**	**Bank**	**Dist**	**Ag**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Mn**	**Ni**	**Pb**	**Se**	**Sn**	**Zn**
Richmond Locks	TQ 168752	N	5														
Kew Bridge	TQ 191779	N	9														
Hammersmith Bridge	TQ 230780	S	15														
Cadogan Pier	TQ 276775	S	22														
South Bank Centre	TQ 308804	S	27														
London Bridge	TQ 327805	S	29														
Greenwich	TQ 388783	S	37														
Woolwich	TQ 439798	N	44														
Beckton	TQ 456817	N	47														
Crossness	TQ 492809	S	51														
Purfleet	TQ 548786	N	58														
West Thurrock	TQ 592770	N	64														
Grays	TQ 614774	N	66	30.8	7.6	3.36	2.43	0.99	163	283	0.22	75.2	7.51	3.97	9.80	0.73	138
Tilbury	TQ 647753	N	70	89.3	12.0	2.66	4.19	1.10	205	266	0.39	61.8	13.40	4.54	35.60	0.91	136
Gravesend	TQ 648745	S	70	69.6	10.1	1.83	1.39	0.98	234	337	0.34	30.4	6.86	3.44	13.32	1.41	125
Coalhouse Fort	TQ 690762	N	75														
Lower Hope Point	TQ 709776	S	77	101.7	16.6	2.28	6.50	1.18	238	335	0.60	68.8	14.43	3.94	31.52	1.46	140
Mucking	TQ 699807	N	80	NA	NA	1.52	3.16	1.20	136	358	0.34	47.4	6.37	3.50	6.47	NA	108
Hole Haven	TQ 774821	N	87	60.4	NA	1.08	1.11	0.73	160	337	0.22	27.0	9.04	2.40	14.63	NA	95
Canvey Island	TQ 800825	N	91	28.6	14.1	0.96	1.22	0.57	141	249	0.19	29.0	7.68	1.92	7.03	0.41	100
Allhallows	TQ 834789	S	91	53.4	14.7	1.79	4.26	1.03	172	411	0.43	95.9	10.67	2.91	19.96	0.77	129
Westcliff	TQ 863852	N	97	45.9	13.1	0.77	1.53	0.55	140	332	0.28	39.8	7.31	3.12	7.88	0.64	91
Grain Flats	TQ 894751	S	99	26.6	12.5	0.83	1.20	0.49	139	221	0.27	38.5	3.50	2.23	4.94	0.59	92
Southend (Thorpe Bay)	TQ 916844	N	102	17.2	12.7	0.58	0.58	0.31	114	252	0.22	36.4	3.72	2.29	3.71	0.43	95
Shoeburyness	TQ 947852	N	106	17.7	14.7	0.68	0.99	0.37	153	253	0.23	51.7	4.39	6.01	3.28	0.52	96
Shell Ness	TR 055682	S	117	15.2	12.1	0.68	1.79	0.32	132	286	0.19	29.5	2.87	3.44	4.39	0.15	112
Foulness	TR 036929	N	117	13.9	18.2	0.49	1.74	0.39	111	208	0.27	80.6	3.54	1.75	2.15	0.25	82
UK minimum*				0.31	6.53	0.25	0.03	0.02	37	117	0.04	9.64	0.68	0.07	0.31	0.003	38
UK maximum*				101.0	101.5	96.19	21.70	28.54	1,089	1,652	29.96	506	18.57	96.79	384.50	11.04	1,576

Underlined values refer to minimum and maximum values recorded in the 1997 Thames survey

* values from PML/MBA database

NA - Not analysed (below detection limit); empty rows -samples not collected at these sites.

Appendix 7. Metals in *Mytilus edulis*, Thames 1997.

				Metal (µg g^{-1} dry weight)													
Site	Mapef	Bank	Dist	Ag	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Se	Sn	Zn
Richmond Locks	TQ 168752	N	5														
Kew Bridge	TQ 191779	N	9														
Hammersmith Bridge	TQ 230780	S	15														
Cadogan Pier	TQ 276775	S	22														
South Bank Centre	TQ 308804	S	27														
London Bridge	TQ 327805	S	29														
Greenwich	TQ 388783	S	37														
Woolwich	TQ 439798	N	44														
Beckton	TQ 456817	N	47														
Crossness	TQ 492809	S	51														
Purfleet	TQ 548786	N	58														
West Thurrock	TQ 592770	N	64														
Grays	TQ 614774	N	66														
Tilbury	TQ 647753	N	70														
Gravesend	TQ 648745	S	70														
Coalhouse Fort	TQ 690762	N	75														
Lower Hope Point	TQ 709776	S	77														
Mucking	TQ 699807	N	80														
Hole Haven	TQ 774821	N	87														
Canvey Island	TQ 800825	N	91	8.75	16.4	3.86	1.68	1.88	9.8	302	0.50	7.4	3.13	5.92	9.58	0.854	288
Allhallows	TQ 834789	S	91	1.35	10.8	2.30	1.29	1.86	10.9	729	0.35	26.1	2.07	7.39	4.95	0.601	225
Westcliff	TQ 863852	N	97	0.88	12.4	1.69	1.07	2.14	13.2	272	0.32	5.5	2.39	8.15	5.35	0.487	187
Grain Flats	TQ 894751	S	99	0.74	9.4	1.48	0.56	1.64	9.3	596	0.30	23.3	1.51	7.32	3.81	0.659	172
Southend (Thorpe Bay)	TQ 916844	N	102	2.08	11.9	1.26	0.69	1.55	11.2	430	0.29	16.8	1.47	6.35	4.37	0.504	156
Shoeburyness	TQ 947852	N	106	1.34	11.5	1.14	0.60	1.65	9.4	633	0.27	24.9	1.35	10.26	4.16	0.453	124
Shell Ness	TR 055682	S	117	0.67	8.2	1.11	0.69	1.03	7.7	356	0.17	16.8	0.65	4.50	3.10	0.293	123
Foulness	TR 036929	N	117	3.50	13.4	1.25	1.33	2.00	9.4	803	0.58	36.7	1.83	7.26	3.22	0.335	137
UK minimum*				0.01	3.4	0.15	0.02	0.19	2.3	56	0.05	2.41	0.14	0.54	0.78	0.001	46
UK maximum*				198	52.5	74.9	8.37	66.1	262	25,271	18.30	291.4	29.8	127	123.4	5.89	884

Underlined values refer to minimum and maximum values recorded in the 1997 Thames survey

* values from PML/MBA database

NA - Not analysed (below detection limit); empty rows -samples not collected at these sites.

Appendix 8. Metals in *Nereis diversicolor*, Thames 1997.

				Metal (μg g^{-1} dry weight)													
Site	**Mapef**	**Bank**	**Dist**	**Ag**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Mn**	**Ni**	**Pb**	**Se**	**Sn**	**Zn**
Richmond Locks	TQ 168752	N	5														
Kew Bridge	TQ 191779	N	9														
Hammersmith Bridge	TQ 230780	S	15														
Cadogan Pier	TQ 276775	S	22														
South Bank Centre	TQ 308804	S	27														
London Bridge	TQ 327805	S	29														
Greenwich	TQ 388783	S	37	2.15	6.4	0.15	11.49	0.142	30.7	535	0.131	24.9	1.16	1.82	9.03	1.47	187
Woolwich	TQ 439798	N	44	7.77	12.5	0.41	18.30	0.340	53.2	696	0.176	15.3	4.09	5.33	11.91	2.87	219
Beckton	TQ 456817	N	47	1.66	13.6	0.10	5.51	0.050	18.3	1,694	0.062	35.4	1.45	2.53	7.65	1.27	200
Crossness	TQ 492809	S	51	1.88	18.0	0.14	8.99	0.318	20.5	1,336	0.115	16.7	1.77	NA	5.70	0.98	191
Purfleet	TQ 548786	N	58	7.39	13.9	0.30	8.18	0.080	37.2	548	0.154	12.0	4.03	3.80	8.14	0.78	229
West Thorrock	TQ 592770	N	64	NA	NA	0.31	11.92	0.039	93.6	511	0.187	12.2	3.58	3.10	9.38	NA	230
Grays	TQ 614774	N	66	NA	14.4	0.26	6.77	0.356	33.4	443	0.174	9.8	3.70	3.14	7.81	1.13	230
Tilbury	TQ 647753	N	70	6.48	9.7	0.10	8.39	0.097	48.9	498	0.131	16.8	1.81	2.06	6.57	1.30	144
Gravesend	TQ 648745	S	70	NA	NA	0.21	13.45	0.268	70.7	518	0.147	15.1	2.03	3.95	8.48	NA	243
Coalhouse Fort	TQ 690762	N	75	5.37	13.1	0.11	21.63	0.177	36.0	730	0.139	17.6	1.61	2.44	7.10	1.18	168
Lower Hope Point	TQ 709776	S	77	7.57	12.5	0.19	21.79	0.404	41.4	568	0.177	12.4	4.04	2.02	9.63	1.42	189
Mucking	TQ 699807	N	80	4.24	13.1	0.27	22.52	0.331	24.9	350	0.235	10.0	3.78	1.91	9.40	1.42	181
Hole Haven	TQ 774821	N	87	2.26	13.3	0.17	6.00	0.167	22.7	433	0.156	8.7	2.15	1.77	4.55	0.42	169
Canvey Island	TQ 800825	N	91	2.58	15.2	0.19	7.20	0.058	17.2	434	0.149	9.1	2.23	1.04	6.81	0.30	149
Allhallows	TQ 834789	S	91														
Westcliff	TQ 863852	N	97	2.40	12.6	0.18	5.34	0.132	21.9	376	0.095	12.5	2.09	2.14	6.85	0.25	172
Grain Flats	TQ 894751	S	99	2.26	10.2	0.10	5.62	0.101	24.7	388	0.145	10.2	1.95	0.93	3.88	0.04	171
Southend (Thorpe Bay)	TQ 916844	N	102														
Shoeburyness	TQ 947852	N	106														
Shell Ness	TR 055682	S	117														
Foulness	TR 036929	N	117	0.88	NA	0.20	25.75	0.540	17.3	302	0.084	11.7	4.57	2.82	1.77	NA	157
UK minimum*				0.05	0.70	0.01	0.29	0.01	7.0	189	0.010	3.03	0.18	0.09	1.27	0.01	55
UK maximum*				36.4	178	10.2	32.1	10.4	2,474	9,246	8.22	123.0	39.3	1,193	80.8	16.4	1,297

Underlined values refer to minimum and maximum values recorded in the 1997 Thames survey

* values from PML/MBA database

NA - Not analysed (below detection limit); empty rows -samples not collected at these sites.

Appendix 9. Metals in *Macoma balthica*, Thames 1997.

				Metal (µg g^{-1} dry weight)													
Site	**Mapef**	**Bank**	**Dist**	**Ag**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Mn**	**Ni**	**Pb**	**Se**	**Sn**	**Zn**
Richmond Locks	TQ 168752	N	5														
Kew Bridge	TQ 191779	N	9														
Hammersmith Bridge	TQ 230780	S	15														
Cadogan Pier	TQ 276775	S	22														
South Bank Centre	TQ 308804	S	27														
London Bridge	TQ 327805	S	29														
Greenwich	TQ 388783	S	37														
Woolwich	TQ 439798	N	44														
Beckton	TQ 456817	N	47														
Crossness	TQ 492809	S	51														
Purfleet	TQ 548786	N	58														
West Thurrock	TQ 592770	N	64	NA	NA	2.12	NA	4.85	255	309	0.44	37.58	3.27	15.69	NA	NA	840
Grays	TQ 614774	N	66														
Tilbury	TQ 647753	N	70	NA	NA	0.43	1.12	2.00	115	325	0.40	14.82	0.73	2.24	3.98	NA	622
Gravesend	TQ 648745	S	70	75.80	NA	0.45	1.00	1.80	208	363	0.45	16.48	0.73	4.14	7.50	NA	723
Coalhouse Fort	TQ 690762	N	75	38.80	9.09	0.24	0.59	1.29	107	268	0.33	11.05	0.69	3.62	5.60	0.987	586
Lower Hope Point	TQ 709776	S	77														
Mucking	TQ 699807	N	80														
Hole Haven	TQ 774821	N	87														
Canvey Island	TQ 800825	N	91														
Allhallows	TQ 834789	S	91	46.58	10.27	0.25	2.38	0.98	48	231	0.29	6.87	0.68	1.37	3.30	0.722	598
Westcliff	TQ 863852	N	97														
Grain Flats	TQ 894751	S	99	NA	NA	0.29	1.75	1.09	50	257	0.24	15.57	0.96	1.05	3.78	NA	492
Southend (Thorpe Bay)	TQ 916844	N	102														
Shoeburyness	TQ 947852	N	106	8.62	13.18	0.22	0.96	0.55	74	237	0.22	13.67	0.98	2.33	4.20	0.549	523
Shell Ness	TR 055682	S	117	5.71	13.94	0.27	1.06	0.53	26	196	0.14	8.24	0.51	0.68	2.80	0.188	486
Foulness	TR 036929	N	117														
UK minimum*				0.18	5.18	0.03	0.16	0.16	10	117	0.06	7.95	0.31	0.39	1.41	0.050	228
UK maximum*				301.0	65.50	9.43	18.40	18.30	1,263	3,663	3.99	411.0	18.70	145.0	138.4	5.88	3,918

Underlined values refer to minimum and maximum values recorded in the 1997 Thames survey

* values from PML/MBA database

NA - Not analysed (below detection limit); empty rows -samples not collected at these sites.

Appendix 10. Metals in *Scrobicularia plana*, Thames 1997.

				Metal (µg g^{-1} dry weight)													
Site	**Mapref**	**Bank**	**Dist**	**Ag**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**	**Mn**	**Ni**	**Pb**	**Se**	**Sn**	**Zn**
Richmond Locks	TQ 168752	N	5														
Kew Bridge	TQ 191779	N	9														
Hammersmith Bridge	TQ 230780	S	15														
Cadogan Pier	TQ 276775	S	22														
South Bank Centre	TQ 308804	S	27														
London Bridge	TQ 327805	S	29														
Greenwich	TQ 388783	S	37														
Woolwich	TQ 439798	N	44														
Beckton	TQ 456817	N	47														
Crossness	TQ 492809	S	51														
Purfleet	TQ 548786	N	58														
West Thurrock	TQ 592770	N	64	NA	NA	0.70	4.26	1.35	76.6	364	0.510	14.1	1.81	21.8	5.45	NA	596
Grays	TQ 614774	N	66	53.1	14.8	1.94	5.68	2.40	51.1	1,338	0.741	39.7	4.10	21.2	9.32	2.56	1,314
Tilbury	TQ 647753	N	70	40.5	15.1	1.22	7.30	2.17	55.3	817	0.583	30.0	3.79	23.2	5.82	1.44	1,057
Gravesend	TQ 648745	S	70	NA	13.1	1.31	3.59	2.57	121.4	693	0.663	38.1	4.07	13.4	6.90	1.54	1,002
Coalhouse Fort	TQ 690762	N	75	32.3	13.3	0.79	3.14	1.60	70.3	657	0.497	27.7	2.78	14.0	6.53	0.94	748
Lower Hope Point	TQ 709776	S	77	24.8	10.3	0.59	2.24	2.12	40.1	990	0.413	32.0	2.09	10.4	6.71	0.92	655
Mucking	TQ 699807	N	80	36.2	12.3	0.90	4.11	3.19	42.1	1,155	0.432	39.6	3.45	19.0	5.81	1.52	841
Hole Haven	TQ 774821	N	87	24.4	15.5	0.61	3.38	1.73	41.6	474	0.407	25.0	3.34	11.2	4.85	0.74	760
Canvey Island	TQ 800825	N	91	15.4	13.0	0.41	2.07	1.23	25.2	523	0.327	31.9	2.69	6.6	5.65	0.24	465
Allhallows	TQ 834789	S	91	34.0	14.9	0.62	4.14	2.25	50.2	949	0.432	30.4	3.04	11.9	7.28	0.75	706
Westcliff	TQ 863852	N	97	18.5	13.6	0.45	2.58	1.01	33.8	577	0.314	31.8	2.78	11.5	4.71	0.47	646
Grain Flats	TQ 894751	S	99	33.0	15.7	0.63	5.26	1.12	74.5	537	0.517	49.1	4.66	12.8	7.17	0.80	767
Southend (Thorpe Bay)	TQ 916844	N	102														
Shoeburyness	TQ 947852	N	106	9.3	17.4	0.42	1.86	0.38	109.1	459	0.326	85.9	4.28	14.1	5.46	0.70	515
Shell Ness	TR 055682	S	117	12.6	12.3	0.45	2.99	0.38	25.2	332	0.190	30.2	1.67	3.8	6.08	0.29	418
Foulness	TR 036929	N	117	16.3	24.6	0.45	3.91	0.60	48.5	382	0.509	96.6	6.16	6.4	5.73	0.13	368
UK minimum*				0.02	4.4	0.10	0.82	0.09	6.8	206	0.015	1.55	0.53	0.45	0.80	0.01	67
UK maximum*				259	297	39.7	97.0	24.8	752	12,702	3.07	405	17.8	1,077	79.00	25.1	5,169

Underlined values refer to minimum and maximum values recorded in the 1997 Thames survey

* values from PML/MBA database

NA - Not analysed (below detection limit); empty rows -samples not collected at these sites.

Appendix 11. Summary of water quality standards (µg l^{-1})

WQO	Fe	Zn	Cu	As	Ni	Pb	Cd	pH
Protection of Estuarine Biology		40 Dem	5 Dem	25 Dem			5 Dem	Range 7-9
EC DSD – Fresh Water	1000 Da	8-125 Ta[1] 30-500T*[1]	1-28 Da[1] 5-112 D*[1]	50 Da	50-200Da[1]	4-20Da[1]	1 Ta	6-9*
EC DSD – Salt Water	1000 Dsa	40 Dsa[2]	5 Dsa	25 Dsa	30Da	25Da	2.5 Dea	6-8.5*

Notes:

EC DSD = EC Dangerous Substances Directive

T = total concentration, µg / l

* = 95 % ile

a = Annual Average

m = annual Maximum

D = dissolved concentration, µg / l :

e, in estuary water;

s, in salt water.

[1] depending on total hardness. QS increases as total hardness of water increases

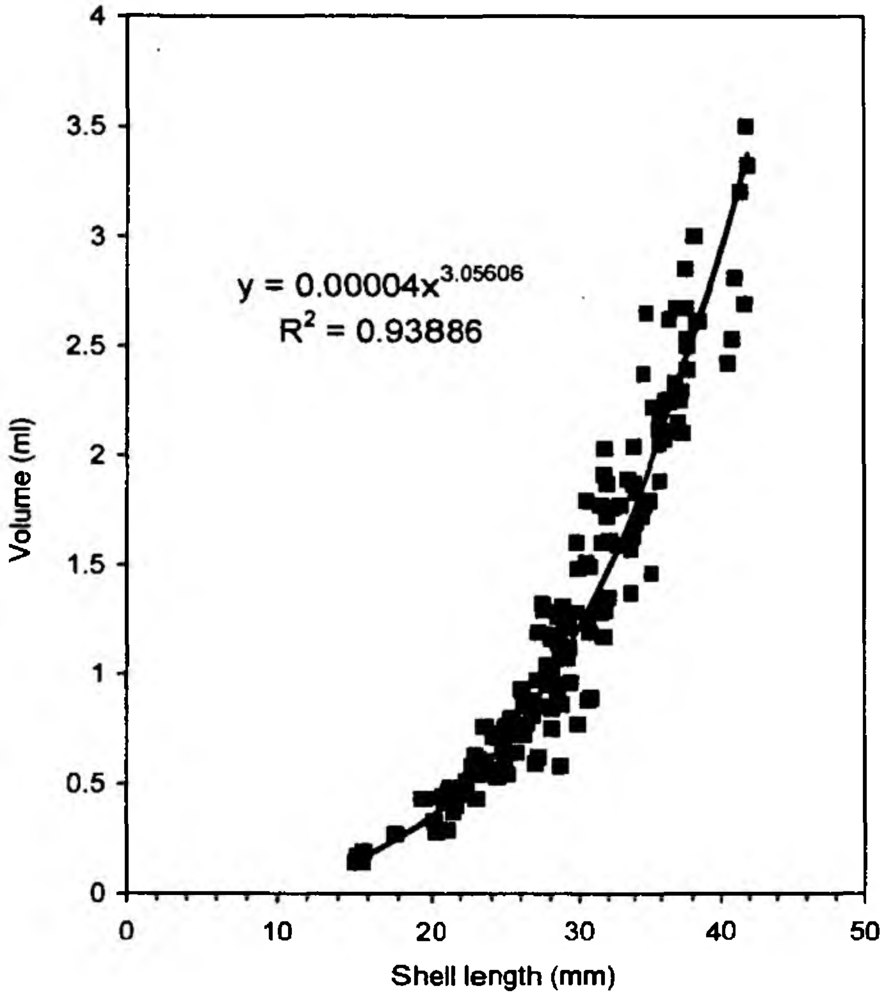
[2] in the future the EQS for Zn may be revised downwards to 10 µg / l

Appendix 12.

Scrobicularia plana: condition index.

For each population this was derived from the equation :
CI = 100 x {dry flesh weight (g) ÷ internal cavity volume (ml)}.

Internal cavity volume was measured by weighing the water held in a selected number of half-shells. By relating this to shell-length (below) the equation could be used to derive the volume of the full collection of *S.plana* (based on measurement of their shell length).



***S. Plana*: relationship between shell length and internal capacity for Thames populations**