Recovery of the Mersey Estuary from Metal Contamination

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Abstract

The Mersey Estuary has received significant quantities of industrial wastes and sewage over several decades. Although contaminant loads are reducing and the estuary is showing signs of recovery, the sediment reservoir remains a repository of historical contamination and still contains high concentrations of trace metals and organic compounds.

A combination of hydrodynamic, sedimentary and geochemical processes are responsible for maintaining trace metal concentrations at present-day levels. The distributions of trace metals in bed sediments reflect changes in granulometry, differences in POC content and the magnitude of past inputs rather than the locations of point sources in the estuary. The association of contaminant metals with SPM varies not only with axial changes in salinity and particle concentration but also in response to the relative magnitudes of freshwater and tidal inflows and cyclic variations in water and particulate chemistry that occur on intratidal, intertidal and seasonal timescales. The most influential of these arise from axial changes in dissolved oxygen and the delivery of organic carbon from both external and internal sources which modify the relative degree of sorptive control exerted by Fe, Mn and organic C at different locations in the estuary and at different times. These factors, combined with the efficient trapping of sediments and possible salting out of neutral metal-organic complexes, assist in the retention and internal recycling of particles and associated metals between the bed and water column. Geochemical reactivity is suppressed in Mersey SPM and metal decontamination is not predicted to occur through the loss of particulate metals to the surrounding coastal zone. Rather, it is envisaged that sediment resuspension and the desorption of metals into fresh and low salinity waters, supplemented by the release of metals from tidally stirred diagenetically modified sediments, are more likely to be important long term cleansing mechanisms, with the latter occurring particularly during the summer months when bacterial numbers and the degradation of accumulated organic detritus becomes more pronounced.

Future declines in metals from bed sediments have been estimated using two methods and two independent data sets. Resulting values are not only metal-dependent but also vary with sediment location. Losses of Cd, Co, Cu, Hg, Ni and Zn are predicted to take up to 40 years, whilst removal of substantially elevated concentrations of Pb in sediments in the upper estuary could span hundreds of years.

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"We have come a long way. We have a long way to go. In between we are somewhere."

(Rheinhold Messner's mantra on his solo and unassisted crossing of Antarctica).

Declaration

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University Award.

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A programme of advanced study was undertaken that included:

- Guided reading in topics relating to marine chemistry and oceanography.
- Development of proficiency in the use of a variety of analytical techniques and instrumentation, particularly in the areas of spectroscopy and radiochemistry.
- Further instruction in estuarine and coastal survey techniques, including successful completion of the RYA Level 4 power boat handling certificate.
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- Research Councils' Graduate School, Otterburn Hall, Otterburn, Northumberland, 04-09 November 1999.
- RYA Level 4 power boat handling, University of Plymouth, June 2000.

Available Data

The original data collected during this study is available as spreadsheets created using Microsoft Excel 97 and stored on the CD-ROM contained in an appendix to copies of this thesis held by the University of Plymouth library.

Conferences and Presentations

- Attendance: **3rd Annual LOIS Conference**, University of East Anglia, 24-26 March 1998.
- Attendance: Royal Society of Chemistry Radiochemical Methods Group **Young Researchers Meeting**, University of Loughborough, 08 July 1998.
- Poster presentation: *'Distribution and reactivity of trace metals in the Mersey Estuary, UK'*, Challenger Society for Marine Science 8th Biennial Conference, **UK Oceanography '98**, University of Southampton, 07-11 September 1998.
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- Oral presentation: *'The distribution and reactivity of trace metals in the Mersey Estuary'*, ECSA Local Meeting **The Coast and Estuaries of North-West England**, Edge Hill College of Higher Education, Ormskirk, 08-09 April 1999.
- Poster presentation: *'Unreactive particles in the Mersey Estuary?'*, 3rd Progress in Chemical Oceanography Conference, **PICO III**, University of Plymouth, September 1999.
- Attendance: Royal Society of Chemistry Environmental Chemistry Group, **Chemical Contaminants in Estuaries and Coastal Waters: Practical Applications of Models**, Scientific Societies' Lecture Theatre, London, 19 November 1999.

- Poster presentation: *'Trace metal reactivity in the Mersey Estuary, UK'*, **3rd SETAC World Congress and Tenth Annual Meeting SETAC-Europe**, Brighton, 21-25 May 2000.
- Oral presentation: *'The transport and flux of sediments, radionuclides and trace metals in estuaries of North-West England'*, Challenger Society Centenary Conference **Marine Science 2002**, University of Plymouth, 09-13 September 2002.
- Oral presentations and weekly attendance at the University of Plymouth Department of Environmental Science Research Seminars.

Signed ...Adrian Watts.......

Dated ...18 October 2004............

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Chapter 1

Introduction

1 Introduction

This work investigates how a combination of hydrodynamic processes and biogeochemical transformations alter the distribution, reactivity and transport of trace metals in the Mersey Estuary. The findings allow a holistic assessment of how spatial and temporal variations in particulate and water chemistry affect metal recycling and the consequences of this in terms of current and future progress in restoration.

1.1 Estuarine management and the regulatory framework

1.1.1 Management issues

Many competing issues and activities affect the coastal environment and inshore waters and with increasing pressures on coastal resources, the need for sustainable management is internationally accepted (JNCC, 2000). Almost two thirds of the global population reside near the coast (Huntley *et al.*, 2001) and within the UK, at least one third of the population lives in towns and cities that are situated on estuaries (Davidson *et al.*, 1991). Britain has 28% of the estuarine resource of the North Sea and Atlantic coasts of Europe, two thirds of which occurs in England.

Estuaries support high population densities, concentrate a diverse range of industrial sites and provide major components in the industrial and transport infrastructure. They can also supply safe anchorage, resources of fish and shellfish and abundant grazing in adjacent marshes. Productive intertidal flats and fringing saltmarshes support internationally important numbers of wintering wading birds and wildfowl, while sand and shingle bars provide breeding grounds for seabirds and seals. A measure of the significance of estuaries for nature conservation in England is that 250 000 hectares have been notified as Sites of Special Scientific Interest (SSSI), equating to 30% of the total area of SSSIs notified (English Nature, 1992).

Estuaries, and coastal waters in general, have traditionally provided convenient disposal of domestic and industrial effluents from onshore developments and water quality in some of the more developed estuaries in the UK (e.g. the Severn, Thames, Mersey, Ribble, Tees and inner Clyde) has suffered as a consequence (JNCC, 2000). Recognition of the extent of impact of anthropogenic activity on estuarine, coastal and marine environments has led to the creation of a wealth of environmental legislation. The enforcement of national and European Directives has resulted in increased pre-treatment of effluents and waste reduction at source through changes to products and waste minimisation. Changes to the industrial structure has occurred in some areas, with reduced operation or closure of manufacturing works and a move to lighter industries also helping to curb pollution. The overall effect has been the gradual improvement in water quality in many estuaries and promotion of more healthy and balanced ecosystems. Increased tourism, waterside regeneration and sustainable development additionally mean that socio-economic benefits can extend far beyond the immediate local community (Mersey Basin Campaign, 2002).

As gross pollution of industrial rivers is reduced, there is greater focus on intermittent and diffuse sources of pollution such as that arising from runoff of agricultural chemicals and fertilisers, and on dealing with past legacies such as contaminated land and sediments and minewater pollution (Edwards, 2001). Key partnerships forged between the research community and environmental management allow greater understanding of processes operating in estuarine environments which can then be incorporated into effective solutions to problems. Computer-based tools for predicting the behaviour and environmental impact of contaminants are being increasingly developed and used and provide important decision support for coastal and estuarine management, as evidenced by the increased use of simulation models by industry and its regulators (Punt, 2000; Jones, 2000, 2002; Spanou and Chen, 2000, 2002).

1.1.2 Legislative control

A range of legislation is in force to control discharges to the aquatic environment in Britain. Information most pertinent to the preservation of water quality has been drawn extensively from the Environment Agency of England and Wales (EA) and UK Marine Special Areas of Conservation Project websites (www.environment-agency.gov.uk and www.ukmarinesac.org.uk, respectively) as well as published sources (NRA, 1995; EA, 2003; JNCC, 2000). Present regulatory drivers that aim to reduce or prevent the pollution of marine, coastal and fresh waters in the UK from industrial, agricultural and domestic activities are provided together with outlines of their main features in Table 1.1.

Table 1.1 refers to the derivation of Environmental Quality Standards (EQS), which are set by the European Union for List I substances and by individual member states for List II substances. Table 1.2 gives current EQS values for dissolved metals appearing in List I and List II for the UK. Values correspond to annual average total dissolved metal concentrations that must be achieved for compliance. Maximum total dissolved metal concentrations reported for a number of major European estuaries are provided for comparative purposes in Table 1.3.

Table 1.1 Table summarising the main legislative drivers for the preservation of water quality in the UK.

Driver	Main features
Dangerous Substances Directive (76/464/EEC)	The establishment of two lists of dangerous substances: • List I: toxic, persistent and bioaccumulative (includes Hg, Cd, HCH, CCl_4 and DDT). Pollution by List I substances must be eliminated. • List II: less dangerous than List I but still have deleterious effects on the aquatic environment. Pollution by List II substances must be reduced. The application of unified emission standards (UESs, also known as limit values) and Environmental Quality Standards (EQSs). Most EU members have adopted UES, whereas EQS is favoured in the UK. Values for EQS are developed on a national level. In the UK, these have been implemented by the Surface Water (Dangerous Substances) (Classification) Regulations 1997 and 1998. Current EQSs for dissolved metals in List I and List II are provided in Table 1.2.
Water Resources Act 1991	Primary statute in England and Wales for controlling the discharge of sewage and industrial or agricultural effluents into freshwater courses and estuaries. Two groups of activities: pollution prevention and control (including waste regulation and water quality) and the management of water resources.
Nitrates Directive (91/676/EEC)	Requires member states to identify waters that are actually or potentially affected by nitrate pollution from diffuse sources and include: • Surface waters, particularly those used for drinking water abstraction where concentrations exceed the mandatory standard of 50 mg l^{-1} nitrate; • Groundwaters actually or potentially containing > 50 mg l^{-1} nitrate; • Freshwater lakes, other freshwater bodies, estuaries, coastal and marine waters which are, or may in the future be, eutrophic. Member states had to designate all areas draining into such waters by 19 December 1993 and establish Action Programmes to control the timing and rate of application of manures & chemical fertilisers in these areas. Sixty-eight Nitrate Vulnerable Zones were duly identified in England and Wales.
Urban Waste Water Treatment Directive (91/271/EEC)	To ensure that all significant discharges of sewage are treated prior to discharge to inland surface waters, groundwater, estuaries or coastal waters. Secondary treatment should normally be provided but discharges to eutrophic-sensitive areas to receive more stringent processing (e.g. removal of N in coastal waters and P in freshwaters). The timetable for the implementation of improvements to estuarine and coastal waters is: • Provision of 2° treatment for discharges > 15 000 population equivalents (pe) by 31 December 2000; • Provision of 2° treatment for discharges of 2 000 – 15 000 pe in estuaries and 10 000 – 15 000 pe in coastal waters by 2005; • Appropriate treatment for smaller discharges by 2005.
Convention for the Protection of the North-East Atlantic (OSPAR Convention)	To prevent and eliminate pollution and to protect the maritime area against the adverse effects of human activities. Entered in to force in 1998. Application of the precautionary and 'polluter pays' principles, best available techniques (BAT) and best environmental practice (BEP), including clean technology. A series of annexes deal with the prevention and elimination of pollution from land-based sources, offshore sources and through dumping or incineration, the assessment of quality of the marine environment and the protection and conservation of ecosystems and biological diversity.
Integrated pollution prevention and control	Within the EU environmental policy since 1996. Attempts to address pollution in a holistic way, taking account of releases to air, water and land and focuses on the prevention, where practicable, of emissions from industrial processes and assists in establishing BEP in industry.
Water Framework Directive (2000/60/EC)	Expansive legislation that attempts to establish a new common management for the delivery of water policy and is anticipated to have a fundamental impact on existing and proposed legislation. Limit values and EQSs to be applied to the control of discharges and in controlling abstractions of surface and groundwaters. Many previously-adopted Directives addressing individual issues (e.g. the control of sewage effluents or dangerous substances) will be drawn together in this Directive, thus enabling an integrated approach towards sustainable water management. Importantly, the Directive will also provide a framework for the inclusion of ecology-based EC legislation such as the Habitats and Biodiversity (conservation) Directives. The WFD was incorporated into UK legislation at the end of 2003 and good water status has to be delivered for most waters by the end of 2015. River basin management plans must be developed (with coastal waters being assigned to the relevant river basin district) and these must register all Protected Areas in the river basin district.

Table 1.2 Environmental Quality Standards for List I and List II metals.

Metal	Annual mean concentration (μg l^{-1})
List I	
Cd and its compounds	5.0
Hg and its compounds	0.5
List II	
As	25
Cr	15
Co	3.0
Cu	5.0
Pb	25
Ni	30
Zn	40

Table 1.3 Maximum estuarine concentrations of dissolved trace metals in a number of major European estuaries.

	Dissolved metal (μg l^{-1})					
Estuary	**Cd**	**Cu**	**Ni**	**Pb**	**Zn**	**Reference**
Forth	0.017	2.5	0.98	0.38	2.5	Balls *et al.* (1994)
Humber	0.48	10	12	-	20	Comber *et al.* (1995)
Loire	0.033	1.4	-	-	-	Waeles *et al.* (2004)
Mersey	0.070	2.4	10	2.5	17	Comber *et al.* (1995)
Scheldt	0.15	1.6	11	0.29	13	Paucot and Wollast (1997); Baeyens *et al.* (1998b)
Seine	0.21	2.3	2.9	-	13	Chiffoleau *et al.* (1994)
Severn	0.42	4.9	-	0.60	18	Apte *et al.* (1990)

The data in Table 1.3 indicate that dissolved metal concentrations comply with regulatory standards for a number of the most heavily industrialised estuaries in Western Europe. The only estuary for which non-compliance is suggested is the Humber, where dissolved Cu reaches a concentration that is double the current EQS whilst in the Severn, dissolved Cu concentrations approach the acceptable limit.

The EQSs in Table 1.2 are only applicable to the water column and currently no equivalent standards have been set for sediments in the UK. Attempts to classify sediments according to contaminant concentration and toxicity thresholds have been made elsewhere however and Table 1.4 gives current Canadian interim sediment quality guidelines for trace metals (CCME, 1999). Also provided in Table 1.5, are mean trace metal concentrations (available to concentrated HNO_3 from the < 100 μm grain size fraction) in a survey of 19 UK estuaries conducted by Bryan and Langston (1992). The data demonstrate that considerable exceedance of these quality guideline limits could occur in sediment-dominated estuaries where: (1) metal inputs are considerable and (2) physical or biogeochemical conditions allow the long-term retention of particles and any particle-reactive contaminants associated with them. Thus, whilst metals in the dissolved phase do not generally pose any environmental concern, the same cannot be said for those in estuarine sediments. This indicates that for some estuaries, substantial measures would be necessary to adequately reduce metals that have accumulated within the sediment reservoir, especially those that have a strong association with estuarine particulate material.

Table 1.4 Interim marine sediment quality guidelines (ISQGs) and probable effect levels (PELs).

Metal	ISQG ($\mu g\ g^{-1}$)	PEL ($\mu g\ g^{-1}$)
As	7.24	41.6
Cd	0.7	4.2
Cr	52.3	160
Cu	18.7	108
Hg	0.13	0.70
Ni	-	42.8*
Pb	30.2	112
Zn	124	271

* Value taken from Buchman (1999), quoted in Spencer and MacLeod (2002).

Table 1.5 Mean metal concentrations ($\mu g\ g^{-1}$) in sediments from a selection of UK estuaries. Figures in bold denote the highest concentrations observed in a total of 19 estuaries.

Estuary	Cd	Co	Cu	Fe	Hg	Mn	Ni	Pb	Zn
Gannel	1.35	**26**	150	25420	0.08	649	38	**2753**	940
Humber	0.48	16	54	35203	0.55	1015	39	113	252
Mersey	1.15	13	84	27326	**3.01**	**1169**	29	124	379
Restronguet Creek	1.53	21	**2398**	**49071**	0.46	485	**58**	341	**2821**
Severn	0.63	15	38	28348	0.51	686	33	89	259
Tamar	0.96	21	330	35124	0.83	590	44	235	452
Thames*	1.30	-	61	28228	0.60	552	34	179	219
Tyne	**2.17**	11	92	28206	0.92	395	34	187	421

* Data are from Attrill and Thomes (1995) and relate to digestion of < 63 μm sediments with HNO_3/H_2O_2.

Care needs to be exercised in the adoption of sediment quality values (SQVs) in the UK, as recent research has suggested limitations to current practice. These include the need to examine vertical metal profiles in estuaries with low sediment accumulation rates, where historically contaminated sediments are in the shallow subsurface zone and where erosion or dredging may occur. Also, the use of total rather than labile metal concentrations may over- or under-estimate the ecotoxicological risk to biota in geochemically dissimilar estuarine sediments (Spencer and MacLeod, 2002). The adoption of regional SQVs in a tiered sediment hazard/risk assessment approach such as an ecological risk assessment may prove more useful but these should also incorporate site-specific data including background concentrations and factors that may influence metal bioavailability (Chapman *et al.*, 1999).

1.1.3 The classification of estuarine status

The UK Environment Agency's General Quality Assessment (GQA) scheme is intended to enable consistent and quantitative comparisons of water quality, both over time and between different geographic areas. The components used in this classification are basic water chemistry, nutrients, biology and aesthetics.

For chemistry and nutrient determinations, around 7 000 sites, representing around 40 000 km of rivers and canals and 2 800 km of estuaries, are sampled 12 times each year (EA, 2002a). Classification is based on the combination of results for three years. Samples are analysed for three indicators of organic pollution: ammonia, biochemical oxygen demand (BOD) and dissolved oxygen (DO). Results for each location are averaged and percentiles are calculated. These are compared with limits set for each of six grades. A grade is assigned to the reach from which the sample was collected and this corresponds to the lowest grade achieved by any of the three chemical determinands. Grading is based on the ability to support salmonid and cyprinid fisheries, the suitability of water for abstraction and perceived perturbation to the ecosystem. Samples are also analysed for nitrate and orthophosphate and grades are assigned according to mean concentrations.

For biological quality, around 6 500 sites are sampled twice by kick sampling during survey years, usually in the spring and autumn. Macro-invertebrates are identified and species diversity is compared to an expected range in a river that is not polluted or physically damaged. This takes account of natural differences in geology and flow and one of six grades are allotted to each stretch.

Around 450 popular tourist sites are sampled for aesthetic quality. Both the water surface and banks accessible to the public are considered. The amount and type of each factor (litter, oil, scum, foam, sewage fungus, colour and odour) are considered separately to assign a class. Individual classes are then combined after weighting for perceived importance to give an overall grade. Oil, scum, foam, sewage fungus and ochre are classified on percentage cover of the water surface, colour by its hue and intensity and odour, by its type and intensity.

Estuarine water quality classifications as determined by the EA for all estuaries in England and Wales in 1990, 1995 and 2000 are shown in Figure 1.1. The percentage of estuarine waters receiving each classification between 1980-2000 is also provided in Table 1.6. The quality of many of the UK's estuaries improved in the 1960s and 1970s as a direct result of investments in sewerage networks and sewage treatment works (STW), the construction of new long sea outfalls to aid the advection and dispersion of effluents away from coastal areas and the diversion of industrial discharges to sewers or treatment plants. Estuary quality stabilised between 1980-1985, but a small deterioration in overall quality was observed between 1985-1990, which was partly explained by prolonged dry spells in 1989 and 1990 causing reduced fluvial inflows into the majority of estuarine systems (EA, 2002a). By 1995, some improvement was made and by 2000 water quality was significantly better than in 1980. Further progress is expected in the next decade as around 800 water company discharges to estuaries will be further improved between 2000-2005 (EA, 2002a).

Table 1.6 Water quality in the estuaries of England and Wales, 1980-2000.

Class	**1980**		**1985**		**1990**		**1995**		**2000**	
	km	**%**	**km**	**%**	**km**	**%**	**km**	**%**	**km**	**%**
Good	1 870	68	1 863	68	1 805	66	1 824	66	1 997	72
Fair	620	23	637	23	655	24	738	27	663	24
Poor	140	5	132	5	178	7	108	4	67	2
Bad	110	4	89	3	85	3	115	4	48	2
All classes *	2 740	100	2 722	100	2 722	100	2 785	100	2 775	100

* Total estuarial length changed in 1995 as a result of re-classification and revised measurements. Source: DEFRA (2003)

Salmon and sea trout have returned to many estuaries in Britain. For example, water quality in the Tees has continually improved since 1970, when the estuary was virtually dead. Discharges of high BOD wastes have substantially declined from over 500 t d^{-1} in 1970 to around 35 t d^{-1} in 2000 and inputs of toxic substances such as

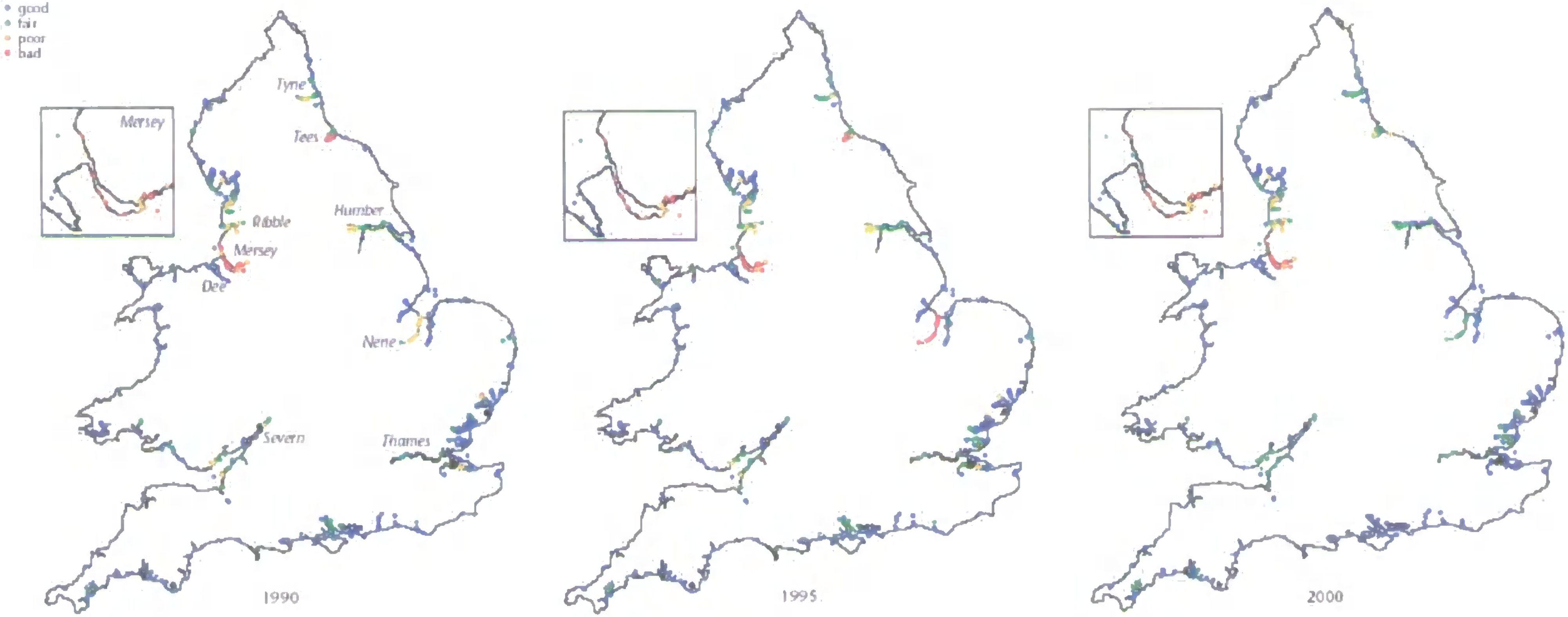


Figure 1.1 Estuary quality in England and Wales, 1990, 1995 and 2000. Source: EA (2002a).

ammonia, organic chemicals and trace metals have also fallen (EA, 2002a). The main estuary is now classed as good or fair quality (Figure 1.1) and the EA estimates that approximately 7 000 salmon and 13 000 sea trout migrated through the Tees Estuary in 2000.

1.2 Processes affecting trace metal behaviour in estuaries

An estuary is a semi-enclosed coastal body of water which has free connection to the open sea, extending into the river as far as the limit of tidal influence, and within which seawater is measurably diluted by freshwater derived from land drainage (Dyer, 1997). Estuaries are both physically and chemically dynamic regions where the mixing of fresh and saline waters results in the production of sharp gradients in the estuarine master variables of salinity, temperature, dissolved oxygen, pH, particle character and concentration. The spatial and temporal variability in physico-chemical conditions encountered throughout an estuary influences the extent to which biogeochemical processes such as sorption, flocculation and the redox cycling of contaminants can take place (Millward and Turner, 1995), as exemplified in Figure 1.2.

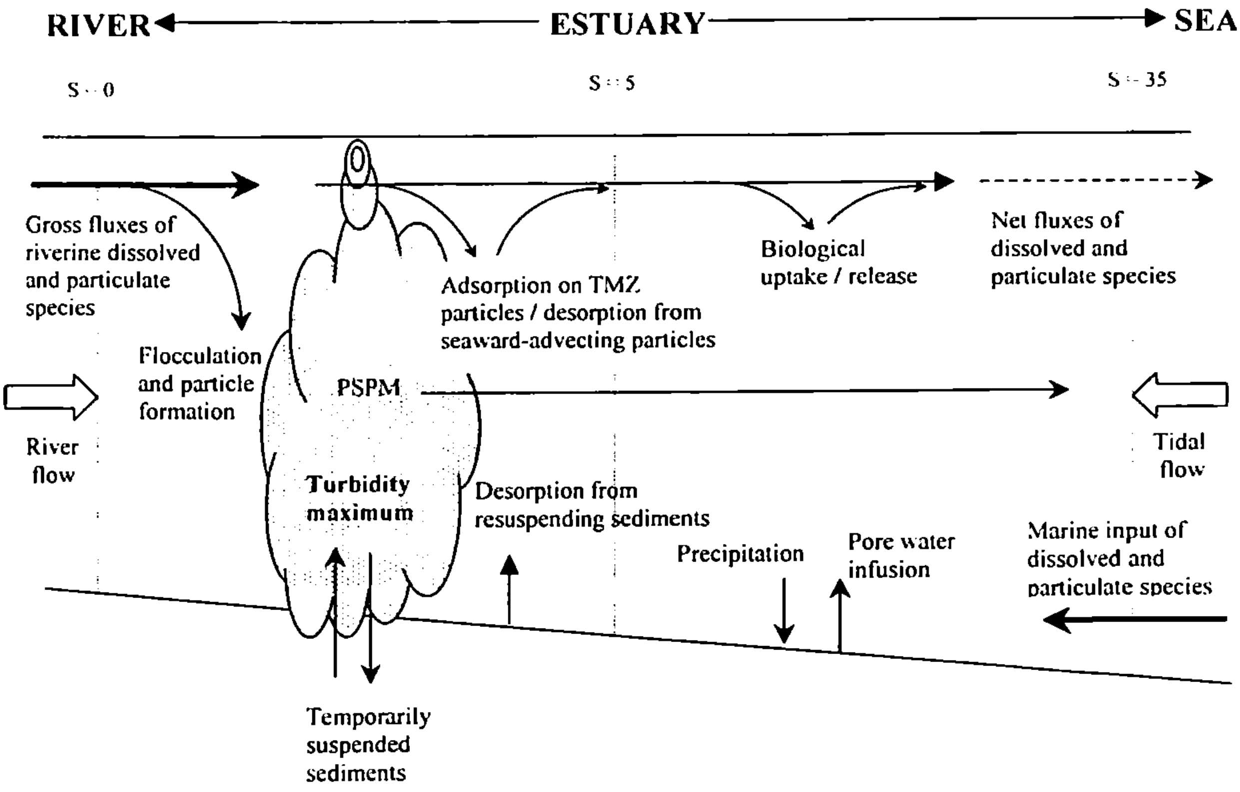


Figure 1.2 Significant processes affecting the transport and reactivity of trace metals in estuaries.

1.2.1 Hydrodynamic processes and particle transport

Estuaries may be classified according to topography and salinity structure, although the limits of each estuarine type are not well defined (Dyer, 1997). The degree of vertical stratification is controlled by circulation and mixing which, in turn, depend on the relative proportions of riverine and tidal forcing in any given system. The extent of mixing has important implications for the physical transport of material and the time available for heterogeneous chemical reactions to take place.

Highly stratified (salt wedge) estuaries are dominated by high and variable fluvial input relative to tidal inflow (Dyer, 1991) and the flow ratio (the ratio of river flow per tidal cycle to the tidal prism) is ≥ 1.0 (Simmons, 1955). Lower density freshwater flows out of the estuary over a denser seawater layer flowing landward near the estuary bed. A sharp halocline exists between the two water masses and there is little entrainment of salt water into freshwater. Rapid increases in salinity and a distinct freshwater-seawater interface (FSI) results (Dyer, 1994). The position of the salt wedge varies with river flow and the tidal range is usually microtidal (< 2 m).

Partially mixed estuaries tend to be mesotidal, having tidal ranges of 2-4 m (Dyer, 1994). Being slightly less influenced by freshwater flow than highly stratified estuaries, flow ratios of ~ 0.25 are observed (Simmons, 1955). The entire water mass moves up and down the estuary in response to tidal oscillation. Friction at the bed caused by tidal currents creates turbulence and this stimulates mixing between river water and seawater. Axial salinity profiles are typically S-shaped, with seawater and freshwater salinities separated by a zone of mixing (Dyer, 1997). The intensity of the salinity structure varies with the spring-neap cycle - stronger tidal currents during spring tides encourage vertical homogeneity in salinity, whilst stratification can occur during less energetic neap tides (Dyer, 1991; Peters, 1997).

Macrotidal estuaries with tidal ranges in excess of 4 m can be well mixed. These estuaries are usually tidally dominated and correspondingly, low flow ratios of < 0.1 are produced (Simmons, 1955). Here, the tidal range is large compared to the water depth and the turbulence produced by the velocity shear on the bed may be significant enough to mix the water column completely and make the estuary vertically homogeneous. Although gravitational circulation is produced by denser water attempting to flow landwards beneath the fresher water, it is insufficient to overcome the strong vertical mixing induced by tidal currents and stratification is impeded (Dyer, 1997).

Increased river flows cause a more rapid circulation of water. Exchange of freshwater with the sea is increased but the volume of freshwater accumulating in the estuary does not increase at the same rate as the fluvial supply. The flushing time (or water residence time), τ, is the time required to replace the existing freshwater in an estuary (or segment thereof) at a rate equal to the river discharge (Officer and Lynch, 1981; Dyer, 1997) and is given by:

$$\tau = \frac{V_f}{Q} \qquad \text{Equation 1.1}$$

where V_f is the volume of freshwater accumulated (m^3) and Q is the river flow ($m^3\ s^{-1}$) (Dyer, 1997). The cumulative flushing time for the entire length of an estuary is usually of the order of tens of days (Dyer, 1997). As the total volume of water in an estuary increases with distance from the head due to widening and deepening, the flushing time also increases (Uncles *et al.*, 1985) and this is additionally influenced by the tidal state (Uncles and Stephens, 1996). The flushing time exerts a key hydrodynamic control on estuarine chemical reactivity by directly influencing the amount of time that can be allowed for the establishment of thermodynamic equilibrium conditions. Approximately 99% conversion of reactants to products can only be achieved if the ratio of the first order reaction half-life to flushing time is < 0.1 (Morris, 1990). Thus, chemical equilibria are more likely to be attained in estuaries with long flushing times. However, realistic estimations of river-ocean fluxes are more complicated in such systems. This is because the actual freshwater discharge at any given time is unlikely to be representative of that when the constituent of interest entered the estuary and this could lead to considerable errors in flux calculations (Paucot and Wollast, 1997; Regnier *et al.*, 1997, Baeyens *et al.*, 1998a). The characteristics of four British estuaries, including tidal range, flushing time and stratification are listed in Table 1.7.

Table 1.7 Physical characteristics of four contrasting British estuaries.

Characteristic	**Tweed**[a]	**Tamar**[b]	**Humber**[c]	**Mersey**[d]
Catchment area (km^2)	4900	900	18100	5000
Mean river flow ($m^3\ s^{-1}$)	50	19	284	30
Typical tidal range (m)	2-4	2-5	3-7	3-10
Flushing time (d)	0.5-3	7-14	40	20 – 50[e]
Stratification	salt wedge/ partly mixed	partly mixed	partly/well mixed	well mixed
Turbidity ($mg\ l^{-1}$)	<0.1-10	10-450	10-5000	15-700[f]
Sediment discharge ($t\ a^{-1}$) *	4.5×10^4	1×10^4	12.6×10^4	4.6×10^4

[a] Uncles and Stephens (1996, 1997); [b] Uncles and Stephens (1993); [c] Gameson (1982); [d] NRA (1995); [e] Jones (1978); [f] this study; * derived from $y = 60x^{0.78}$ (Wilmot and Collins, 1981) where y = sediment flux ($t\ a^{-1}$) and x = catchment area (km^2).

An area of enhanced turbidity, the turbidity maximum zone (TMZ) exists in the low salinity region of macrotidal estuaries (Uncles *et al.*, 1985; Bale *et al.*, 1985). This is generated by estuarine gravitational circulation (Dyer, 1997) and maintained by tidal resuspension of cohesive bed sediment and the upestuary 'pumping' of resuspendable material by tidal asymmetry (Uncles *et al.*, 1985; Ackroyd *et al.*, 1986; Uncles and Stephens, 1989; Dyer, 1994). Concentrations of suspended particulate matter (SPM) are considerably higher in the TMZ than in riverine or marine end-members (Muller *et al.*, 1994) and the zone is generally one of pronounced geochemical reactivity due to the physical selection and chemical modification of estuarine particles (Morris *et al.*, 1982a, 1986; Morris, 1990; Turner *et al.*, 1991). The TMZ is usually located at, or near to, the freshwater-saltwater interphase (FSI), but can shift up- or downestuary in response to low or high river flows, respectively (Uncles and Stephens, 1989). However, its position also varies semidiurnally and with the fortnightly spring-neap cycle (Dyer, 1997, Guézennec *et al.*, 1999). The TMZ is pushed further upestuary during springs than neaps due to increased mean water level at the head of the estuary caused by the higher tidal range during spring tides. Guézennec *et al.* (1999) have shown that maximum downestuary fluxes of SPM could occur during the spring-neap transition (Figure 1.3).

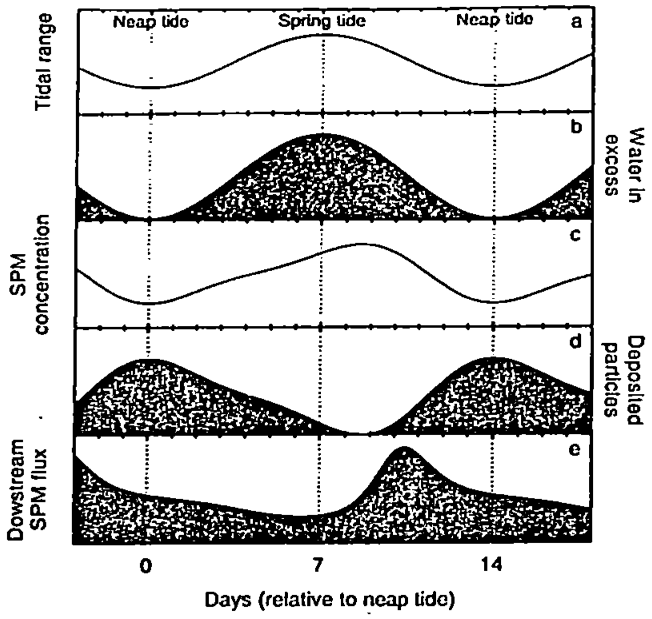


Figure 1.3 Spring-neap variations in particle transfer in the upper Seine Estuary during low river discharge. Source: Guézennec *et al.* (1999).

Fine-grained mobile particles in the FSI/TMZ may originate as either river-borne sediment or as tidally-advected particles of marine origin. Particle size is governed by turbidity, turbulent shear, salinity and organic content. Particles flocculate upon contact with saline water, forming larger aggregates. As effective particle size increases, densities decrease but settling velocities increase. The specific surface area (SSA) is a conceptual measure of particle reactivity (Turner *et al.*, 1991). It has been demonstrated in the Elbe, Humber and Tamar estuaries that significant maxima in SSA of particles exist and each time a TMZ is formed, the total SSA lies between 5 and 20 $m^2\ l^{-1}$. This represents a considerable amount of active surface and therefore implies the favoured removal of dissolved constituents (Millward *et al.*, 1990). *In situ* laser particle sizing experiments in the Tamar Estuary (Bale *et al.*, 1990), have shown that peak current velocities assist in the generation of the highest SPM concentrations and that this SPM is composed of relatively small, rapidly settling, discrete particles with a median size of 10 - 30 µm. When current velocity decreases to a minimum, such as occurs at slack water, the particle population is comprised of much larger (median size of 100 µm) fragile, low density aggregates. This transition from one particle type to another has been interpreted as reflecting selectivity in the behaviour of grains resuspended from the bed combined with the destruction of fragile aggregates through tidal shear.

These studies have led to the hypothesis that physical processes in the TMZ may combine to generate two particle types - permanently suspended particulate matter (PSPM), which tends to predominate at low SPM concentrations and temporarily suspended particulate matter or TSPM, the prevalence of which increases as turbidity increases (Williams and Millward, 1998). PSPM is thought to be a major carrier of trace constituents and is composed of small, low-density detrital material with high SSAs and low settling velocities. It is suggested that these particles could therefore undergo significant seaward advection and pass the estuarine freshwater-saltwater interphase. Conversely, TSPM is composed of larger, denser material with smaller specific surface areas, is derived from the resuspension of bed sediment by tidal shear and exists as flocs as well as discrete particles. These particles are usually higher in mineral content, have higher settling velocities and could consequently be subject to a more limited axial transport. A full understanding of the physical and chemical nature and mobility of these different particle types is therefore essential for accurate determinations of land-ocean fluxes of contaminants and to quantify the exchange of components between dissolved and particulate phases (Turner *et al.*, 1994).

Repeated alternating cycles of erosion (during the flood and ebb) and deposition (during periods of slack at high and low water) promotes the regular cycling of particulate material and associated particle-reactive contaminants between the bed and water column. A feature of considerable importance in muddy estuaries lies in the fact that these particles become trapped and can remain associated with the TMZ for considerable lengths of time (Dyer, 1997). For example, in the Tamar Estuary, particles are estimated to be retained in the TMZ for 1.4 years (Bale *et al.*, 1985) compared to a flushing time of 7-14 days (Uncles *et al.*, 1985). Similarly, the residence time of SPM in the Humber Estuary is estimated at 18 years, whereas that for water is up to 40 days. Thus, estuaries are often sinks for sediment (e.g. Calmano *et al.*, 1996; Ridgway and Shimmield, 2002; Spencer *et al.*, 2003). The possession of high surface areas and long residence times allow the composition of fine estuarine particles to reflect both contemporary and historical inputs (Turner, 2000), although some evidence suggests that particle reactivity diminishes with age (Moore and Millward, 1988). Nevertheless, substantial periods may be required for decontamination of estuarine sedimentary regimes that have been impacted by human activity (Cato *et al.*, 1980). This is likely to be significant in some estuaries in the UK where metal concentrations in bed sediments are considerable, such as those shown in Table 1.5 for example.

1.2.2 Estuarine trace metal distributions

Rivers transport trace metals to the ocean in dissolved, colloidal and particulate forms. The estuarine reactivity of dissolved elements are usually described by comparing its concentration against that of a (quasi-) conservative element (typically salinity), to generate a mixing curve (Morris, 1990) as in Figure 1.4. The theoretical dilution line (TDL), joining two end members of constant composition, signifies conservative (noninteractive) behaviour where the distribution of a dissolved constituent is simply the result of mixing and dilution. Positive and negative deviations from the TDL imply inputs

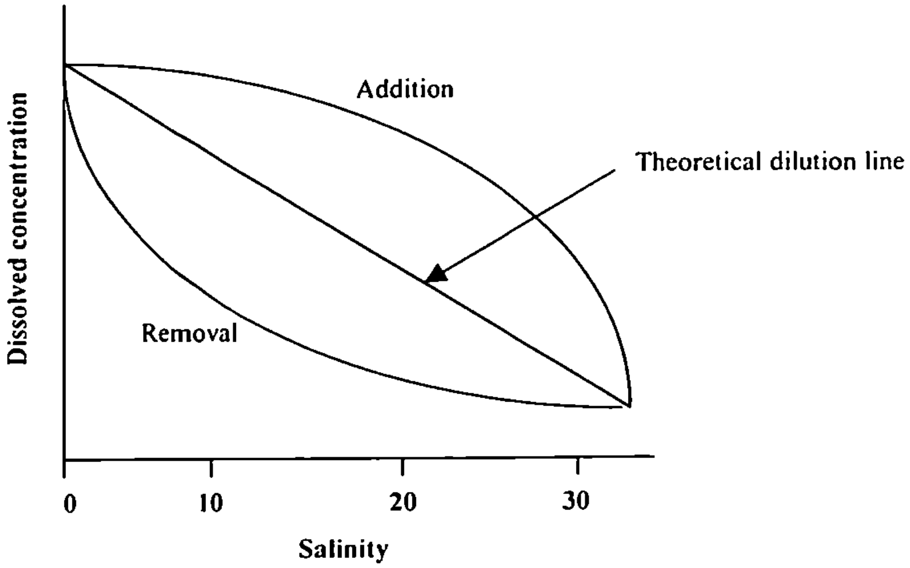


Figure 1.4 Representation of the estuarine distributions of a dissolved constituent under steady-state conditions.

to the dissolved phase (from anthropogenic sources, tributaries, porewater infusion or desorption from contaminated particles) or removal onto the particulate phase, respectively, arising either from non-conservative behaviour or temporal variability in end member composition (Cifuentes *et al.*, 1990).

Axial distributions of trace metals can exhibit considerable interestuarine variability in response to the unique biogeochemical and hydrodynamic conditions of individual systems, as illustrated for dissolved and particulate metals in Tables 1.8 and 1.9.

Table 1.8 Field observations of dissolved metal behaviour in the estuaries described in Table 1.7.

Estuary	Metals	Behaviour	References
Tweed	Cd, Cu	Conservative	Tappin *et al.*, 2001
	Mn	Addition	Tappin *et al.*, 2001
	Pb	Removal at low salinity, addition/conservative at higher salinities	Tappin *et al.*, 2001
	Ni, Zn	Unresolved	Tappin *et al.*, 2001
Tamar	Cd, Cu, Mn, Ni, Zn	Removal at low salinity, Midestuary addition	Morris *et al.*, 1982b,1986; Ackroyd *et al.*, 1986; Liu, 1996
Humber	As, Cu	Conservative/ slight addition	Comber *et al.*, 1995
	Cd, Ni, Zn	Addition	Campbell *et al.*, 1988; Comber *et al.*, 1995
Mersey	Cd, Cr, Cu, Zn	Removal at low to mid salinities	Comber *et al.*, 1995
	Ni, Pb (inorganic)	Addition	Riley and Towner, 1984; Comber *et al.*, 1995

Table 1.9 Concentration ranges (where available) of selected dissolved and suspended particulate trace metals for three of the estuaries described in Table 1.7.

		Metal concentration			
Estuary		**Cd**	**Cu**	**Ni**	**Zn**
Tamar[a]	*Dissolved* ($\mu g\ l^{-1}$)	0.0050-0.12	0.50-13	0.40-2.5	2.50-12
	Particulate ($\mu g\ g^{-1}$)	-	150-760	-	260-1100
Humber[b]	*Dissolved* ($\mu g\ l^{-1}$)	0.060-0.48	1.8-10	3.0-12	3.5-20
	Particulate ($\mu g\ g^{-1}$)	-	32, 34, 62	3.5-45	180, 280, 280
Mersey[c]	*Dissolved* ($\mu g\ l^{-1}$)	0.015-0.070	0.90-2.4	2.3-10	7.5-17
	Particulate ($\mu g\ g^{-1}$)	0.49-1.2	24-56	19-55	310-450

[a] Morris *et al.* (1986). Particulate data refer to total metals released by *aqua regia* + HF. [b] Data for dissolved metals are from Comber *et al.* (1995). Data for particulate Ni (available to 1M HCl) are for samples taken from the Humber plume by Millward *et al.* (2002). Data for particulate Cu and Zn are mean concentrations (available to 1M HCl) in winter, spring and summer respectively, in SPM sampled near the mouth of the Humber where S>30 from Turner and Millward (2000). [c] Data for dissolved metals are from Comber *et al.* (1995). Data for particulate metals are from Laslett (1995) using conc. HNO_3.

The concentration and geochemical composition of particulate matter, which naturally varies both in space and time, fundamentally influences the cycling of trace metals in estuaries (Ackroyd *et al.*, 1986; Balls, 1990; Turner *et al.*, 1992a,b; Wood *et al.*, 1995; Millward and Turner, 1995; Tipping *et al.*, 1998). Estuarine particles are derived from catchment and coastal erosion. Consequently, underlying lithogenous phases may comprise a heterogeneous mixture of clays, quartz, feldspars and carbonates. Flocculation in slightly saline water and *in situ* biological production can produce further phases (Millward and Turner, 1995). Hydrous Fe and Mn oxide precipitates coat mineral phases, have high adsorptive capacities and are therefore important for the sequestration and transport of trace metals in natural waters (Turner, 2000). Particles also possess surface coatings of organic compounds, which can be of marine or terrestrial (including anthropogenic) origin. Organic matter is able to modify the solubility, redox potential and precipitation behaviour of trace metals and this occurs primarily through the complexation of metals with sedimentary humic compounds (Sholkovitz, 1976; Duinker, 1980). Unlike Fe and Mn oxides, which are implicated in enhancing the SSAs of particles (Martin *et al.*, 1986; Glegg *et al.*, 1987), the presence of organic carbon reduces SSA (Millward *et al.*, 1990), although this is dependent on the nature and reactivity of organic matter present, the latter of which can be altered by masking effects (Garnier *et al.*, 1993).

The transfer of metals to and from the dissolved phase *via* desorption and adsorption from particulate matter is critically dependent on the speciation, colloidal interaction, redox sensitivity, microbial mediation, pre-existing particulate metal loading and particle composition (Oakley *et al.*, 1981; Morris, 1986; Millward *et al.*, 1990; Wen *et al.*, 1997; Tipping *et al.*, 1998; Benoit and Rozan, 1999; Zwolsman and van Eck, 1999; Martino *et al.*, 2002). Each of these factors may additionally be subject to temporal (intratidal, intertidal and seasonal) and spatial variations (Church, 1986; Morris, 1986; Chiffoleau *et al.*, 1994; Zwolsman *et al.*, 1997; Uncles *et al.*, 1998b; Veyssey *et al.*, 1999). To avoid repetition, a description of processes affecting the extent of recycling or elimination of trace metals in estuaries is provided later in Section 1.3.

1.2.3 Solid-solution partitioning

Central to the prediction of trace metal behaviour in estuaries is the use of the conditional distribution coefficient, K_D, which defines the ratio of adsorbed or particulate concentration (P, w/w), to dissolved concentration (C, w/v) of a chemical constituent:

$$K_D = \frac{P}{C} \qquad \text{Equation 1.2}$$

Partition coefficients are often derived from field measurements of particulate and dissolved metal concentrations in estuaries and coastal waters (Valenta *et al.*, 1986; Balls, 1989; Turner *et al.*, 1992b; Balls *et al.*, 1994; Paucot and Wollast, 1997; Achterberg *et al.*, 2003; Zhou *et al.*, 2003). However, there are several limitations to their use. Firstly, analytically determined particulate concentrations are highly dependent on the acid digest employed and resulting total or partial extractions often over-represent the fraction of exchangeable metal that is naturally available for solid-solution interaction (Turner, 1996). Secondly, a wide variety of acid leaches are used and this presents difficulties when trying to elucidate inter-estuarine differences in metal partitioning. Conventional filtration techniques can lead to the inclusion of colloidal metals within the dissolved fraction, thus introducing another bias in the quantification of K_D (Benoit and Rozan, 1999). The speciation of dissolved components may also have an effect on K_D as can the natural variability of SPM concentration. With the latter, changes in suspended load are often accompanied by changes in particle character and this often produces an inverse dependency of K_D on particle concentration (Turner, 1996). The so-called 'particle concentration effect' has been demonstrated both in the laboratory and in the field for a wide variety of chemicals and sorbent phases and is likely to result from an assortment of physical and chemical mechanisms including colloidal interactions, sorption reversibility and experimental artefacts (Turner and Millward, 2002). Alternatively, particle-water interactions may be replicated by using radioisotopes in laboratory experiments where salinity and turbidity are controlled (Li *et al.*, 1984a,b; Jannasch *et al.*, 1988; Turner *et al.*, 1993; Millward *et al.*, 1994). This possesses several advantages over field K_Ds including the direct measurement of immediately reactive components, but the commonly employed batch mixing experiments do not account for the often considerable natural *in situ* variability of both water and particle composition (Turner, 1996).

The comparison of K_Ds determined in short-term sorption experiments and those of constituents in the natural environment is a critical domain. Li *et al.* (1984b) found a difference of two orders of magnitude between radiotracer and stable element K_Ds as demonstrated in Figure 1.5. This contrariety is primarily due to a high exchangeability of surface-available constituents with radionuclides against elements that are held less exchangeably within the particle matrix. Similarly, Balls (1989) found that field and laboratory partition coefficients for Cd and Zn, using samples obtained from a number of coastal environments, varied by 1-2 orders of magnitude. In contrast, K_Ds were more similar for stable Hg and ^{203}Hg, suggesting that this metal exhibits a greater particle affinity which allows for differences in analytical methodology to be overcome.

The distribution of trace metals between dissolved and particulate phases is primarily controlled by variations in salinity and particle concentration (Turner, 1996). Whilst K_Ds are estuary-specific and metal-specific, they also vary with more localised changes in temperature, pH, solution composition and the physical and chemical properties of SPM (Li *et al.*, 1984a; Turner *et al.*, 1992b; Wood *et al.*, 1995). Temporal variability in both SPM type and concentration induced by short-term events such as tidal resuspension or longer-term seasonal variability, will influence the capacity of SPM to adsorb dissolved trace metals although in turbid systems, metals are mainly carried in the particulate phase (Turner and Millward, 1994). Seasonal variations in determinands are linked to changes in river flow, temperature and biological processes such as diatom and algal growth (Robson and Neal, 1997; Luoma *et al.*, 1998). Thus, apparent relationships may not hold at different times of year in the same estuary. Also, it should not be assumed that the extent of metal partitioning in any one system can be anticipated in another experiencing entirely different hydrodynamic and biogeochemical controls (Koelmans and Radovanovic, 1998).

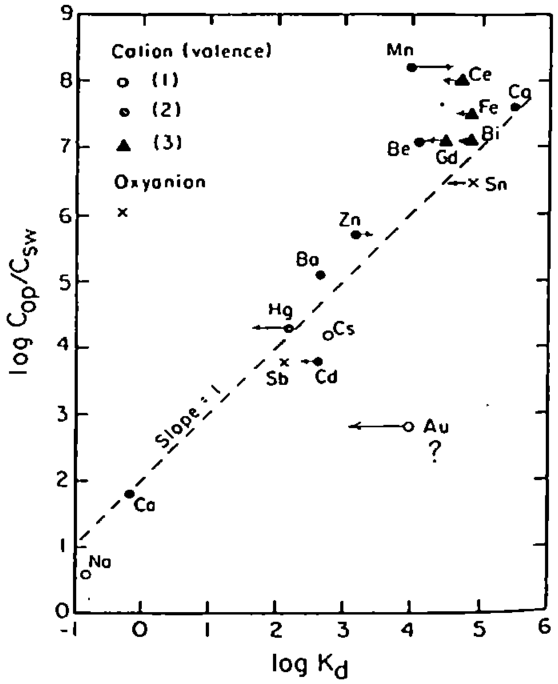


Figure 1.5 Comparison of the natural partition coefficient for some elements (x-axis) with 'adsorption' K_Ds (y-axis) determined for various radiotracers and a red clay suspension of particle concentration 400-1700 mg l^{-1}. Source: Li *et al.* (1984b).

Ackroyd *et al.* (1986) have used K_Ds to evaluate the relative contributions to midestuarine dissolved metal inputs from porewater infusion and desorption from resuspendable sediment. Equilibrium sorption models have been used to describe salinity-induced desorption (Li *et al.*, 1984a; Williams and Millward, 1998) and desorption from and adsorption to resuspending sediments (Martino *et al.* (2002) and Morris (1986), respectively) in the vicinity of a TMZ. It is assumed that sorption processes are effectively instantaneous and fully reversible and that chemical equilibrium has been achieved (Li *et al.*, 1984a; Srivastava and Srivastava, 1990; Turner *et al.*, 1993). Whilst this theory may hold for certain chemical reactions, others are slow to reach equilibrium or be only partially reversible. In rapidly flushed estuaries and/or those receiving subsidiary metal sources or where compositionally distinct particle populations take part in sorption reactions, disequilibrium may occur between dissolved and particulate phases (Morris, 1990; Turner *et al.*, 1992b, Turner, 1996). Thus, in these systems, a more complex approach to sorption modelling may be necessary such as the inclusion of chemical kinetics and/or multiple steps (Nyffeler *et al.*, 1984; Comber *et al.*, 1996). Appropriate experimental protocols may also need to be revised to take account of seasonal variations in particulate and water chemistry, thus enabling more accurate determinations of sorption constants for predictive model use.

The wide use of K_D by trace metal geochemists and numerical modellers signifies its usefulness in predicting the flux and fate of estuarine contaminants. As partitioning controls the fate, transport, bioavailability and potential toxicity of trace metals to aquatic life, it is crucial to accurately define specific sorption components so that environmental models are adequately parameterised and specific objectives such as the setting of EQSs can be met (Comber *et al.*, 1996). Defining relationships of K_D as functions of salinity and turbidity are vital in the development of coupled hydrodynamic-chemistry models which can be used to evaluate dispersion of contaminants from diffuse or point sources, an approach that has had successful applications in several instances (Ng *et al.*, 1996; Falconer and Lin, 1997; Wu *et al.*, 1998).

1.3 Estuarine decontamination

Trace metals may be introduced into estuaries from a variety of sources, particularly in areas experiencing high urban pressure. The superimposition of anthropogenic signals from direct and indirect discharges from industry, contributions from municipal works in surrounding conurbations, atmospheric deposition and the reintroduction of historical contamination from sediment resuspension and porewater diffusion to natural background trace metal concentrations can assist in maintaining the pollution burden of an estuary if conditions allow.

1.3.1 Mechanisms of decontamination

Sediment decontamination, through decreasing, diluting or embedding pollutants, is generally a slow process. Several factors can affect the contaminant content of estuarine sediments (Cato *et al.*, 1980):

- A decrease or cessation of the pollutants discharged;
- Good ventilation of the water mass;
- Mixing-in of uncontaminated sediments;
- Physical and biological re-working of sediments, including dredging;
- Physico-chemical and/or microbiological mobilisation and subsequent release of contaminants to the overlying water column;
- Persistence of different pollutants;
- Sedimentation of uncontaminated sediments with subsequent embedding of the contaminated sediment cover.

☐ *A decrease in pollutant loading*

The reduction or abatement of an effluent would naturally be anticipated to have a positive effect on pollution within an estuary. Evidence of increased contamination has been illustrated in many studies utilising sediment cores to reconstruct historical trends of intensified anthropogenic disturbance in the sedimentary record. Vertical profiles of contaminants and in some instances, a knowledge of industrial production chronology, have been used to assess sediment accumulation rates, the dating of significant discharge events and the identification of pre-industrial background concentrations (e.g. Zwolsman *et al.*, 1993; Hutchinson and Prandle, 1994; Fox *et al.*, 1999). The accurate delineation of cores provides a useful tool for gauging the enrichment of contaminants relative to both peak or baseline concentrations and can thus give a measure of the effectiveness of input reduction. However, bioturbation, sediment granulometry, smearing of the core sample during collection and sediment erosion can lead to perturbation of the sedimentary record (Fletcher *et al.*, 1994; Mudge *et al.*, 2001). Inconsistencies in sampling, analytical measurement and choice of extraction technique present further difficulties (Grant and Middleton, 1990). Appropriate evaluation or minimisation of these factors is necessary if any trends are to be defined accurately.

☐ *Adequate ventilation*

Tides, meteorological forcing and estuarine circulation generally ensure good ventilation of the water mass and exchange with adjacent seas. Consequently, a contaminated water mass is unable to maintain itself in an estuary, although several of the mechanisms mentioned earlier (e.g. the flocculation and deposition of colloidal species and fine-grained particles and the existence of flood dominance and tidal pumping in macrotidal systems), can assist in holding the suspended load or transporting it back into the estuary on flood tides. This can have significant implications in muddy estuaries where the majority of any escaping dredged material may quickly resettle within the estuary (van den Berg *et al.*, 2001). Under such conditions, the greatest loss of contaminants to the coastal region is predicted to occur through transport in the dissolved phase rather than by association with SPM (Turekian, 1977; Duinker, 1980).

- *Mixing-in of uncontaminated sediments*

The mixing-in of uncontaminated particles has been used to explain seaward decreases in the trace metal content of sediments (particularly in the lower reaches) in some estuaries. For example, declines of 65-98% of bed sediment metal concentrations in the Elbe (Müller and Förstner, 1975) and 20-60% of leachable Cu, Fe and Zn in SPM from the Rhine Estuary and southern Bight (Duinker and Nolting, 1976) were attributed to the dilution of sediments by less contaminated particles entering from the North Sea. Other evidence for this process has been provided by Cato (1977) who demonstrated that C:N ratios reduced with progression towards the mouth of the Valen Estuary, due to a concomitant decrease in terrestrial organic matter with a steadily increasing presence of marine humus. Similar patterns have since been observed in the Humber-Ouse (Uncles *et al.*, 2000) and Tay (Thornton and McManus, 1994).

- *Physical and biological re-working*

Bioturbation during feeding, burrowing or tube construction increases the release and mixing of contaminants in sediments. Biological re-working can lead to either the burial or upward migration of contaminants, from the direct transfer of sediment particles or by aiding dissolution, and bioaccumulation in benthic fauna can also release particle-bound pollutants (Sharma *et al.*, 1987; Gagnon *et al.*, 1997). The degree of bioturbation is likely to reduce up an estuary as salinities decline and the benthic fauna composition is altered (Cato *et al.*, 1980). Remobilization may also occur through physical re-working induced by dredging (Tramontano and Bohlen, 1984; Petersen *et al.*, 1997; Simpson *et al.*, 1998; van den Berg *et al.*, 2001), the venting of sediments by tidal action (Campbell *et al.*; 1988; Martino *et al.*, 2002) and erosion (Harland *et al.*, 2000; Spencer *et al.*, 2003).

- *Diagenetic and microbial processes*

The decomposition of aquatic detritus in bed sediment results in changes in pH, redox potential, DO, sulphide and organic molecules. This may lead to changes in the chemical form in which trace elements are associated with sediment particles, possibly shifting them into more exchangeable positions and increasing their availability to the overlying water. A further result of diagenesis in organic-rich sediments is the increase in dissolved metal concentrations in interstitial waters and considerable evidence points to the existence of a relatively large reservoir of dissolved trace metals in the upper layers of reducing sediments (Elderfield and Hepworth, 1975; Gaillard *et al.*, 1986; Ciceri *et al.*, 1992). Elderfield and Hepworth (1975) proposed that metal enhancement of around 10% can occur in surface muds simply through diagenetic processes alone.

The majority of trace metals tend to be adsorbed to or occluded within hydrogenous and biogenic coatings on natural particle surfaces (Turner *et al.*, 1991; Thomas and Bendell-Young, 1999, Dong *et al.*, 2003). Oxyhydroxides of Fe and Mn are significant phases for trace metal sequestration as they have high adsorptive capacities. Microbial decomposition of sedimentary organic matter results in the bacterial utilisation of O_2 and other electron acceptors such as NO_3^-, MnO_2, $Fe(OH)_3$, and SO_4^{2-} (Farmer, 1991; Buckley *et al.*, 1995). The reduction of Fe^{3+} and Mn^{4+} species results in the mobilisation of these (and any other metals associated with them) as oxide precipitates become reduced and solubilised (Duinker *et al.*, 1979). Reprecipitation of Fe and Mn oxides occurs under increasingly oxic conditions at the sediment-water interface or in the water column (Morris *et al.*, 1982b). Other metals (e.g. Co) may be co-precipitated with Mn (Zwolsman and van Eck, 1999). Autocatalysis can also take place whereby the presence of Mn on particle surfaces promotes the adsorption of dissolved Mn. Repeated cycles of oxide dissolution and precipitation reduce their crystallinity and thus aid the incorporation of metal ions (Chao, 1984) but it is important whether the species to be adsorbed is present during hydrous oxide formation as the amount adsorbed on freshly precipitated oxides is considerably greater than on aged precipitates (Duinker, 1980). Elevated pH, existing with progression along a salinity gradient or resulting from phytoplankton blooms, has also been linked with removal of Fe and Mn from solution (Li *et al.*, 1984a; Admiraal *et al.*, 1995; Zwolsman *et al.*, 1997; Guieu *et al.*, 1998).

Metal concentrations in interstitial waters may be many orders of magnitude larger than the solubility values of sulphides, even in the presence of H_2S within the sediment column. Metals may be solubilised from their precipitated sulphides by aerobic bacterial activity. Alternatively, mobilisation can also occur through redox alterations induced by high nutrient supply. The formation of stable complexes between trace metals and an excess of dissolved organic molecules is believed to be a major contributing factor as metals such as

Cu, Mn, Co, Ni and Zn can be solubilised from their carbonate and sulphide species by interaction with organic matter (Rashid and Leonard, 1973; Emerson *et al.*, 1983). Vertical concentration gradients in dissolved organic matter therefore provide an important pathway through which upward ionic or molecular diffusion can take place. Whilst Fe and Mn can be released to bottom waters under reducing conditions, elements such as Cd, Cu, Ni, Pb and Zn are removed from seawater as sulphides. Competition can therefore exist between inorganic precipitation and organic complexation.

In addition to the effects of microbial and photosynthetic activity on oxygen saturation and pH and the consequences of these on the precipitation or dissolution of Fe and Mn oxides, metals may also be adsorbed by particulate organic carbon (POC) (Church, 1986; Paulson *et al.*, 1994). High concentrations of POC may originate from the introduction of organic-rich soils eroded from the catchment during high river flows (Neal *et al.*, 1997), from phytoplankton blooms or from anthropogenic discharges. These factors will assume greater or lesser importance at different times of year and can induce seasonal changes in particle composition (Balls, 1990; Zwolsman and van Eck, 1999). The coagulation or salting out of neutral organic compounds from solution at higher salinities promotes the adsorption of organic carbon (and any associated contaminants) onto SPM (Turner and Rawling, 2001). Removal of metals from the dissolved phase in this manner could represent an important additional pathway for particulate trace metal retention in estuaries such as the Beaulieu and Mersey which experience high concentrations of dissolved organic carbon (DOC) (Turner *et al.*, 2001b, 2002).

In macrotidal estuaries, the tidal pumping of metal-depleted particles may provide the appropriate thermodynamic drive for the adsorption of trace metals from the water column when these particles are resuspended by strong tidal action (Ackroyd *et al.*, 1986; Morris, 1986,1990). Instead, dissolved metal maxima have often been observed in many turbid and moderately contaminated macrotidal estuaries throughout western Europe (Duinker *et al.*, 1985; Apte *et al.*, 1990; Turner *et al.*, 1992; Chiffoleau *et al.*, 1994; Laslett and Balls, 1995; Kraepiel *et al.*, 1997). Desorption, rather than adsorption, may be favoured in the low salinity region or TMZ in these estuaries, if resuspending particles are loaded with metals compared to SPM at equilibrium with metals dissolved in the water column (Martino *et al.*, 2002).

Controls on the phase distribution of trace metals may also arise from changes in salinity during estuarine mixing due to the coupled processes of chloride complexation and cation competition (Comans and Van Dijk, 1988; Chiffoleau *et al.*, 1994; Paalman *et al.*, 1994; Kraepiel *et al.*, 1997). Metals may enter the dissolved phase by the formation of highly stable complexes with Cl^-, SO_4^{2-} and CO_3^{2-} and competition with seawater ions such as Na^+, K^+, Ca^{2+} and Mg^{2+} for active sites on particles. As the ionic strength of seawater increases, so the effectiveness of these processes is enhanced and metal readsorption is progressively hindered, although the extent of metal release is variable (Hegeman *et al.*, 1992; Paalman *et al.*, 1994).

☐ *Persistence*

The stability or persistence of a contaminant will also influence the recovery process. Certain trace metals (e.g. Cu, Hg and Pb) tend to exhibit a high affinity for particulate matter, especially if organic carbon or biopolymers are present on particle surfaces (Paulson *et al.*, 1994; Turner *et al.*, 2001b; Guibaud *et al.*, 2003). These metals are more likely to be retained unless physico-chemical alterations to the sediment or water column intervene. Elements such as Cd, which generally shows weaker associations with estuarine particles, is more readily released to the dissolved phase, largely as a result of salinity-induced desorption (Kraepiel *et al.*, 1997). The rate at which sediment may be cleansed of trace metals will, in part, vary simply as a consequence of the relative ability of individual elements to bind with particulate matter. Microbial methylation provides an additional pathway for the release of Hg, Pb and As (Wood, 1984), but these are very slow processes and are limited to the upper layers of deposited sediments where bacterial numbers are considerably higher than at depth (Gagnon *et al.*, 1997). However, the environmental consequences of such processes are significant. For example, CH_3Hg is more toxic than inorganic Hg and is readily accumulated by aquatic organisms (Bloom, 1992; Morse, 1994).

☐ *Sedimentation and burial*

The introduction of a steady supply of sediment either from catchment erosion or offshore sources will allow an almost continuous deposition of fresh uncontaminated (or less contaminated) material that will cover polluted layers. With time, and sufficiently high rates of deposition, contaminated strata are withdrawn from the sediment-water interface and embedded. The vertical redistribution of pollutants may then only arise through bioirrigation or other, more energetic, physical disturbances.

1.3.2 Examples of estuarine remediation

It is through the increasingly stringent control of domestic and industrial discharges in combination with some of the above processes that significant improvements in the quality of waters and sediments of many European estuaries have been observed. The Scheldt and Thames estuaries are two such examples.

The Scheldt basin, draining over 20 000 km^2, covers one of the most populated and industrialised areas of Europe (Paucot and Wollast, 1997). It is characterised by a small mean annual river discharge, which is subject to large seasonal fluctuations (Paucot and Wollast, 1997), a tidal range of 4-5 m and a residence time of 2-3 months under normal river flows (~ 120 m^3 s^{-1}) (Regnier *et al.*, 1997). The estuary is generally well mixed but the upper estuary may become partially mixed during peak fluvial discharges.

The Scheldt has experienced a high degree of both organic and inorganic contamination, arising from a large number of domestic, industrial and agricultural waste inputs entering the upper estuary. The decomposition of substantial organic loads contributed to the development of an anoxic water column at low salinities at most times of the year (Zwolsman and van Eck, 1999). However, the same authors have shown dramatic reductions in the particulate metal burden of the estuary in the period 1980-1995, with decreases of 88% for Cd, 85% for Hg, 74% for As, 59% for Cu and 50-54% for Cr, Ni, Pb and Zn in fluvial SPM. Most notably, the Mn content of riverine particles has more than doubled between 1974-1996, reflecting the gradual increase in riverine DO concentrations. Metal loss was largely attributed to the mixing of fluvial and marine particulates, porewater infusion from and resuspension of reducing sediments, co-precipitation of Ni and Co with Mn oxides and the uptake of Cd and Zn by phytoplankton. Desorption of metals such as Cd, Cu and Zn was considered a relatively minor effect compared to particle mixing. Particulate metal concentrations in the Scheldt were still relatively high when compared to those in a number of other impacted estuaries (Baeyens, 1998).

The Thames basin covers an area of 10 000 km^2 and includes large urban and industrial centres (Habib and Minski, 1982). The Thames is also macrotidal and water level is regulated by a series of weirs along its length. Minor stratification has been recorded, but for most purposes the system is considered well mixed. Freshwater flows of < 10 m^3 s^{-1} are common in summer and large quantities of water are abstracted for potable supplies. Consequently, dilution is reduced and a net seaward movement of only 2 km d^{-1} has been estimated which strictly limits the polluting load that can be accepted under such conditions (Lloyd and Whiteland, 1990).

Numerous industrial sites, storm overflow drains and STW are sited along its banks (O'Reilly Wiese *et al.*, 1997a) and the main source of metal input into the estuary is from the final effluent discharged from STW which contain both urban and industrial wastes (Rossin *et al.*, 1983). Significant organic loads led to < 5% DO being recorded for around half the length of the estuary in 1950 and much of this was completely anaerobic in summer (Wood, 1980). Attrill and Thomes (1995) demonstrated (see Table 1.5) that concentrations of most metals studied in surficial sediments of the Thames were comparable to or elevated above those observed in other contaminated estuaries in the UK in the late 1980s (Bryan and Langston, 1992).

Reduction in the pollution load has largely occurred through the updating of major STW in the area in 1959 and 1963 and water quality began to improve in the 1960s (Wood, 1980). Analysis of 10 m sediment cores collected from a disused dock basin in the lower estuary indicate that a 30-50% decrease in Ag, Cd, Cu, Pb and Zn and a 70% decrease for Hg concentrations occurred in the period 1944-1966 (O'Reilly Wiese *et al.*, 1997a). In addition, through-core distributions of Mn implied that sediments were deposited under anoxic conditions prior to 1960 but that after this date Mn concentrations have increased up to a factor of 2, demonstrating the effect of increased DO levels in estuarine waters due to the increased efficiency of STW. Whilst metal concentrations at depth agree with the findings of Attrill and Thomes (1995), surface concentrations now place the metal contamination status of the Thames in a more favourable position compared to many of the estuaries studied by Bryan and Langston (1992). In a concurrent study utilising the same cores, O'Reilly Wiese *et al.* (1997b) found that metal mobility followed the order Cd > Ag > Cr > Ni, Zn > Co, Cu, Pb. Cadmium and Ag also showed a tendency (at surface and at depth) to partition towards the exchangeable phase indicating the potential for long-term leaching of these metals from the sediments. Evidence to support this theory has been provided in saltmarsh sediments situated 25 km downstream in the outer Thames Estuary, which are shown to be enriched with Cd (Fletcher *et al.*, 1994).

Whilst overall improvements in water oxygenation have occurred, occasional short-term rapid declines in DO concentrations occur. These are induced by large quantities of storm sewage entering the estuary, which arise during periods of heavy rainfall onto a highly impermeable catchment and such incidences resulted in several fish mortalities in the 1970s and 1980s. The solution was the introduction of a rapid-response vessel capable of pumping oxygen directly into the water column to prevent the formation of lethal DO sags (Lloyd and Whiteland, 1990). The Thames has now become a major nursery ground for key economic and conservation fish species, including eel and salmon (Colclough *et al.*, 2002), attesting to the success of restorative measures over the last 4 decades.

The effects of remediation in the Scheldt and Thames show some commonality between the two systems. Overall, despite the fact that the quality of inputs has improved over many years, both estuaries may be considered as partially rather than fully restored at the present time and similar rates of progress would therefore be anticipated in other similarly impacted estuaries.

1.4 The study area

1.4.1 Physical parameters of the Mersey Estuary

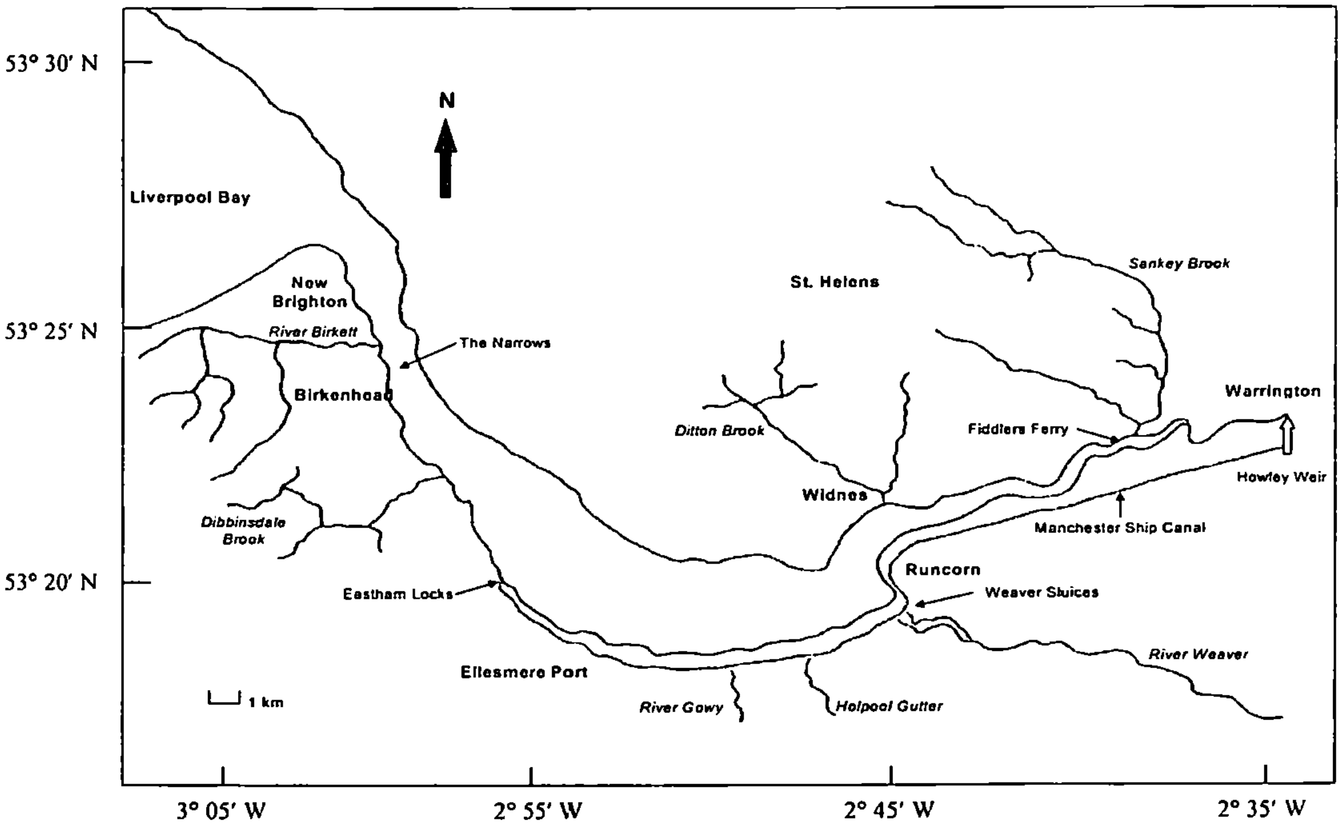


Figure 1.6 Map of the Mersey Estuary, showing the locations of tributaries and major towns. Adapted from NRA (1995).

The Mersey Estuary (Figure 1.6) is approximately 50 km long from the tidal limit to the mouth and can be divided into four main sections. The upper estuary is a narrow meandering channel that extends for 17 km between Howley Weir and the Runcorn/Widnes Gap, where the channel widens briefly upstream of a North to South sandstone ridge constricting the estuary. Surface sediments in the upper estuary possess a moderate silt content (20-60%) with the remainder being very fine sand (Harland and

Riddle, 1997). The estuary rapidly widens below Runcorn and Widnes and forms a large, shallow basin known as the inner estuary. This basin is 20 km long and has a maximum width of 4.8 km, with extensive intertidal mudflats and saltmarshes on its southern margin, almost all of which dries out at low tide. The bed here is largely sand with silt located on both the northern and southern banks which are unstable and evidence suggests that mobilisation of previously consolidated sediments is taking place (Harland and Riddle, 1997; Harland *et al.*, 2000). Further downstream in the Narrows, the estuary changes to a straight, narrow channel approximately 1 km wide and 10 km in length with depths reaching 30 m even on low spring tides. The unusually narrow mouth gives rise to tidal current velocities in excess of 2 m s^{-1} during spring tides, resulting in a strong tidal scour and high concentrations of SPM (NRA, 1995). Silt content here is generally low but a large silt bar does exist (Harland and Riddle, 1997). The outer estuary begins at New Brighton and extends out into Liverpool Bay. It consists of a large area of intertidal sand and mud banks through which the navigation channels are constrained by 16-km long training walls and are continuously dredged to keep them navigable. A submerged sandbank at the seaward end of the channels represents the physical limit of the estuary. The mean silt content of the estuary was found to be around 26% in 1997 (Harland and Riddle, 1997).

The Mersey Estuary is a highly energetic system. For example, on exceptionally high spring tides (9.2-10.7 m), saltwater incursion frequently overtops the weir, an artificial tidal limit in Warrington, some 50 km from the mouth. High dynamicity is also evident at the seaward end, with an estuarine-type circulation extending for 22 km from New Brighton out into Liverpool Bay (Bowden and Sharif el Din, 1966; Abdullah and Royle, 1973). Tidal bores are frequently observed on spring tides. Under favourable conditions and particularly during periods of dry weather, upestuary progression of the bore is rapid such that it may reach Howley Weir just prior to high water at Liverpool (Proudman Oceanographic Laboratory, 2003). Freshwater flow is relatively small for the size of the estuary catchment. The subsequent flushing time is around 32 days under normal conditions but increases to about 50 days at times of low flow (Jones, 1978). This represents a considerable residence time for chemical components in the estuarine environment and could lead to the establishment of equilibrium conditions for sorptive reactions in the upper estuary (Millward and Turner, 1995).

The generation of a turbidity maximum in the upper estuary is most pronounced during spring tides, when SPM concentrations can reach as high as 2 g l^{-1} (Taylor, 1986). Prandle *et al.* (1990) estimated a net transport into and out of the estuary of around 15 000 m^3 of suspended sediment for a mean tide. The mean SSA of Mersey SPM is 9.6 m^2 g^{-1}, is relatively constant throughout the whole estuary and is lower than the average SSA measured in a number of other macrotidal systems (Millward *et al.*, 1990). It has been suggested that the low SSA of Mersey SPM could be attributed to a greater amount of organic carbon, possibly in the form of humic acids or anthropogenically-derived carbon which themselves have very low SSAs and which act to reduce the amount of active surface available for adsorption by blocking the pores (Millward *et al.*, 1990).

1.4.2 Inputs into the Mersey Estuary

The Mersey Basin drains an area of 5 000 km^2 including the major conurbations of Liverpool and Manchester and supports a population of over 5 million. The estuary is an important interface coupling a heavily industrialised area with the Irish Sea. Significant inputs of water from riverine sources are listed in Table 1.10. The two main freshwater sources are the River Mersey, entering the estuary at Howley Weir in Warrington and the Manchester Ship Canal, which receives additional water from the River Weaver.

Table 1.10 Significant freshwater inputs into the Mersey Estuary. Data adapted from NRA (1995).

Watercourse	**Mean flow (m^3 s^{-1})**
River Mersey	19
Manchester Ship Canal (including River Weaver)	12
Sankey Brook	4
Ditton Brook	1
River Gowy	1
Holpool Gutter	<1
Dibbinsdale Brook	<1
River Birkett	<1

The source of the River Mersey is in Stockport and is formed by the confluence of the Rivers Tame and Goyt. It then flows through a number of densely populated areas before entering the Manchester Ship Canal. The river and canal separate and run parallel to each other as far as Eastham (Figure 1.6). Water from the canal enters the estuary *via* two locks and associated sluiceways at Eastham or through the Weaver Sluices below Runcorn (Figure 1.6). Until 1989, excess water brought into the canal by high spring tides was levelled and this effectively flushed the canal between Eastham and the Weaver Sluices.

Since then, additional gates at Eastham have been used to close off the canal from the estuary thereby eliminating levelling, reducing siltation and lowering the average salinity of the canal.

The estuary has received significant quantities of industrial wastes, sewage and run-off from agriculture and contaminated land into its tidal and non-tidal reaches over the last two centuries, adding a considerable polluting load into the estuary (NRA, 1995; DoE, 1996). The estuary and its hinterland saw the start of the British chemical industry and the growth of major manufacturing centres at Ellesmere Port, St. Helens, Warrington and Widnes (Figure 1.6). It continues to be a focal point for a wide range of manufacturing activities and retains its status as a major port. Evidence of past industrial contamination is found in its salt marsh sediments (Fox *et al.*, 1999).

Improvements in the water quality of the Mersey and Ribble estuaries have been slower in comparison with other industrialised systems like the Tyne, Tees, Severn and Thames and for the Mersey in particular, little apparent change is observed between 1990 and 2000 (see Figure 1.1). However, this evidence is somewhat misleading as gradual improvements have been achieved. Between 1995-2000, the 16 km stretch from Howley to Runcorn (Figure 1.6) improved from a position of historically bad quality and the entire estuary is now classified as being either of fair or poor quality (Figure 1.7). This amelioration is

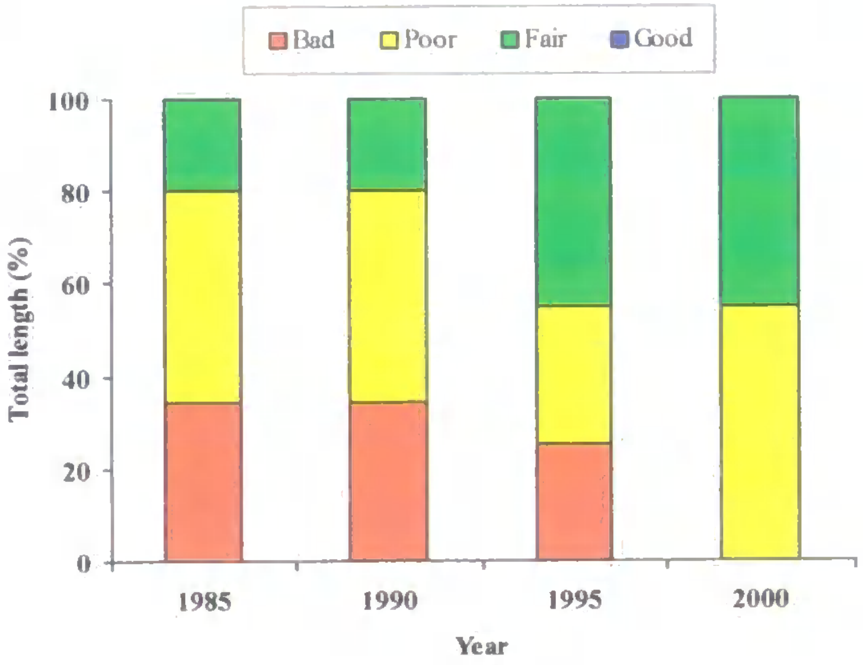


Figure 1.7 Water quality in the Mersey Estuary, 1985-2000. Source: EA (2002a).

primarily due to the investment of more than £60 million by United Utilities Ltd. (formerly North West Water) to improve the quality of waste discharged from STW at Davyhulme, Widnes and Warrington, which between them serve over 1.5 million people. The effect of systematically reducing concentrations of ammoniacal nitrogen entering the estuary at Howley Weir for example, has been to significantly reduce BOD and subsequently increase oxygenation of the water column (Figure 1.8). In total, more than £1.5 billion has been spent to date on related projects located within the estuary catchment. Due to the successful partnership forged between the EA and its predecessor, the National Rivers Authority, water companies, local industry and the Mersey Basin Campaign, DO levels are now high enough to support fish populations throughout the estuary. The operation of humane fish traps and catches by anglers indicate that the numbers and diversity of fish species in the River Mersey and its estuary have risen steadily in the last decade and now includes salmon, brown trout, sea trout, lamprey, dace, bream, cod and whiting (EA, 2003). Some parts of the Mersey and Wirral foreshore are designated as SSSI and RAMSAR sites and part is a candidate for designation as a Special Protection Area under the Conservation of Wild Birds Directive (79/409/EC) (NRA, 1995).

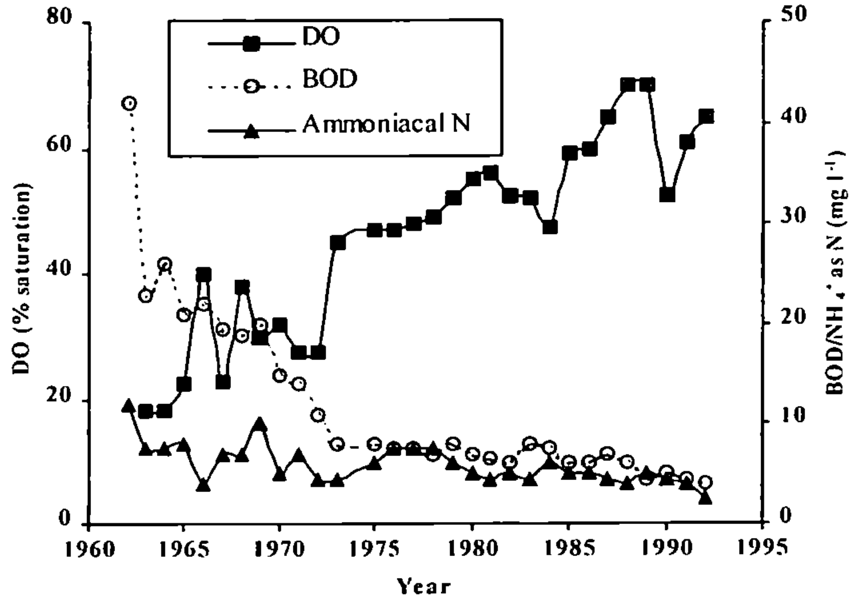


Figure 1.8 Annual trends in ammoniacal nitrogen concentration, biochemical oxygen demand and dissolved oxygen levels at Howley Weir, 1962-1992 (Jones, 2000).

Despite the aforementioned improvements, DO saturation still varies quite considerably at all points along the estuary and significant differences exist on seasonal, inter-tidal and intra-tidal timescales (Figure 1.9). Higher water temperatures prevailing during the summer months can lead to a decrease in the amount of DO retained in the water. This, combined with the degradation of organic matter from continuing effluent discharges can produce a distinct oxygen sag, which is especially evident in the upper reaches of the estuary where occasional anoxia can be observed. Dissolved oxygen minima are discernible, to greater or lesser degrees, at most times of the year (NRA, 1995). Thus, since 1980, the majority of routine surveys of the Mersey Estuary by the Environment Agency (and hence this work) have been performed monthly on spring tides in order to record conditions when DO is anticipated to be at a minimum.

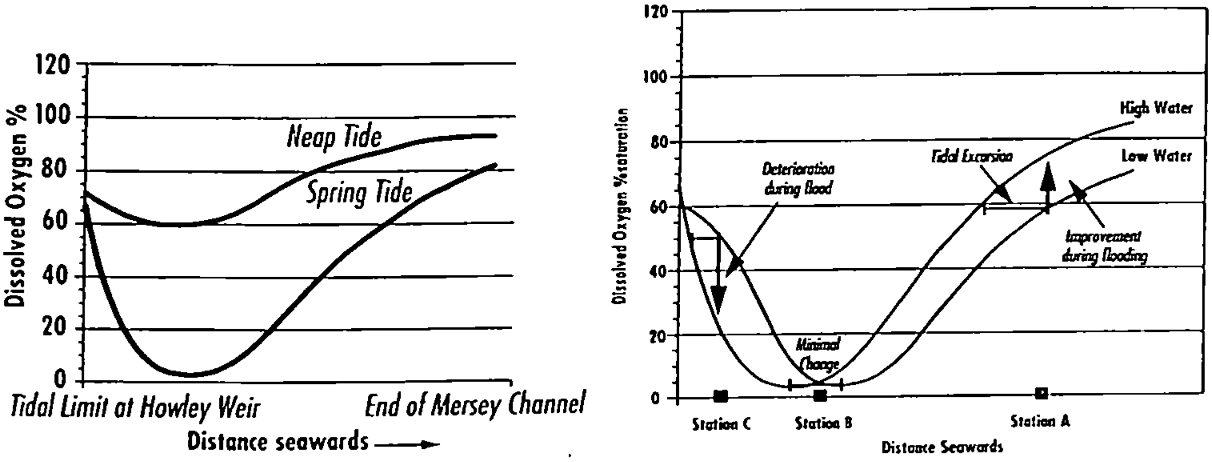


Figure 1.9 Typical observed differences in dissolved oxygen (a) between spring and neap tides and (b) during a single tidal cycle in the Mersey Estuary. Source: NRA (1995).

Trace metal concentrations and fluxes have been widely investigated in the Mersey and its environs in recent years (Bartlett and Craig, 1981; Airey and Jones, 1982; Langston, 1986; Campbell *et al.*, 1988; Bryan and Langston, 1992; Camacho-Ibar *et al.*, 1992; Laslett, 1995; Comber *et al.*, 1995; Williams *et al.*, 1998). Bryan and Langston (1992) reviewed the bioavailability, bioaccumulation and biological effects of several heavy metals in sediment-dominated UK estuaries, with the Mersey showing relatively high concentrations of Cd, Cu, Zn and, in particular, Hg (Table 1.5). Highest Hg concentrations of all estuaries studied were consistently found in the Mersey. Sources of Hg to the Mersey are numerous and diverse (Table 1.11) but the overall distribution in sediments is consistent with known major emissions in the area (Taylor, 1986; Harland and Riddle, 1997; Harland *et al.*, 2000). Complexation by organic matter and rapid adsorption onto particles means that Hg becomes predominantly (80%) associated with particulate material in the polluted upper estuary (Airey and Jones, 1982).

Discharges of metals to the estuary have decreased significantly over the last 30 years

(NRA, 1995) and the metal loads reported for 1998 and 1999 in Table 1.11 (P. Jones, EA, pers. comm.) register further declines in metals delivered to the system. A general reduction in contaminant concentrations is now evident for a range of organic pollutants and metals due to large financial investments in sewage treatment and tighter controls on industrial discharges (Taylor, 1986; Fox *et al.*, 1999; Harland *et al.*, 2000; Jones, 2000).

Table 1.11 Mersey Estuary dangerous substances load data (t a^{-1}) and percentage contributions from different sources in 1998 and 1999.

Discharge	**Cd**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
1998						
Rivers						
Mersey %	54	57	10	62	28	60
Weaver %	38	24	36	23	8	16
Sewage works						
Warrington %	2	9	<1	3	<1	8
Widnes %	<1	<1	<1	1	<1	1
Liverpool %	6	10	2	11	5	15
Industry						
ICI %	0	0	47	0	0	0
Octel %	0	0	5	0	57	0
TOTAL (t a^{-1})	**0.44**	**246**	**0.55**	**16.2**	**52.8**	**888**
1999						
Rivers						
Mersey %	43	57	6	54	23	49
Weaver %	27	23	19	27	5	13
Sewage works						
Warrington %	1	2	<1	1	<1	5
Widnes %	<1	1	<1	6	<1	<1
Liverpool %	10	15	1	11	9	31
Industry						
ICI %	0	0	72	0	0	0
Octel %	19	2	2	1	63	<1
TOTAL (t a^{-1})	**0.37**	**18.7**	**0.50**	**15.0**	**38.6**	**80.2**

Examples include the chlor-alkali industry which now discharges a mercury load of less than 1 tonne per year compared to nearly 60 tonnes in the mid 1970s (NRA, 1995). The number of point sources for Ni, Zn, Cr, Cd and Cu has diminished and inputs are now dominated by non-tidal riverine contributions (NRA, 1995; Jones, 2000). However, sediments still contain relatively high concentrations of pollutants and much of the estuary experiences poor water quality, particularly in the summer (NRA, 1995). Importantly, perturbations in metal reduction trends in the Mersey have been reported in recent years with dissolved and particulate concentrations showing evidence of stabilisation rather than a continuance of the rapid declines that were previously observed in the 1980s (Laslett, 1995; Fox *et al.*, 1999; Harland *et al.*, 2000). The focus of this research therefore is the investigation of causative mechanisms that may be responsible for the apparent slow-down in metal decontamination in the estuary.

1.5 Study aims

The overall aim of this project is to investigate factors affecting the temporal and spatial variability of estuarine water and particulate chemistry and the consequences of these in terms of the medium- to long-term cleansing of trace metals from sediments in the Mersey Estuary. Variations in the axial distribution, phase partitioning, reactivity and transport of trace metals will be understood in relation to changing estuarine physico-chemical parameters and the hydrodynamic regime and used to assess the underlying mechanisms controlling the cycling and fate of trace metals in the estuary. Specific objectives of the study are as follows:

- To undertake a co-ordinated programme of measurement of estuarine master variables and selected trace metals in the Mersey Estuary;
- To investigate seasonal axial distributions of total and non-detrital particle-associated concentrations of the priority pollutant metals Cd, Co, Cu, Ni, Pb and Zn in SPM and surface sediments;
- To examine any preferential associations of stable trace metals with different particle populations derived from settling experiments and inference thereof to subsequent estuarine transport processes;
- To integrate data on seasonal axial distributions of dissolved Cd, Co, Cu, Ni, Pb and Zn in collaboration with other works;
- To incorporate complementary archived data from the Environment Agency's Marine Monitoring Programme surveys to assist in defining the underlying geochemical conditions present in the estuary;
- To use other techniques for the geochemical characterisation of estuarine particles such as the analysis of Fe, Mn, C and N and measurement of SSA;
- To undertake key particle-water interaction experiments designed to study the *in situ* partitioning of ^{203}Hg onto bulk and density-separated fractions of SPM to investigate the

reactivity of Hg toward different particle types;

- To evaluate recent progress in trace metal decontamination in the Mersey and to assess the implications for further restoration based on the knowledge gained in relation to key hydrodynamic and biogeochemical controls operating within this complex system.

Chapter 2

Sampling and Analysis

2 Sampling and Analysis

Field studies have been undertaken to characterise the distributions of trace metals in waters (Martino, 2000), sediments and SPM in order to draw inferences on their transport and reactivity. Process-orientated studies using a radiotracer were employed to investigate variations in the sorptive behaviour of different suspended particle types.

2.1 Field studies

2.1.1 Overview of the sampling campaign

A flow diagram summarising the sampling strategy and overall experimental protocol of the surveys is given in Figure 2.1. Sampling normally took place on the same days as the routine monthly monitoring surveys of the Environment Agency (EA). The EA water samples were collected for a wide variety of routine analyses, including organic contaminants, trace metals and nutrients. *In situ* determinations of the estuarine master variables, salinity, temperature, pH and dissolved oxygen were also made. Contemporaneous sampling allowed coherence between the EA and University of Plymouth datasets, including archival data held by the EA. Contiguous sampling by the University of Liverpool research group working on organic contaminants was also achieved, thus providing even greater unity between project partners. This was of vital importance for the validation and subsequent implementation of a geochemical model of the Mersey Estuary developed at the University of Cardiff.

Seven axial surveys were performed on the Mersey Estuary between July 1997 and July 2000 and covered the seasonal cycle. Details of the field campaign pertaining to the collection of water samples are shown in Table 2.1. Field measurements and near-surface water sampling were undertaken for the collection of SPM at EA designated stations (Figure 2.2). Boat surveys were usually carried out at high water (± 2 hours) during spring tides on board the EA vessel 'Seajet' or the EA RIB 'Seafury', enabling optimum access along the entire length of the estuary within tidal time constraints. This approach minimised the effect of tidal state when comparing estuarine constituent distributions. It also meant that sampling was performed under conditions when relatively low concentrations of DO were anticipated (see Section 1.4.2). The resulting field data were consistent and allowed systematic tidal corrections to be made, thereby interfacing with the modelling component of the research programme.

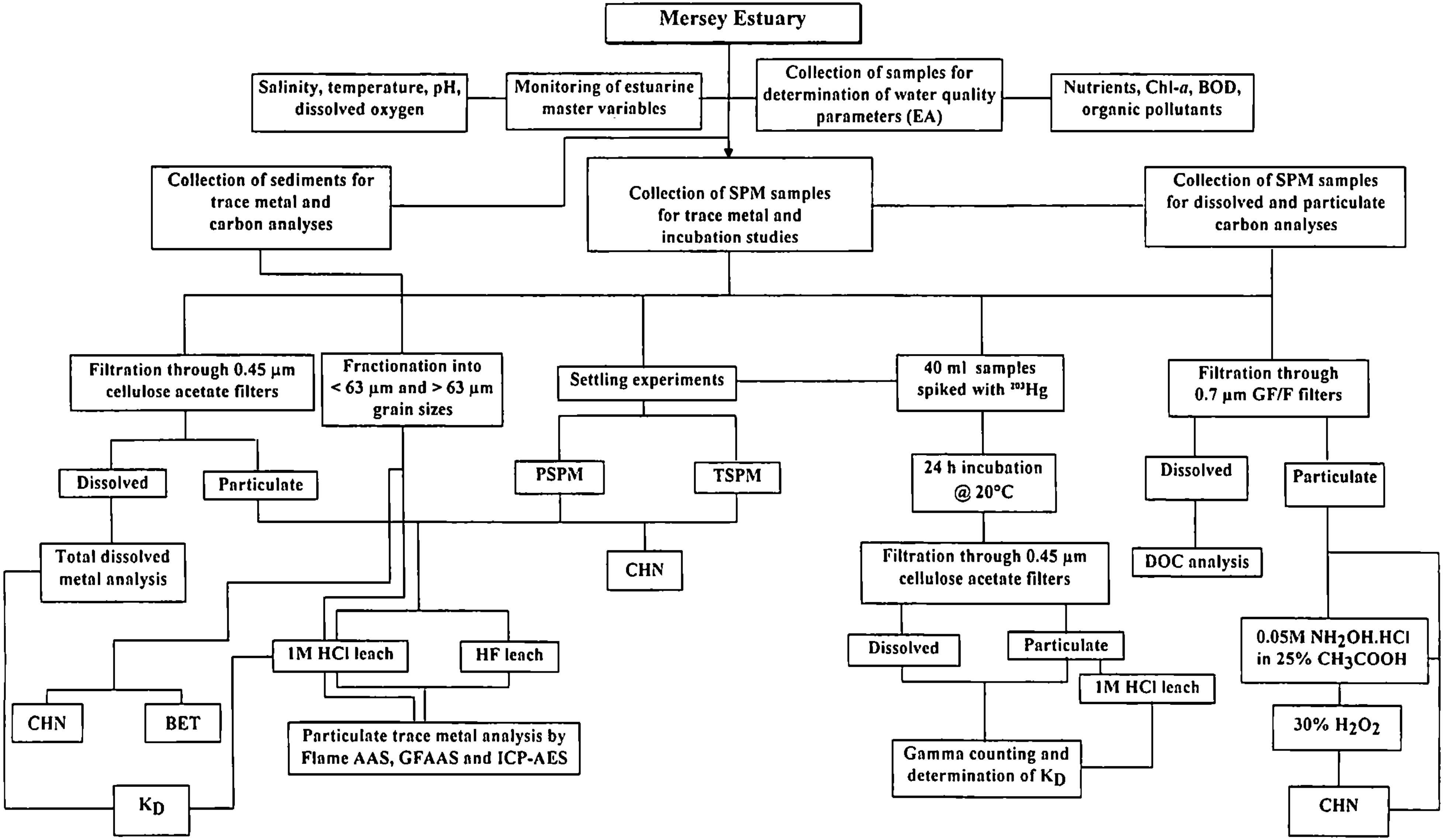


Figure 2.1 Flow diagram illustrating the sampling strategy and experimental protocol adopted.

Table 2.1 Summary of the axial transects, hydrological conditions and analyses performed on the water samples collected.

Date	Q (m^3s^{-1})	Survey	Tidal state	Tidal range (m)	n	S	SSC	T	pH	DO	Nutrients	Chl-*a*	Carbon		Metals		Settling experiments	Radiotracer studies	SSA
													P	D	P	D			
15-Jul-97	17.6	Axial transect	HW-neaps	5.0	12	✓	✓	✓	✓	✓	EA	✓	✓		✓		✓		
16-Dec-97	28.5	Axial transect	HW-springs	8.9	12	✓	✓	✓	✓	✓	EA	✓	✓	✓	✓	MM	✓		
30-Mar-98	47.2	Axial transect	HW-springs	10.9	18	✓	✓	EA	EA	EA	EA	✓	✓	✓	✓	MM	✓	✓	
25-Jun-98	29.1	Axial transect	HW-springs	9.2	21	✓	✓	EA	EA	EA	EA	✓	✓	✓	✓	MM	✓	✓	
20-Oct-98	82.4	Axial transect	HW-springs	8.2	20	✓	✓	EA	EA	EA	EA	✓	✓	✓	✓	MM	✓	✓	
04-May-00	10.1	Axial transect	HW-springs	9.4	21	✓	✓	EA	EA	EA	EA	✓	✓	✓					✓
03-Jul-00	30.5	Axial transect	HW-springs	9.6	8	✓	✓	EA	EA	EA	EA	✓	✓	✓					✓

Q = mean river flow; HW = High water; n = number of stations sampled; S = Salinity; SSC = determination of suspended solids concentrations; T = Temperature; DO = dissolved oxygen; EA = measured by Environment Agency personnel; P = particulate; D = dissolved; MM = analysed by M. Martino, University of Plymouth (Martino, 2000); SSA = specific surface area measurements.

The symbol ✓ signifies measurements conducted as part of this thesis.

The December 1997 survey was abandoned at EA station 11 due to adverse weather conditions. Subsequent samples were taken from the shore at locations approximating to EA stations 16, 19, 22 and 2 km below the weir. Riverine water and sediments were always gathered approximately 100 m above the artificial tidal limit at Howley Weir in Warrington (Figure 2.2).

In July 1997, bed sediments were sampled at discrete points along the estuary (Figure 2.3) that were assumed to represent a variety of contaminant sources and sediment types (P. Jones, EA, pers. comm.). On this occasion, samples were obtained from the boat using a van Veen grab. In July 1999, surface sediments were collected from the shore, concentrating on sampling within the upper estuary (Figure 2.3).

2.1.2 Equipment preparation for field studies

During sample collection, attempts were made to minimise sample contamination. Disposable plastic gloves were worn throughout all sampling and experimental work. High purity reagents, including high purity water (purified by reverse osmosis, Milli-RO, 18 MΩ cm resistivity, followed by ionic exchange, Milli-Q, Millipore) were employed for sample preparation and washing. Where possible, sample manipulation was carried out under a Class-100 laminar flow hood.

Unless stated otherwise, all plastic materials used were first cleaned in 5% Decon for 24 hours then, after rinsing, transferred to 10% HCl (AnalaR, BDH) for a further 24 hours and rinsed three times with Milli-Q water before being dried in a laminar flow hood. Cellulose acetate filters (47 mm, 0.45 µm pore size, Sartorius) were washed in 0.1M HCl (AristaR, BDH) for 24 hours before being rinsed thoroughly with Milli-Q water. Each filter was transferred to an acid-washed petri dish and dried to constant weight in a laminar flow hood. Glass bottles for the collection of DOC samples and a Millipore glass filtration unit were soaked in 5% Decon for 48 hours, then rinsed thoroughly with Milli-Q water and ashed in a muffle furnace for 8 hours at 450 °C. After cooling, the glassware was wrapped in combusted Al foil and stored until use. Aluminium foil inserts were made and placed underneath the plastic bottle caps from the collection bottles, in order to prevent any contamination of the water samples with organic carbon from the caps. Glass fibre filters (Whatman GF/F, 47 mm, 0.7 µm pore size) for the retention of suspended particulates for total C analysis were also ashed in a muffle furnace at 450 °C for 8 hours, before being weighed and stored in pre-combusted Al foil until required.

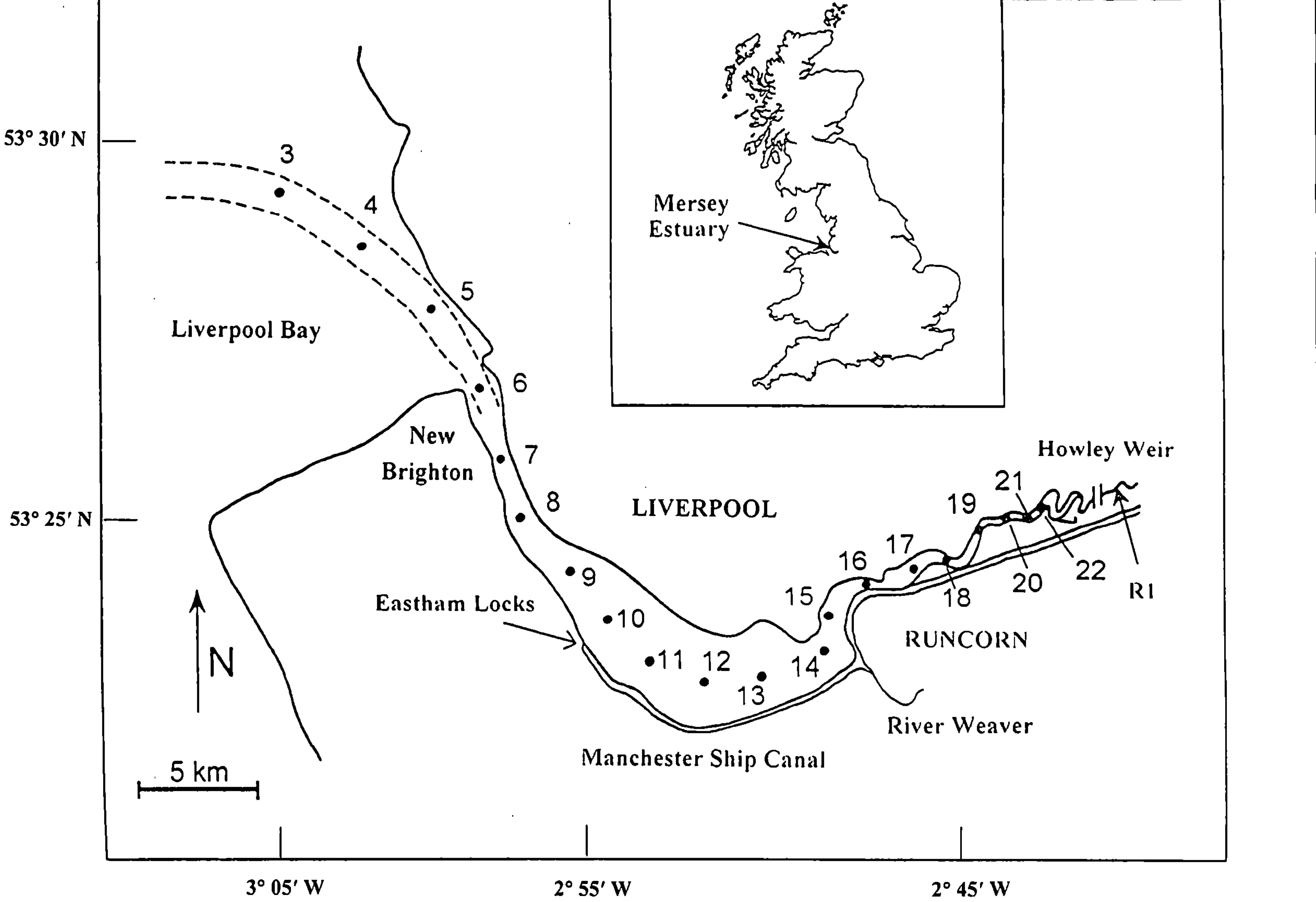


Figure 2.2 Location of the Mersey Estuary and Environment Agency monitoring stations used for the collection of water samples. R1 is the sampling point for riverine water.

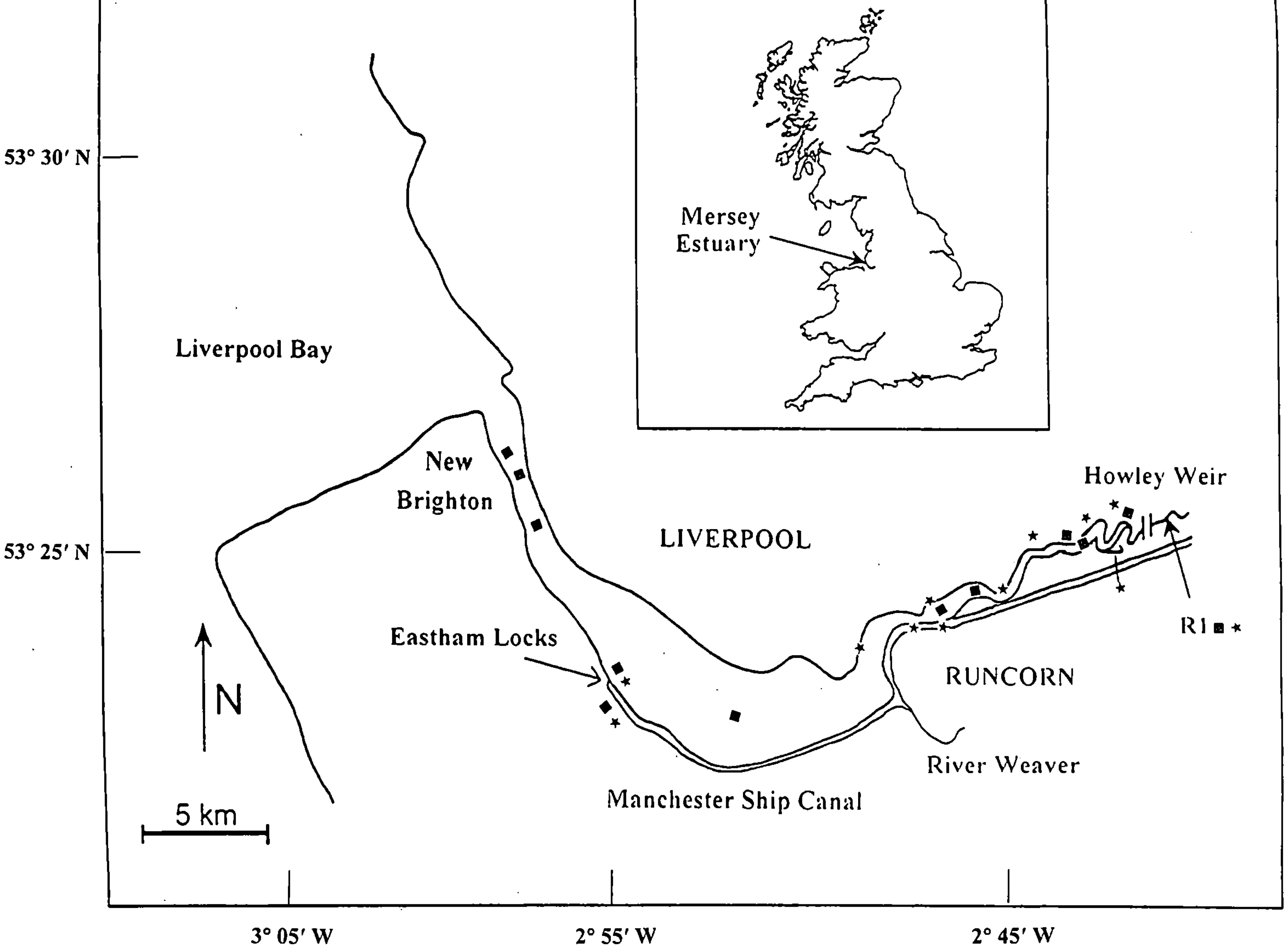


Figure 2.3 Location of the sampling positions for sediments obtained in July 1997 (■) and July 1999 (★). R1 is the sampling point for riverine sediments.

2.1.3 Sample collection and pre-treatment

2.1.3.1 Water

Samples of SPM for trace metal analysis were collected in Decon- and acid-washed 10-l plastic carboys. The closed carboys were each opened under the water so as to avoid surface microlayer contamination and rinsed three times with the sample before being filled. In order to preserve *in situ* solid-solution partitioning, filtration was performed as soon as possible after collection. This was achieved either immediately after a survey, in the Life Sciences Department at the University of Liverpool or exceptionally, upon return to Plymouth (within 24 hours of sample collection).

Distinction between particulate and dissolved phases is operationally defined by the nominal pore size of the filter used, which is conventionally 0.45 µm. However, a variety of metal species such as metals bound in colloids with clay, Fe and Mn oxides and humic acids in the size range 10-450 nm; metal-organic complexes at 1-10 nm; inorganic complexes such as metal hydroxides and chlorides; and free inorganic ions at <1 nm diameter may pass through the filter (Hall *et al.*, 1996). In addition, it is now recognised that a number of other factors may contribute to significant variability in the 'dissolved' concentrations of elements such as Al, Co, Cu, Fe, Ni, Pb and Zn (Horowitz *et al.*, 1992, 1996; Hall *et al.*, 1996). Differences in the pore size, pore type, diameter and type of filter used, the volume of sample processed, sample turbidity and the amount of organic matter present in the sample for example, have all been shown to affect resulting dissolved metal concentrations. Nevertheless, the majority of variations in dissolved element concentrations are thought to be due to the inclusion/exclusion of colloidal metals in the filtrate (Horowitz *et al.*, 1996). One method that may be employed to minimise the presence of colloidal artefacts is to use 'exhaustive filtration' of natural water samples, whereby the aliquot of filtrate retained for dissolved metals analysis is retrieved after several portions of water have passed through the same filter (Shiller and Boyle, 1987; Taylor and Shiller, 1995). The volume required to initially pass through the filter would be dependent on such factors as the turbidity and organic matter content of the native sample. Pre-loading the filter in this way reduces the effective pore size of the filter and consequently limits the amount of colloidal material being incorporated into the final dissolved sample and is the favoured technique in this study. Additionally, the same make and type of filters have consistently been used for the capture of dissolved and particulate trace metals in order to help achieve consistency in sample preparation throughout this analysis programme.

Native water samples were gently turbidised and vacuum-filtered using Nalgene polycarbonate filtration units through 47 mm, 0.45 μm pore size Sartorius cellulose acetate filters. Filtrate volumes were recorded, allowing the estimation of SPM concentrations. Between 200-500 ml of water sample were typically filtered before a sub-sample of filtrate was taken for the measurement of dissolved metals. Filtrates were collected into acid washed HDPE bottles and acidified to pH < 2 with concentrated HCl (AristaR, BDH) and stored at 4 °C to prevent hydrolysis of the metal ions, deter microbial action and reduce adsorption onto the container walls (Millward and Turner, 1995). After filtration, the SPM was rinsed with 20 ml of Milli-Q to remove any sea salts, although it is acknowledged that this may potentially desorb loosely bound metals (Millward and Turner, 1995). The washing step was included so as to (a) remove the contribution of salts to dry weight determinations, and (b) reduce spectral interferences in the spectroscopic measurement of trace metals. After drying under vacuum, the filters were replaced in petri dishes and left to dry to constant weight in a laminar flow hood before being re-weighed and later stored at -18 °C until analysis. Some filters were retained as blanks. Operational blanks were prepared by filtering a known volume of Milli-Q before and after filtering each batch of samples in order to assess the cleanliness of the protocols (Martino, 2000). It is important to note that in this investigation, the measurement of dissolved and particulate metals was always achieved from the same original whole water samples.

Near-surface water samples for dissolved and total suspended particulate carbon analysis were collected in 250 ml Decon-washed and pre-combusted glass bottles in the same manner as described earlier for sampling with carboys but additional care was taken not to introduce any air into the bottles. Turbidised samples were vacuum-filtered using glass filtration units through 47 mm, 0.7 μm pore size Whatman GF/F filters. The filters were then air-dried in a laminar flow hood, re-weighed, wrapped in Al foil and frozen until required. Filtrates were collected in ground glass-stoppered glass bottles and acidified with concentrated H_3PO_4 (300 μl per 100 ml of sample, AristaR, BDH), wrapped in Al foil and stored at 4 °C until analysis (Tupas *et al.*, 1994). The operational blank consisted of Milli-Q water treated in exactly the same way as the samples. Concentrations of DOC in H_3PO_4 were always below the detection limit.

Near-surface water samples were also filtered through unashed GF/F filters for chlorophyll *a* analysis with the volumes of water filtered being recorded each time.

2.1.3.2 Settling experiments

Suspended particulate material from some of the water samples was separated into two components, permanently suspended particulate material (PSPM) and temporarily suspended particulate material (TSPM), based on differences in their settling characteristics. A maximum of six settling experiments were performed for each survey, with samples selected to cover a broad salinity and turbidity range each time. Samples were homogenised by gentle agitation of the carboy and a 1 litre sub-sample was immediately transferred to a measuring cylinder, in which the particles were allowed to settle under gravity for 30 minutes. This period was selected as it is representative of the water residence time within the upper half of the estuary where most of these samples originated. After 30 minutes, the majority of the suspension was carefully siphoned off, giving a decanted fraction containing only PSPM. The remaining settled material therefore consisted of TSPM, together with a residual portion of PSPM. For trace metal analyses, the decanted PSPM-only sample was filtered through cellulose acetate filters as described previously. The filtrate volume was recorded, after which the filtrate was added to the small volume of TSPM in order to resuspend the settled particles, which were then also filtered using a second cellulose acetate filter. The volumes of water filtered at each stage of the process were recorded, thus allowing the determination of PSPM and TSPM concentrations in the original sample. For example, by knowing the concentration of PSPM in the decanted sample, it was then possible to correct the TSPM concentration for residual PSPM. The same procedure was adopted for the separation of PSPM and TSPM for total suspended particulate carbon determinations, the only differences being that the bulk water samples were collected in glass bottles and filtered through ashed GF/F filters (see Sections 2.1.2 and 2.1.3.1).

2.1.3.3 Sediments

Surface sediment samples were collected either by van Veen grab from the boat in mid-channel (July 1997) or by hand from the shore (July 1999) (Figure 2.3). In each case, the surface (1-2 cm) layer was removed using a polyethylene spatula and stored in plastic containers. In the laboratory, the sediments were fractionated into <63 μm and >63 μm components prior to acid digestion. Approximately 1g of sample was wet sieved through an acid-washed 63 μm nylon mesh using a few mls of Milli-Q. The sieving was aided manually by gently stirring the sediment with a plastic spatula. The mesh was placed on the top of a 47 mm filtration unit and a few drops of Milli-Q added around the edge to create a vacuum seal around the top of the cup. The fine-grained fraction was received into the filtration unit and instantly filtered through a cellulose acetate filter. On completion of the sieving, the filter was washed with 20 ml of Milli-Q and dried to constant weight in a laminar flow hood. The coarse-grained sediment portion was washed from the mesh, filtered through another cellulose acetate filter and similarly dried. The sediment samples were stored at -18 °C until required.

2.1.4 Master variables

2.1.4.1 Measurement of temperature, salinity, pH and dissolved oxygen

Temperature, salinity, pH and dissolved oxygen were measured using previously calibrated instruments *viz*: an MC5 T-S bridge, a Hanna pHOX 52E pH meter and a Clandon YSI-58 dissolved oxygen meter, respectively. Where necessary, conductivity measurements were made using a WPA CM35 conductivity meter.

2.1.4.2 Analysis of dissolved organic carbon

Dissolved organic carbon was determined immediately after filtration using an automatic Shimadzu Total Organic Carbon-5000 analyser. The instrument was calibrated with standard solutions of $NaHCO_3$ for inorganic carbon and potassium hydrogen phthalate for total carbon, to provide a working range of 0-20 mg C l^{-1}.

2.1.4.3 Analysis of chlorophyll a

Glass fibre filters loaded with SPM were analysed for chlorophyll *a*. Each filter was placed in a boiling tube to which 20 ml of methanol was added such that the filter was covered. The tube was then stoppered and the contents warmed in a hot water bath kept at 65 °C. The methanol was boiled for 10 seconds, and the stopper periodically removed to release pressure inside the tube. The tube was then removed from the water bath, re-stoppered and kept in the dark for 5 minutes. The filter paper was carefully removed and squeezed to minimise solvent removal and the solution consequently centrifuged at 3500 rpm for 7 minutes to yield a clear solution. The solution was carefully decanted into a glass cuvette having a path length of 2 cm and the absorbance of the solution was measured in a UV/visible spectrophotometer zeroed on methanol (Strickland and Parsons, 1972). Absorbance measurements were made at two wavelengths, 665 nm, the absorbance maximum of chlorophyll *a*, and 750 nm to compensate for background turbidity. The chlorophyll *a* concentration was calculated as:

$$\text{Chl a} = \frac{13.9 * A * v}{d * V} \qquad \text{Equation 2.1}$$

where A = the difference in absorbance (units) at the two wavelengths; v = volume of methanol (ml); V = volume of filtrate (l); d = cell path length (cm); units are μg l^{-1}. The constant (13.9) is the reciprocal of the specific absorption coefficient of methanol x 10^3.

2.1.5 Analysis of particulate trace metals

2.1.5.1 Digest method for extractable trace metals in SPM and surface sediments

Some of the cellulose acetate filters and retained SPM were digested at room temperature for 24 hours in covered PTFE reactors using 25 ml of 1M HCl (AristaR, BDH made up with Milli-Q). Three filters were separately digested for each station. For fine- and coarse-grained sediment fractions, approximately 0.7 g of material was digested in each reactor. Digests were performed in triplicate on both grain-size fractions from each sediment sampling site.

The 1M HCl digest removes weakly bound trace metals, believed to correlate more closely with bioavailability than other extraction methods (Luoma, 1983; Bryan and Langston, 1992). This digest also attacks amorphous oxides and clays, although recoveries of lattice-bound metals are low compared to a total extraction (Millward *et al.*, 1996). It is noted therefore that the metal component liberated by 1M HCl cannot be truly allied with any specific particulate phase (Luoma and Bryan, 1981) and possibly over-estimates the true fraction available to aquatic organisms. Enzymatic digestion techniques aimed at simulating conditions in the gut are now under investigation for the evaluation of 'bioavailable' or 'gut soluble' fractions of carbon, nitrogen, mineral and trace metals from contaminated sediments (Turner *et al.*, 2001a). However, consistent use of the 1M HCl leach within the research group (Williams, 1995; Millward *et al.*, 1996; Sands, 1997; Dixon, 1998) and by other workers in the UK (e.g. Langston, 1986; Tappin *et al.*, 1995), allows for direct comparisons between data sets for different estuaries.

After digestion, each sample was filtered through a 47 mm, 0.45 μm cellulose acetate filter contained within a Nalgene polycarbonate filtration unit. The filters and PTFE beakers were rinsed with a few mls of 1M HCl and the leachate transferred to a 50 ml polyethylene volumetric flask which was then made up to the mark with 1M HCl. Procedural blanks were prepared in the same manner using unused filters. Reagent blanks were also prepared each time a batch of filters or sediments were digested by placing 25 ml of acid alone in a

Teflon beaker and continuing as for a normal sample, including filtration. The resulting digest solutions were stored in high density polyethylene (HDPE) bottles prior to analysis by Flame Atomic Absorption Spectrophotometry (FAAS) and Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS). Samples of Certified Reference Materials (CRMs) BCSS-1 and PACS-1 supplied by the Canadian National Research Council (CNRC) and an in-house standard prepared from <63 µm grain size North Sea sediment were co-digested (in triplicate) with each batch of estuarine samples. Approximately 0.7 g of material was used in each instance and treated in exactly the same manner as the Mersey sediment samples. The results of these analyses are presented in Section 2.2.

2.1.5.2 Digest method for total metals in SPM

An HF digestion method was employed for the extraction of total metals (Williams, 1995). Weighed filters and associated SPM were placed in PTFE reactor vessels to which 1 ml of *aqua regia* and 1 ml of HF was added. The vessel was then placed in a boiling water bath for 1 hour, after which the remaining sample was evaporated to dryness. The vessel was washed several times with small volumes of 1M HCl (AristaR, BDH) and the washings transferred to a 25 ml polyethylene volumetric flask. The digest solution was then carefully made up to the 25 ml mark with 1M HCl before being filtered through pre-weighed cellulose acetate filters in order to remove charred remains of the original filters, (shown to produce interference in preliminary analysis by GFAAS). The resulting filtrates were stored in HDPE bottles for later analysis by FAAS and Inductively Coupled Plasma Atomic Emission Spectophotometry (ICP-AES). Blank filters, reagent blanks and the Certified Reference Sediments BCSS-1 and PACS-1 (approximately 0.7 g) were also digested in the same manner, to provide Quality Assurance data, the results of which are discussed in Section 2.2.

2.1.5.3 Analysis of extractable trace metals in SPM and surface sediments

Flame AAS determination of particulate Fe, Mn and Zn in the digests was made using a PTFE microcup attached to a Varian SpectrAA 300/400 Plus flame atomic absorption spectrophotometer connected to an on-line printer. The instrumental parameters and standards used for each metal are given in Williams (1995). Deuterium background correction was applied for the measurement of Zn to reduce spectral interference caused by scattering. Samples were injected manually into the air-acetylene flame *via* the microcup using 200 µl volumes. Sample absorbance was recorded digitally by the instrument and was based on peak height. Concentrations of Fe, Mn and Zn were calibrated using linear calibration and a minimum of four standards prepared from Spectrosol standards (BDH) made up in 1M HCl (AristaR, BDH) to maintain a consistent matrix between estuarine digest samples and standards. All standards were analysed in triplicate and a calibration curve fitted using the mean absorbance for each standard. The acceptance criterion for all calibrations was $R \geq 0.995$. Samples were analysed in triplicate and the batch analytical precision, as relative standard deviation of the method was <10% for each determined concentration. Samples were diluted if necessary using 1M HCl (AristaR, BDH) so that their absorbance readings fell within the linear ranges of the calibrations and re-calibration was performed after every 10 samples. Detection limits were taken as being three times the standard deviation of the blank values and these, along with the blank concentrations obtained for Fe, Mn and Zn using FAAS are reported in Table 2.2.

Surface sediment and SPM samples digested with 1M HCl were analysed for Cd, Co, Cu, Ni and Pb by GFAAS using a Perkin Elmer 4100ZL with Zeeman background correction connected to a Perkin Elmer AS-70 autosampler. Optimisation of the GFAAS temperature programmes was performed so as to identify the temperature that gave maximum absorbance and smoothest peak profile. Calibration was by the linear method using a minimum of four standards made from Spectrosol standards (BDH) made up in 1M HCl (AristaR, BDH). All standards were analysed in triplicate and a calibration curve was fitted using the mean blank corrected peak area for each standard. The same acceptance criteria were employed for calibrations and sample measurements as described previously for FAAS.

The analysis of marine and estuarine samples is often complicated by an array of matrix or 'salt' effects (Sturgeon, 1989). Matrix interferences arise when the physical characteristics of the sample and standard differ considerably, *i.e.* a high salt content within estuarine or marine samples compared to acidified standards. This may occur, even if measures are taken to remove seawater salts by extensive washing of the particles upon initial filtration. The use of matrix modifiers combined with selection of the correct instrumental conditions can reduce or eliminate such effects (Tsalev *et al.*, 1990). Matrix modifiers work by reacting with the analyte, stabilising the metal so that higher pyrolysis temperatures can be used to obtain smoother peak profiles.

Full details of the furnace programmes used, instrument operating parameters, standards and matrix modifiers employed are given elsewhere (Williams, 1995). Optimisation of the

Table 2.2 Blank concentrations and detection limits for Fe, Mn and Zn determinations using FAAS.

	Blank concentration						Detection limit					
Survey	**Jul/97**	**Dec/97**	**Mar/98**	**Jun/98**	**Oct/98**	**Jul/99**	**Jul/97**	**Dec/97**	**Mar/98**	**Jun/98**	**Oct/98**	**Jul/99**
SPM												
1M HCl												
Fe (mg l^{-1})	0.07	nd	nd	nd	nd	#	0.92	0.31	0.68	0.16	0.27	#
Mn (mg l^{-1})	0.09	nd	nd	nd	0.06	#	0.83	0.16	0.33	0.10	0.16	#
Zn (mg l^{-1})	nd	nd	nd	0.01	nd	#	0.02	0.05	0.05	0.02	0.12	#
SPM												
HF												
Fe (mg l^{-1})	#	nd	0.15	nd	nd	#	#	0.31	0.32	0.62	0.56	#
Mn (mg l^{-1})	#	nd	0.02	nd	nd	#	#	0.16	0.13	0.18	0.23	#
Zn (mg l^{-1})	#	0.02	0.17	0.01	0.01	#	#	0.03	0.26	0.03	0.03	#
SEDIMENT												
1M HCl												
Fe (mg l^{-1})	0.13	#	#	#	#	0.07	0.38	#	#	#	#	0.44
Mn (mg l^{-1})	0.39	#	#	#	#	nd	0.27	#	#	#	#	0.28
Zn (mg l^{-1})	0.03	#	#	#	#	nd	0.02	#	#	#	#	0.02

nd = below limits of detection; # = not part of sampling/analytical programme

Table 2.3 Blank concentrations and detection limits for Cd, Co, Cu, Ni and Pb determinations using GFAAS.

	Blank concentration						**Detection limit**					
Survey	**Jul/97**	**Dec/97**	**Mar/98**	**Jun/98**	**Oct/98**	**Jul/99**	**Jul/97**	**Dec/97**	**Mar/98**	**Jun/98**	**Oct/98**	**Jul/99**
SPM												
1M HCl												
Cd (μg l^{-1})	0.17	0.10	0.01	nd	0.01	#	0.95	0.15	0.07	0.23	0.21	#
Co (μg l^{-1})	#	nd	nd	nd	nd	#	#	1.18	2.76	2.59	1.65	#
Cu (μg l^{-1})	0.42	nd	nd	nd	0.09	#	1.98	1.02	1.75	1.19	0.61	#
Ni (μg l^{-1})	#	nd	nd	0.43	nd	#	#	1.25	3.14	4.02	3.01	#
Pb (μg l^{-1})	nd	1.79	0.28	nd	0.09	#	3.98	3.75	1.73	4.38	1.28	#
SEDIMENT												
1M HCl												
Cd (μg l^{-1})	nd	#	#	#	#	nd	0.12	#	#	#	#	0.11
Co (μg l^{-1})	#	#	#	#	#	1.02	#	#	#	#	#	1.61
Cu (μg l^{-1})	0.27	#	#	#	#	nd	3.95	#	#	#	#	1.50
Ni (μg l^{-1})	#	#	#	#	#	nd	#	#	#	#	#	0.89
Pb (μg l^{-1})	1.67	#	#	#	#	0.02	3.01	#	#	#	#	1.41

nd = below limits of detection; # = not part of sampling/analytical programme furnace programmes was performed as necessary for each metal, by cycling through different combinations of char and atomisation temperatures. Detection limits (determined as 3σ of the blank) and blank concentrations obtained for particulate Cd, Co, Cu, Ni and Pb using GFAAS are provided in Table 2.3.

The HF-extractable trace metals were analysed by ICP-AES on a Varian Liberty 200. The acceptance criteria for the determination of total trace metal concentrations were the same as for FAAS and GFAAS. Blank concentrations and detection limits for measurements of total particulate Cd, Co, Cu, Ni and Pb by ICP-AES are given in Table 2.4.

Table 2.4 Blank concentrations and detection limits for Cd, Co, Cu, Ni and Pb determinations using ICP-AES.

	Blank concentrations				Detection limits			
Survey	**Dec/97**	**Mar/98**	**Jun/98**	**Oct/98**	**Dec/97**	**Mar/98**	**Jun/98**	**Oct/98**
Cd (μg l^{-1})	1.46	1.01	2.29	2.16	2.43	3.43	1.76	3.26
Co (μg l^{-1})	4.49	1.58	1.07	0.84	4.98	4.74	4.99	4.98
Cu (μg l^{-1})	3.96	1.17	1.56	2.89	4.64	2.14	3.67	4.48
Ni (μg l^{-1})	2.46	1.16	2.10	1.69	3.25	1.50	3.28	2.71
Pb (μg l^{-1})	1.71	1.45	1.59	1.42	4.93	3.02	3.12	2.73

2.1.6 Particulate carbon analysis

Particulate organic carbon was initially estimated by the loss on ignition (LOI) method for the July 1997 and December 1997 surveys. Filters (GFF) and size-fractionated sediments were ashed at 450 °C for 8 hours and the percentage weight loss calculated. However, this method has previously been reported to overestimate POC by around 10% at this temperature. It is thought this is due to the loss of structural water associated with clay lattices and other inorganic materials at or below 450 °C (Mook and Hoskin, 1982). The results were used only to provide a guide for subsequent analyses and are not reported further here. The carbon and nitrogen contents of freeze-dried sediment and SPM samples collected in later surveys were measured using a Carlo Erba EA1110 Elemental Analyser, calibrated with acetanilide, cyclohexanone and EDTA standards.

Reliable determinations of elements such as C and N in sediments are requisite for biogeochemical and partitioning studies. Accurate elemental concentration data are essential for the validity of C:N ratios, for example, that help to identify the origins of organic matter in estuarine and marine systems (Matson and Brinson, 1990; Meyers, 1994; Thornton and McManus, 1994, Hellings *et al.*, 1999). It has been suggested that differences in analytical methods may explain much of the observed variability in oceanic C concentrations (King *et al.*, 1998). Percentage organic carbon contents of sediments are traditionally achieved through the removal of carbonates by acidification of the sample, either by the direct addition of concentrated acid or by vapour acidification (Ryba and Burgess, 2002 and references therein). The direct application of 1M HCl has been recommended for the accurate determination of organic carbon in marine sediments (Ryba and Burgess, 2002) but should not be used for H, N, O or S measurements. However, after much consultation it was decided that fuming would not be used to remove $CaCO_3$. The analysis of SPM on filters therefore represents that of total C.

For bulk SPM, PSPM and TSPM loaded on GF/F filters, small discs were cut with an 8 mm diameter metal cork borer. Three discs were removed from each filter and three filters were used for each station and each sample type. This was done to account for any differences in SPM distribution across individual filter surfaces. Thus, a total of nine discs representing every station or sample type were analysed by CHN. The discs were individually placed in weighed tin foil capsules and the combined weight of each capsule and disc recorded. Correction was made for the contribution to the total mass made by the portion of filter material present before the sample mass was entered on the computer program. The tops of the capsules were carefully sealed and the capsules squeezed with metal tweezers to make them as small as possible for loading into the autosampler carousel.

For the last two surveys (May 2000 and July 2000), water remaining in the carboys after sub-sampling for filtration, was allowed to settle out over a period of 3 hours. The settled material was then carefully harvested, filtered and freeze-dried. This procedure is therefore not the same as that described for the routine settling experiments in Section 2.1.3.2 but was performed so that as much SPM as possible could be recovered. The same carbon analyses could then be performed upon both this material and size-fractionated bed sediments as follows.

Small portions (typically around 10 mg) of freeze-dried size-fractionated sediments and bulk settled SPM were carefully introduced into the foil capsules using a small metal spatula and then treated in the same manner as the SPM samples. These samples were prepared in triplicate and measurements made upon them therefore relate to total carbon and nitrogen present in unaltered (natural) samples. The remaining bulk settled SPM and fractionated sediments were subjected to a sequential digest as used by Thomas *et al.*, (1994) and adapted by Bayon *et al.*, (2002). In this method, a combination of hydroxylammonium chloride and acetic acid is used to remove both carbonate and Fe-Mn oxide fractions from sedimentary material, thereby allowing the measurement of organic carbon in a sample. It is the preferred digest in this study as it is thought to be less destructive than 1M HCl (Ryba and Burgess, 2002) but just as effective at eradicating the Fe and Mn oxyhydroxide and inorganic carbon phases. Approximately 2 g of each natural sample was digested for 24 hours with 0.05M $NH_2OH.HCl$ in 25% CH_3COOH. The samples were filtered, washed, air-dried and then freeze-dried before aliquots were taken for further CHN analyses. Of the remaining material, approximately 0.5 g was further digested in 30% H_2O_2 at 85 °C for 2 h to oxidise any organic matter prior to measurement of C, H and N. Results from this material provided data on any residual particulate carbon remaining that was resilient to the initial (moderate) and second (harsh), acid digests employed.

Triplicate analyses of the samples and blanks gave consistent coefficients of variation of within ± 5% (typically < 2 %), the precision being maintained regardless of sample type (*i.e.* SPM on filters, bulk material, total C, organic C and residual C). The total carbon contents of the CRMs BCSS-1 and PACS-1 were also measured in order to assess the accuracy of the technique and the results of these analyses are given in Section 2.2.

2.1.7 Specific surface area analysis of SPM and sediments

Natural and digested samples of bulk settled SPM and sediments arising from the July 1999, May 2000 and July 2000 surveys were analysed using the multi-point BET N_2-adsorption technique (Millward *et al.*, 1990). This was done to assess the effects of removing inorganic and organic carbon (as outlined in the previous section) upon the amount of 'active' surface present on Mersey particles. As the material was relatively fine, only around 0.2 – 0.3 g was used each time and the evacuation rate was lowered to 50.0 mm Hg min^{-1} to prevent loss from the sample tube. The instrument, a Micromeritics Gemini 2360 Surface Area Analyser was calibrated using kaolinite standards, the specific surface area of which was consistently found to lie within 4% of the certified value.

2.1.8 Dissolved metal analysis

Dissolved trace metals were determined by voltammetry using either a µ-Autolab

(Ecochemie) voltammeter connected to a Metrohm 663VA mercury drop electrode, or an Autolab (Ecochemie) voltammeter connected to a PAR 303A mercury drop electrode (Martino, 2000). All reagents for sample analysis were of AristaR analytical grade (BDH and Sigma); details of the reagents and analytical procedures are found elsewhere (Turner *et al.*, 1998). Briefly, the acidified samples were UV-irradiated for 4 hours with a 400 W high-pressure Hg-vapour lamp to destroy organic matter, and analysed according to established methods (Martino, 2000). The accuracy of the technique was assessed by replicate analyses of CRM CASS-3 (coastal water) and SLRS-2 (river water), the results of which are provided in Table 2.10.

2.2 Quality Assurance

During analysis of trace metals arising from the first two surveys, an in-house reference sediment, originating from the North Sea was co-digested with each batch of sediment and SPM samples. The results of these quality control samples are provided in Table 2.5. This material had been analysed previously within the laboratory using the same leach and thus provided a historical data set of 'certified' values (Williams, 1995). Cobalt and nickel determinations were not made for the first (July 1997) survey. Concentrations of Fe, Mn, Cd, Cu, Ni and Pb determined in this study were all within 10% of historical values. A two-tailed t-test was performed on the data in Table 2.5. As calculated values for t are less than tabulated values in all cases, the results of the test indicate very highly significant agreement at the 99.9% confidence level between the means of observed and historical concentrations for all metals.

Table 2.5 Certified and detected concentrations of trace metals available to 1M HCl in an in-house reference sediment, where n = number of determinations, and t_{calc} and t_{crit} are calculated and critical values for t obtained in a t-test.

	Observed Concentration			**Historical Concentration**				
Metal	**Mean**	**RSD**	**n**	**Mean**	**RSD**	**n**	t_{calc}	t_{crit}
Cd ($\mu g\ g^{-1}$)	0.40 ± 0.08	20	6	0.38 ± 0.08	20	8	0.18	4.32
Co ($\mu g\ g^{-1}$)	7.9 ± 0.4	14	6	7.6 ± 1.1	14	8	0.26	4.32
Cu ($\mu g\ g^{-1}$)	26.4 ± 3.5	13	6	28.6 ± 4.5	16	8	0.39	4.32
Fe ($mg\ g^{-1}$)	18.3 ± 1.8	10	8	16.8 ± 1.9	11	11	0.57	3.97
Mn ($\mu g\ g^{-1}$)	691 ± 46	7	8	675 ± 121	18	10	0.12	4.02
Ni ($\mu g\ g^{-1}$)	22.6 ± 3.7	16	6	22.4 ± 7.8	15	8	0.02	4.32
Pb ($\mu g\ g^{-1}$)	117 ± 10	9	6	119 ± 12	10	8	0.13	4.32
Zn ($\mu g\ g^{-1}$)	141 ± 23	13	8	130 ± 12.6	10	10	0.42	4.02

For subsequent surveys, the CRMs BCSS-1 and PACS-1 were analysed after being subjected to the 1M HCl leach, the results of which are presented in Table 2.6. Unfortunately there are no certified concentrations for 1M HCl-extractable trace metals available and therefore the accuracy of these analyses cannot be fully assessed. However, comparisons of the percentages of each metal recovered using this digest to that yielded using a total digest indicates variability, not only between metals but also the sediments themselves, thus highlighting the selectivity of 1M HCl as a leaching agent. Moreover, the percentage recoveries closely match those determined in two other studies.

Table 2.6 Percentage metal recovered by 1M HCl on the certified reference sediments BCSS-1 and PACS-1, where n = number of determinations. The values indicate the mean of observed recoveries compared to the mean of the certified total metal concentration.

CRM	**n**	**Cd**	**Co**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
BCSS-1									
This work	12	80	41	46	22	24	24	92	49
Sands (1997)	4	-	-	-	22	23	30	-	42
Dixon (1998)	5	105	-	45	24	26	-	104	-
PACS-1									
This work	12	77	46	64	35	28	46	94	83
Sands (1997)	4	-	-	-	37	28	47	-	82
Dixon (1998)	5	105	-	67	37	28	-	100	-

Quality Assurance for the measurement of total metals was provided by analysis of the same CRMs (BCSS-1 and PACS-1) using ICP-AES, the results of which are provided in Table 2.7.

Table 2.7 Total metals analysis of BCSS-1 and PACS-1 by ICP-AES. Number of determinations made in this study for each CRM = 9. Concentrations are in $\mu g\ g^{-1}$, apart from Fe ($mg\ g^{-1}$).

CRM	**Cd**	**Co**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
BCSS-1								
Measured	0.29 ± 1.0	12.6 ± 1.9	17.3 ± 2.5	31.7 ± 1.3	220 ± 25	51.4 ± 3.8	31.5 ± 3.0	136 ± 19
Certified	0.25 ± 0.04	11.4 ± 2.1	18.5 ± 2.7	32.9 ± 1.0	229 ± 15	55.3 ± 3.6	22.7 ± 3.4	119 ± 12
PACS-1								
Measured	2.40 ± 0.40	18.9 ± 1.2	473 ± 40	44.6 ± 1.7	468 ± 66	43.8 ± 2.4	410 ± 26	777 ± 56
Certified	2.38 ± 0.20	17.5 ± 1.1	452 ± 16	46.9 ± 0.8	470 ± 12	44.1 ± 2.0	404 ± 20	824 ± 22

The results indicate that generally, detected concentrations are within 10% of certified values. There is evidence of slight sample contamination resulting in over-estimations of Pb and Zn for BCSS-1, which is believed to be due to the preparation of 3 BCSS-1 samples coinciding with a period of laboratory refurbishment at the University of Plymouth. A t-test is not possible on the data in Table 2.7, as the number of determinations made on the CRMs by CNRC in order to derive the certified metal concentrations is not indicated on the certificate accompanying the CRM samples.

Accuracy of the CHN analyses was also checked. This was achieved by the measurement of total particulate carbon in BCSS-1 and PACS-1, the findings of which are presented in Table 2.8. The results show that the analytical protocols employed were highly reproducible, with measured values being consistently within 4% of the certified values. A t-test is not possible on the data in Table 2.8, as the number of determinations made on the CRMs by CNRC is not indicated.

Table 2.8 Analyses of total carbon in BCSS-1 and PACS-1, where n = number of determinations made in this study.

	BCSS-1	PACS-1
n	18	18
Measured (%)	2.10 ± 0.07	3.54 ± 0.13
Certified (%)	2.19 ± 0.09	3.69 ± 0.11

The dissolved metal analyses were tested against two CRMs, CASS-3 and SLRS-2, which give a range of concentrations normally encountered in estuarine waters (Martino, 2000). Again, as for BCSS-1 and PACS-1, a statistical comparison of measured and certified metal concentrations in CASS-3 and SLRS-2 cannot be made as the number of determinations made on the CRMs by CNRC is not known.

Table 2.9 Analysis of CRM CASS-3 and SLRS-2 (nM), where n = number of determinations; nd = below the limit of detection (Martino, 2000).

CRM	Cd	Co	Cu	Ni	Pb	Zn
CASS-3						
Measured (n =6)	0.35 ± 0.07	0.51 ± 0.14	8.0 ± 0.75	5.8 ± 0.50	nd	22.4 ± 1.3
Certified	0.27 ± 0.02	0.70 ± 0.08	8.1 ± 0.50	6.6 ± 0.50	0.06 ± 0.01	19.0 ± 1.5
SLRS-2						
Measured (n = 5)	0.56 ± 0.06	0.85 ± 0.04	40.2 ± 1.8	19.8 ± 0.7	0.64 ± 0.02	49.6 ± 1.4
Certified	0.25 ± 0.02	1.0 ± 0.10	43.4 ± 1.4	17.5 ± 0.9	0.62 ± 0.03	50.9 ± 1.2

2.3 Laboratory studies

Radiochemical experiments were performed in the laboratory using native water samples from the March, June and October 1998 surveys (Figure 2.1). The high specific activity γ-emitting radioisotope ^{203}Hg (E = 279 keV; $t_{1/2}$ = ~ 47 days) was used to examine the extent of metal uptake by estuarine SPM. The method assumes that the very small amount of radioactive Hg introduced behaves in the same way, chemically, as stable Hg and does not perturb the pre-existing chemical equilibrium of the sample (Anderson *et al.*, 1987).

2.3.1 Preparation of equipment for radiochemical experiments

All bottles, carboys, filters and filtration units for the collection, filtration and storage of water samples used in these experiments were cleaned as described in Section 2.1.2. In addition, a small Millipore glass filtration unit capable of taking 25 mm filters and 60 ml Nalgene polycarbonate bottles were soaked in 5% Decon for 24 hours, rinsed thoroughly with Milli-Q water and soaked in 1M HCl (AnalaR, BDH) for 48 hours. They were then rinsed with Milli-Q and dried in a laminar flow hood. Cellulose acetate filters (25 mm, 0.45 μm pore size, Sartorius) were washed for 24 hours in 0.1M HCl (AristaR, BDH) before being rinsed in Milli-Q and placed in individual acid-washed petri dishes. The filters were dried overnight in a laminar flow hood and then weighed.

2.3.2 Sample collection and pre-treatment

Near-surface water samples were collected in acid-washed 10-litre carboys as described in Section 2.1.3 (see also Figure 2.1). Some of the SPM used in the radiotracer experiments was derived from settling experiments, the procedures for which are also outlined in Section 2.1.3. (Figure 2.1). All samples set aside for incubations were stored in the dark at 4 °C until use.

2.3.3 Incubation experiments

The sorptive behaviour of inorganic mercury has been investigated by undertaking 24 h uptake experiments using the radiotracer ^{203}Hg. Incubation times may be varied according to the reactivity of the metal being applied. For instance, a period of five days has been utilised in studies using ^{65}Zn, ^{109}Cd and ^{137}Cs, when added to samples taken from estuaries with considerable flushing times (Turner *et al.*, 1992a). In these instances, results indicated that five days was a suitable timescale for these metals with low particle reactivities to achieve equilibration between dissolved and particulate phases. However, Hg has a strong affinity for particles and the uptake of ^{203}Hg is virtually instantaneous, with almost complete adsorption occurring within one minute (Le Roux, 2000). Therefore, incubations with unfiltered water samples were accomplished for the calculation of 1-day K_ds, the procedures for which are illustrated schematically in Figure 2.4.

Laboratory studies are often conducted in discrete, parallel experiments which inadequately reproduce the *in situ* variability of salinity, turbidity, the chemical composition of SPM and the relative dominance of different particle types in suspension. A batch mixing method is often employed in radiotracer partitioning experiments, whereby freshwater sediment slurry of known turbidity is added to waters that are made up of combinations of filtered river and marine end-member water samples that have been previously equilibrated with radioisotope. Under such conditions, turbidity and salinity are controlled. The investigations made in this study have involved the addition of radiotracer to ambient water samples of naturally varying compositions. It is envisaged that results will therefore indicate the degree of *in situ* radiotracer partitioning under more realistic (*i.e.* natural) estuarine conditions.

Natural water samples from all 18 stations sampled during the March 1998 survey were used for initial incubation studies but because of the large number involved, this batch of experiments was only performed in duplicate. However, this did allow a study of ^{203}Hg uptake by SPM samples from the entire axial transect. For the June and October 1998 surveys, only water samples from sites used in settling experiments were utilised. These sites were chosen primarily to cover a wide range in salinity and turbidity and the smaller number of samples allowed for each set of assays to be performed in triplicate.

Prior to the incubation experiments, acid-washed polycarbonate bottles were conditioned overnight with the estuarine samples and stored at 4 °C thereby limiting adsorption of radiotracer to the container walls. Fresh sample (40 ml) was then introduced and spiked with 20 μl of ^{203}Hg solution previously prepared using filtered river water and radioisotope stock supplied by Amersham International ($HgCl_2$/HCl). A final activity of the isotope of approximately 100 Bq ml^{-1} was achieved in the reaction vessels. These concentrations were in the nanomolar range *i.e.* close to those encountered in the marine environment. The samples were shaken at 300 rpm for 24 hours at a constant temperature of 20 °C before filtration through pre-weighed cellulose acetate filters. The pH of each sample was monitored before and after addition of the spike and at the end of the incubation period.

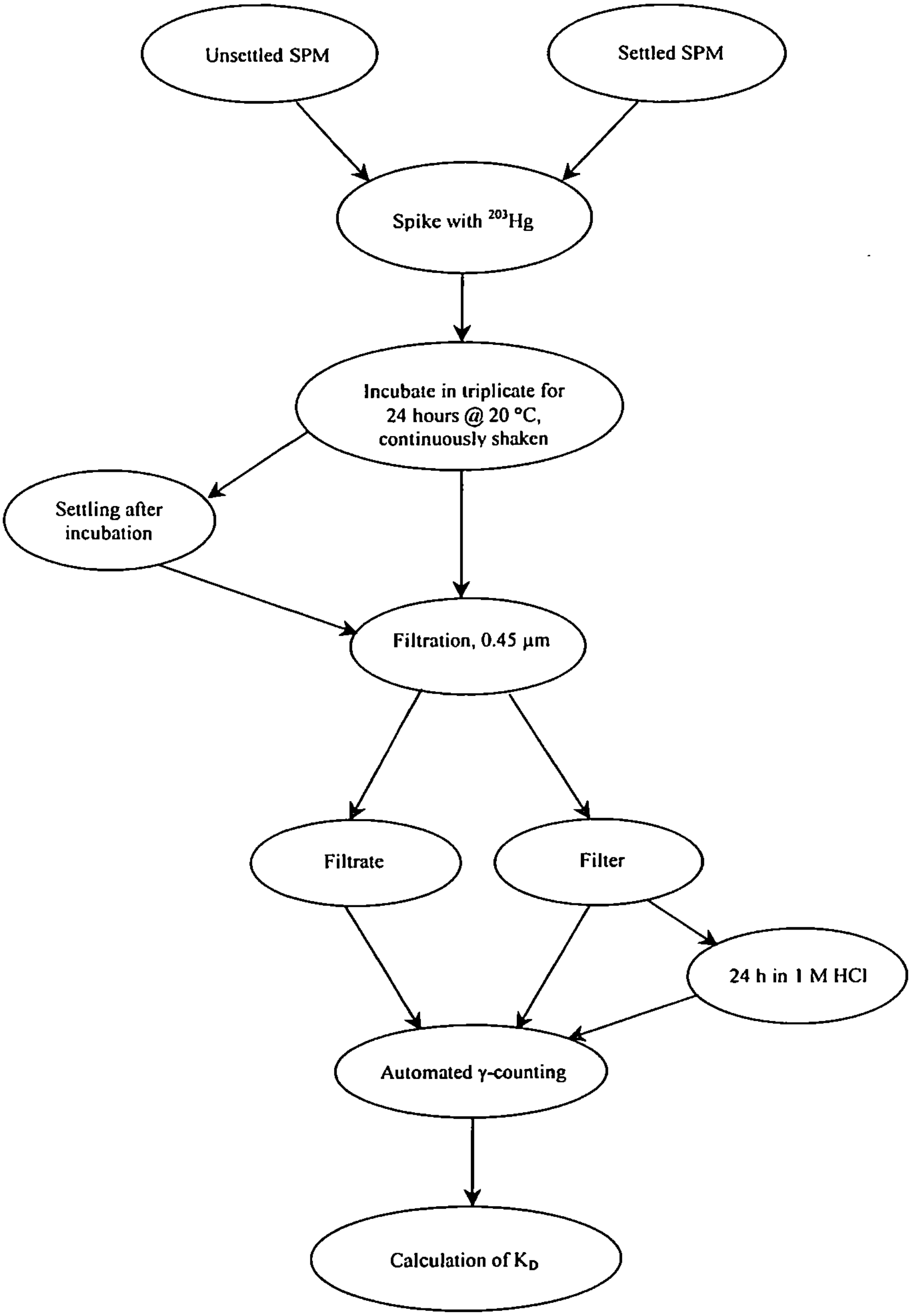


Figure 2.4 Protocols for radiochemical experiments.

Sample pH was virtually unaltered by the addition of the radioisotope, only varying by ± 0.2 pH units. The filters and 20 ml of the filtrates were then placed into acid-washed scintillation vials to measure particulate and dissolved ^{203}Hg activity. Gamma-energies were counted using a high performance Wallac 1480 'Wizard 3' Gamma Spectrometer with NaI detection; each sample was counted three times for 1 000 s and automatically background corrected. After counting, filters were dried and re-weighed. Radioactive decay correction was calculated for all activities measured due to the relative length of the experiments and the short half-life of the radioisotope. The range of counting errors was usually < 1% for filters and < 5% for filtrates. Partition coefficients (K_Ds, l kg^{-1}) were calculated as follows (Turner *et al.*, 1993):

$$K_d = \frac{A_p * V * 10^3}{A_s * m * f} \qquad \text{Equation 2.2}$$

where A_p and A_s are the blank corrected activities on the filter and in solution respectively; V is the volume of solution in ml; m is the dry mass of SPM on the filter in mg; and f is the geometric correction factor, determined from the ratio of measured activity per spike absorbed in a blank filter and dissolved in 20 ml of ultra-pure water.

Samples of PSPM and TSPM from the March, June and October 1998 transects were isolated by settling and also incubated with ^{203}Hg in the same manner as previously described, thereby allowing an examination of radiotracer uptake by the two different suspended particle populations. Another experiment was undertaken using the March 1998 samples in which bulk SPM was differentiated by settling for 30 minutes after the 24-hour incubation period (Figure 2.4). After 30 minutes, the PSPM was carefully removed using a dropping pipette and filtered. The filter was replaced with a new one and the TSPM remaining in the polycarbonate bottle was then also filtered. Both filters and 20 ml of the corresponding filtrates were then counted as described earlier. Comparison of the results issuing from this experiment and that conducted with previously fractionated SPM showed very little difference in results between the two protocols. Therefore, the post-incubation settling experiment was not repeated for later surveys.

Half of the samples in each type of experiment performed in March 1998 were poisoned with 5% (w/w) NaN_3 (10 µl per 10 ml of sample) in order to assess the effect of potential biological activity upon ^{203}Hg uptake. Normally, $HgCl_2$ would be used as a metabolic inhibitor but its use in these experiments was avoided, as the presence of additional Hg would have negated the findings. Insignificant differences in partitioning were observed between poisoned and unpoisoned samples, indicating that biological activity appeared minimal in March 1998. Nevertheless, the use of NaN_3 was continued in subsequent experiments in case microbial or photosynthetic activity became more prevalent for other seasons.

After counting, the dried and weighed filters from experiments conducted in June 1998 and October 1998 were placed in acid-washed 20 ml Sterilin tubes and subjected to a partial acid digest. 5 ml of 1M HCl (AristaR, BDH) was added and the filters left for 24 hours, after which time the digests were carefully re-filtered using the same filter. Filters and leachates were placed into scintillation vials for γ-counting. The filters were then dried at room temperature and re-weighed. Leachable ^{203}Hg fractions were calculated from the activities measured in leachates after the extraction and the activities on the filters used for mass balance calculations.

The relative standard deviation for three replicate experiments ranged from 4 - 27% and average ^{203}Hg recoveries were around 80%. Owing to its high particle reactivity, losses of ^{203}Hg by wall adsorption were sometimes observed during the overall experiment despite pre-conditioning the reaction vessels (after Li *et al.*, 1984a). Washing out the containers with 1M HCl after incubation and filtration has indicated that wall adsorption can account for up to 15% of the lost ^{203}Hg (Le Roux, 2000). However, percentage loss was significantly reduced with increasing salinity and also the increased presence of suspended material. Turbidities of the ambient samples used in this study varied widely from 30 – 580 mg l^{-1}, which leads to the hypothesis that if the number of particles present is relatively low, then loss of radiotracer to the container walls may be increased. Results showed that this could indeed be the case where SPM concentrations were below 100 mg l^{-1}, as recoveries of the radioisotope were generally lowest and rsd values were highest in these less turbid waters.

Recoveries of particulate radioisotope after the acid leach were calculated from the initial activity on the filters and the sum of the activities on the filters and in the leachates after the extraction. Reproducibility of the procedure was better than ± 2% (n = 3) and an average radiotracer recovery of 96 ± 2% was attained.

Chapter 3

The Chemical Framework

3 The chemical framework

The purpose of this chapter is to define the prevailing biogeochemical conditions existing within the Mersey Estuary in order to support interpretation of the trace metal data. Results from the axial surveys, pertaining to the measurement of surface water master variables, particulate carbon and nitrogen and specific surface areas of estuarine particles are presented here. River flow data and estuarine nutrient concentrations kindly supplied by the EA have been incorporated to complement the discussion.

3.1 Freshwater input to the estuary

The River Mersey has a total catchment area of 2 030 km^2 (Davidson *et al.*, 1991), a mean annual flow of 31 m^3 s^{-1} (Buck, 1993) and is the dominant source of fresh water to the estuary (see Section 1.4.2). Mean daily flow data, provided by the EA, have been used to construct an episodicity curve for the River Mersey (Figure 3.1) covering the period 01/01/1997 – 01/10/2000. Flow measurements were taken at the same time each day (0900 hrs) at the river flow gauging station in closest proximity to the 'normal' tidal limit at Howley in Warrington. At Howley, a mechanically operated weir can be used to regulate freshwater input. It is also notable that the weir may be overtopped during extreme spring tides, pushing the limit of saline intrusion upstream of its usual position (P. Jones, EA, pers. comm.). The gauging station, 'Westy Flow' (NGR SJ629884), is situated approximately 2.5 km upstream from Howley Weir and covers a catchment area of 660 km^2 (Davidson *et al.*, 1991). The episodicity curve is fairly platykurtic, suggesting that

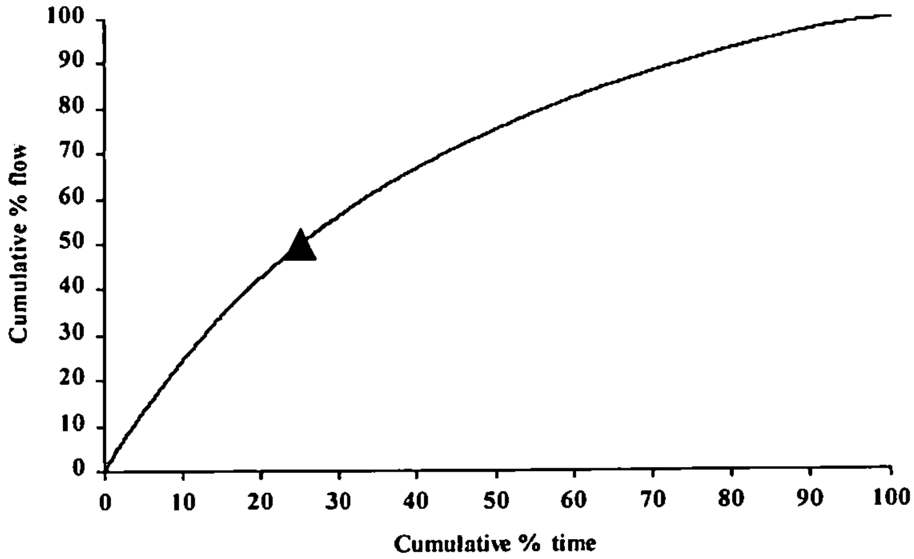


Figure 3.1 Episodicity curve for the River Mersey. The triangle represents the time for 50% of the cumulative flow.

the flow of the River Mersey is generally relatively low and consistent. The profile indicates that 50% of the flow occurs within 25% of the time. This is in contrast to the River Tamar for example, where analysis of long-term data reveals that 50% of the fluvial flow takes place over 17% of the time, resulting in a more pronounced curve.

The same flow data have been utilised for the calculation of mean daily and monthly flows for the River Mersey between January 1997 and September 2000 (Figure 3.2). Daily mean flows were highly variable, ranging from 2 $m^3 s^{-1}$ on 24 June 1999 to 132 $m^3 s^{-1}$ on 03 December 1999 (Figure 3.2a). The average mean daily flow for the period covering all surveys within this study (July 1997 – July 2000) was 43 $m^3 s^{-1}$. River flow gradually decreased through the spring and summer then rapidly increased again in the autumn. Spring and autumn were generally characterised by frequent, but short, periods of flood. The most persistent drought and flood events occurred between June 1999 and June 2000. The range of flows within each month (indicated by the error bars in Figure 3.2b) also varied and was usually greatest in the winter and spring compared to the summer. Comparing the monthly ranges (Figure 3.2b) to mean daily flows recorded on the days of axial surveys of the estuary (see Table 2.1, Section 2.1.1) confirms that nearly all field sampling during this project was conducted within flow regimes that were typical for those months. The only exception to this was during the 16 December 1997 survey when the flow (28.5 $m^3 s^{-1}$) was only half that of the average discharge for that month (59.4 $m^3 s^{-1}$). In general therefore, surveys were accomplished under normal flow conditions for the different times of year.

3.2 Master variables

Figure 3.3 displays the master variables plotted as a function of distance from the normal limit of saline intrusion. Data for chlorophyll *a* and dissolved organic carbon have also been included as these parameters help to further characterise underlying chemical conditions present within the water at the times of sampling. Salinity (Figure 3.3a) shows an exponential increase with movement downestuary. The plots generally lack the characteristic S-shaped profiles normally indicative of a partially mixed system (Dyer, 1997). Assuming the freshwater flow, Q_f, into the Mersey generally ranges between 25 and 200 $m^3 s^{-1}$, this produces a mean flow ratio (Q_f x 12.42 h/volume between high and low water) of approximately 0.01 (Prandle *et al.*, 1990). As the flow ratio is < 0.1, the estuary tends towards a well-mixed type (Dyer, 1997). However, during part of the tidal cycle, certain sections only undergo partial mixing. This is thought to be due to the unusual

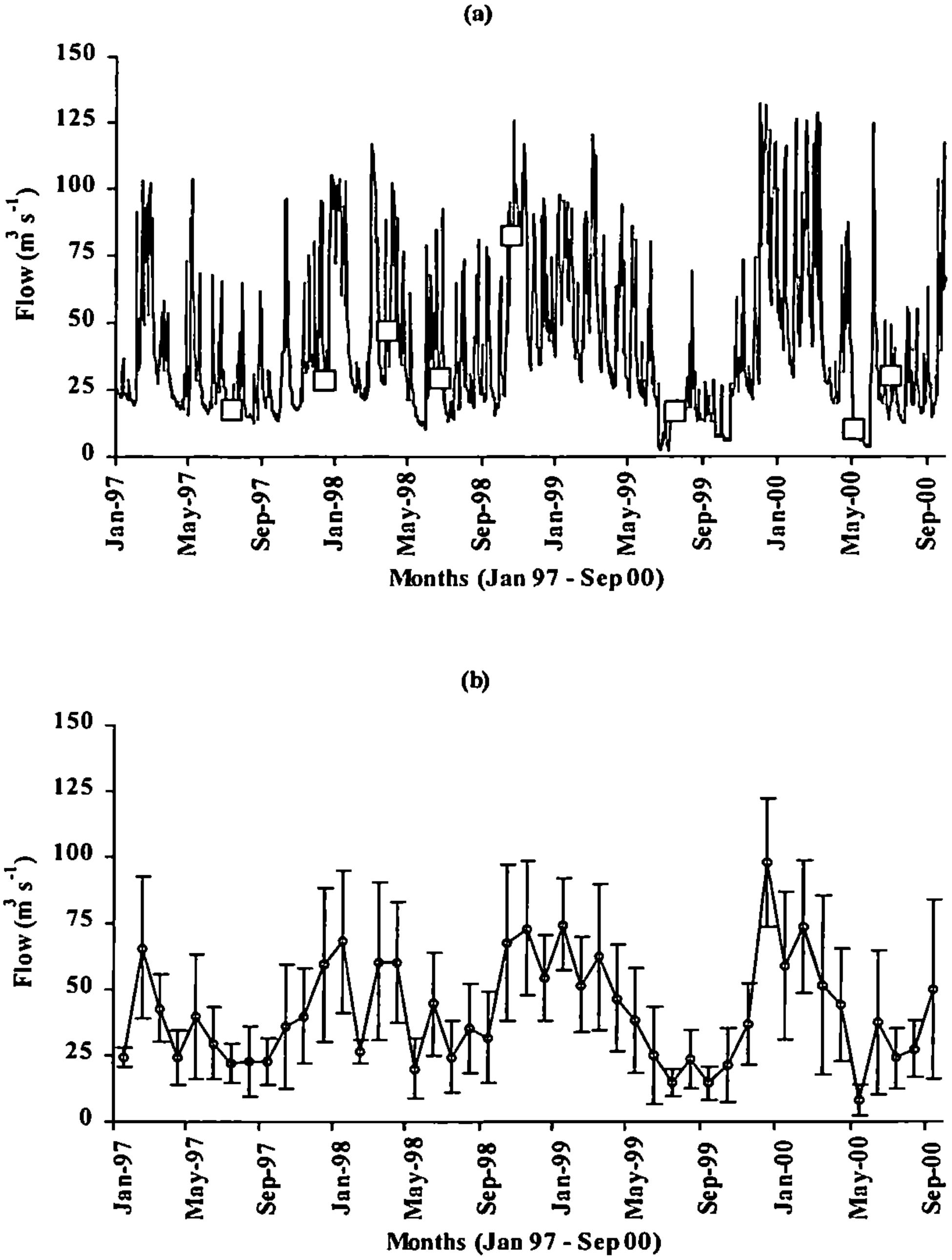


Figure 3.2 Mean (a) daily and (b) monthly, river flows in the River Mersey at Westy Flow river flow gauging station during the period January 1997 to September 2000. Source: Environment Agency. The timing of surveys is indicated by ☐ in (a).

morphology of the estuary, which has a narrow entrance channel broadening into a wide and shallow inner basin (Figure 1.4). Similarly, when river flow is relatively high, as in October 1998 (82 m^3 s^{-1}), the waters in the upper estuary become only partially mixed. The most prominent feature of Figure 3.3b is the presence of a turbidity maximum located almost 10 km from the tidal limit. Highest concentrations of SPM, at around 700 mg l^{-1}, occur here in December 1997. The TMZ is shifted seawards during October 1998 due to

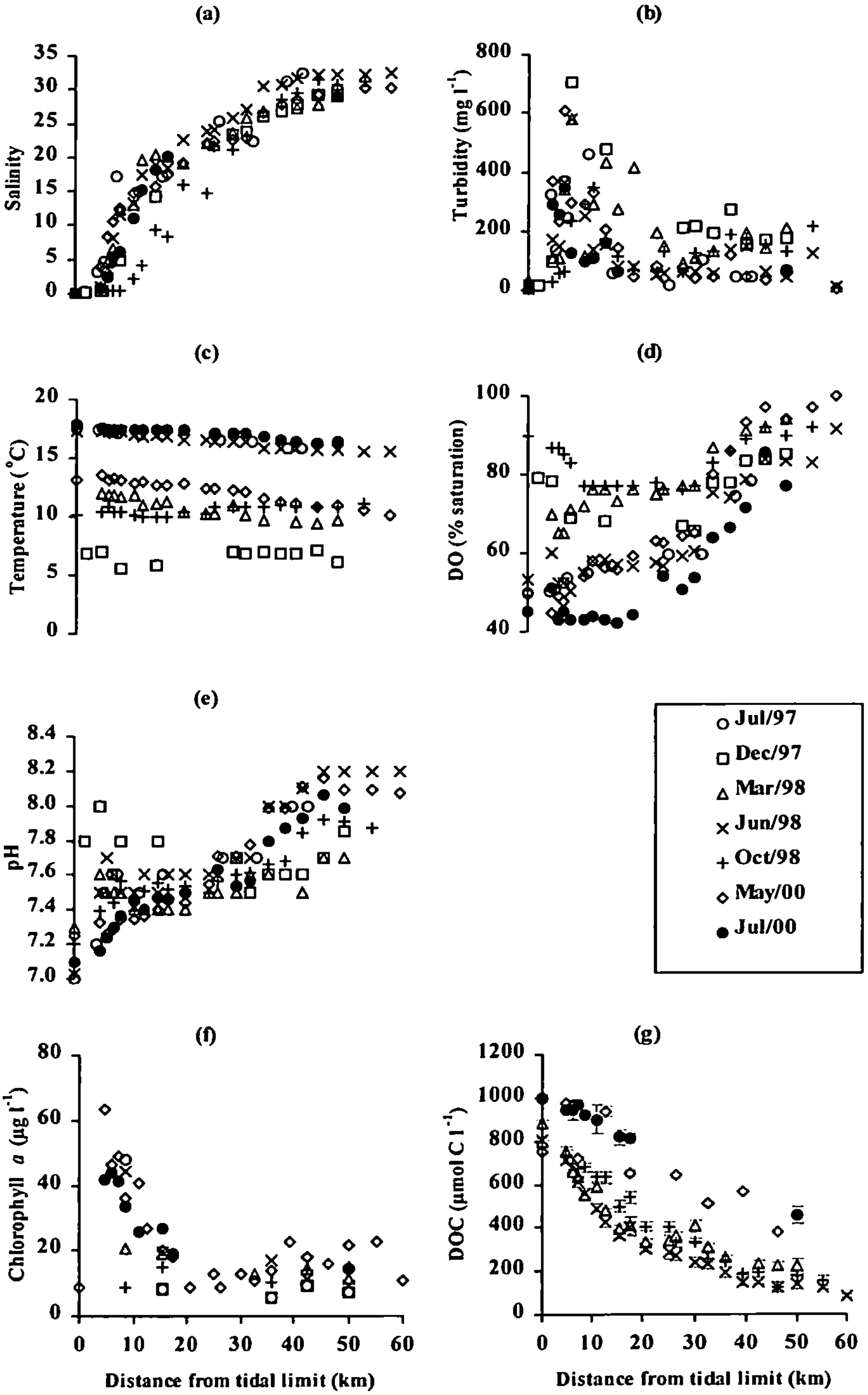


Figure 3.3 Seasonal trends in master variables along the Mersey Estuary for (a) salinity, (b) turbidity, (c) temperature, (d) dissolved oxygen, (e) pH, (f) chlorophyll *a* and (g) dissolved organic carbon.

the higher river flow. This is a common feature of macrotidal estuaries, where ebb tides generally extend for longer periods than flood tides. Higher current velocities generated during flood tides compared to ebb tides effectively 'pump' erodable bed sediments and other particulate matter into the upper reaches of the estuary, particularly when freshwater input is low (Uncles *et al.*, 1985; Morris *et al.*, 1986; Uncles and Stephens, 1989). Further upestuary advection of particles is prevented when fluvial flows balance tidal pumping which occurs at the estuarine null point. By contrast, during periods of spate, tidal pumping is repressed and the TMZ relocates further down the estuary (Morris *et al.*, 1986; Uncles *et al.*, 1994). Lyons (1997) found that variation in tidal velocities during the spring-neap tidal cycle altered the degree of tidal pumping, producing oscillations in the position of the TMZ in the Ribble Estuary. Temperature (Figure 3.3c) exhibits obvious seasonal differences. Highest water temperatures are recorded in July 1997, June 1998 and July 2000 and the lowest in December 1997, whilst intermediate temperatures are measured in March 1998, October 1998 and May 2000. Dissolved oxygen saturation is lowest in July 1997, June 1998, May 2000 and July 2000 (Figure 3.3d) and there is evidence of an oxygen sag in the upper-middle reaches, extending over a distance of approximately 30 km before gradually improving in the lower estuary. This trend is most marked during July 2000. The broad oxygen sag coincides with a general decrease in pH (Figure 3.3e) and is due to the bacterial degradation of organic loads from effluent discharges combined with tidally-resuspended, organic-rich bed sediments and decaying plankton (NRA, 1995; Jones 2000). A smaller sag, apparent at ~ 2-7 km from the tidal limit during the March 1998, June 1998 and May 2000 surveys, is most likely associated with either the TMZ or the null point. However, it is notable that oxygen saturation has dramatically improved since the start of the clean-up campaign due to reductions in oxygen consuming wastes entering the estuary (NRA, 1995; Jones, 2000). Comparisons of chlorophyll concentrations measured in Liverpool Bay in December 1997 with measurements made for the other surveys suggests the presence of phytoplankton blooms in the estuary in June 1998, May 2000 and July 2000 (Figure 3.3f). Phytoplankton populations detected in the estuary are expected to derive from both riverine and marine end-members, transported by freshwater and tidal inflows to the null point, where marine and fluvial fronts converge. Here, increased sediment resuspension would result in the release of degraded and/or aged mineral-bound organic material from sediment matrices, thus aiding the release of nutrients into the dissolved phase and hence into a form readily accessible for uptake by phytoplankton (Komada *et al*, 2002). However, nutrients are anticipated to be unlimited in the Mersey due to the number of effluent discharges and the potential for significant diffuse inputs issuing from an extensive catchment. The UK interpretation of the EC Urban Waste Water

Treatment Directive (91/271/EEC) suggests that an exceedance of 10 $\mu g\ l^{-1}$ chlorophyll *a* is indicative of the presence of algal blooms, although not necessarily characteristic of eutrophication. Concentrations in excess of this value have been found in the Dee and Mersey estuaries, the Ouse, Wash, Tees and Thames with highest chlorophyll *a* concentrations occurring on the largest scale in the South-Eastern Irish Sea (EA, 1999). Restricted circulation in the Irish Sea produces an extended flushing time in Liverpool Bay, which is estimated to be between 7-16 months (Gowen *et al.*, 2002). It is thought that the high concentrations of estuarine suspended sediment largely inhibits the growth of microalgae in estuaries such as the Thames, Mersey, Humber and Severn due to light limitation (EA, 1999). Even so, a fairly strong relationship exists between chlorophyll *a* and turbidity as, and with the exception of October 1998 when $R^2 = 0.13$, R^2 values of ≥ 0.86 (where $P \leq 0.01$) are obtained. The apparent 'blooms' observed in the Mersey in this study are therefore more likely to originate in Liverpool Bay and be tidally advected into the estuary rather than being produced *in situ*. Riverine DOC concentrations (Figure 3.3g) are high compared to other UK estuaries (Table 3.1).

Table 3.1 End-member concentrations of dissolved organic carbon (mg l^{-1}) for six UK estuaries. REM: Riverine End-Member (S < 0.3); MEM: Marine End-Member (S > 30).

Estuary	REM	MEM	Distribution	Reference
Beaulieu	9 – 18	1.2 – 2.3	Removal	Turner *et al.* (1998)
Humber	3.6 – 7.1	0.96 – 1.32	Conservative/addition	Alvarez-Salgado and Miller (1999)
Mersey	9.1 – 10.6	1.0 – 5.5	Conservative/addition	This study
Severn	3.1 – 7.8	0.7 – 2.2	Conservative	Mantoura and Woodward (1983)
Tamar	5.7	1.3	Conservative/addition	Miller (1999)
Tweed	3.1 – 5.8	1.3 – 3.1	Conservative	Martino (2000)

Previous authors (Turner *et al.*, 2001b, 2002; Martino *et al.*, 2002) have proposed that a significant fraction of Mersey DOC is likely to be of anthropogenic origin, mainly arising from the discharge of domestic and industrial effluents into the River Mersey. By way of contrast, the Beaulieu estuary is rich in natural dissolved organic matter and this is reflected in the elevated DOC concentrations found there. Small localised inputs combined with a more general trend of DOC removal at distances of 5 – 50 km from the tidal limit during the March, June and October 1998 surveys are suggested in Figure 3.3g. However, if these distributions are plotted against salinity, largely conservative behaviour is exhibited (Figure 3.4), with data from the March, June and October 1998 transects showing little seasonal variability. In contrast, axial DOC profiles from May 2000 and July 2000 reveal that considerable addition is taking place throughout the mixing zone. This was initially thought to correlate with the growth and decay of phytoplankton blooms with autolysis, mechanical breakage or active excretion of metabolites releasing DOC to the surrounding water. However, Cole *et al.* (1982) have shown that photosynthetically produced dissolved organic carbon (PDOC) is an important carbon source for planktonic microbes and that the metabolism of PDOC is rapid, proceeding at almost the same rate at which it is produced by algae. Miller (1999) proposed that DOC addition in the Tamar Estuary arose from the mixing of organic-rich porewaters, desorption from particles, and/or disaggregation of macroaggregates by the tidal scouring of bed sediments. In the same paper it was implied that these mechanisms could also assist in explaining occasional non-conservative behaviour of DOC in the Humber (Alvarez-Salgado and Miller, 1999) and it would appear reasonable to suggest that the same processes could be occurring in May and July 2000 in the Mersey.

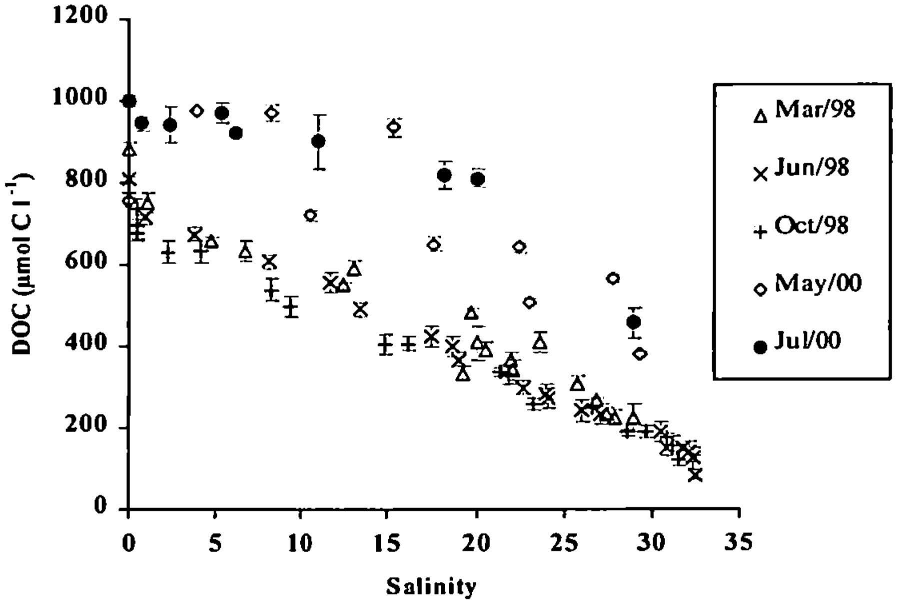


Figure 3.4 Axial concentrations of dissolved organic carbon as a function of salinity.

3.3 Nutrients

3.3.1 Estuarine nutrient distributions

Dissolved nutrient species often display seasonal and shorter-term variability in concentrations and distribution patterns in estuaries. These arise from changes in a variety of temporally and spatially variant controls, such as rates of input and export, homogeneous and heterogeneous chemical transformations, biological uptake and regeneration processes (Morris *et al.*, 1985). Estuarine distributions of dissolved nitrate, nitrite, ammonium, phosphate and silicate from the six surveys conducted between December 1997 and July 2000 are presented in Figure 3.5.

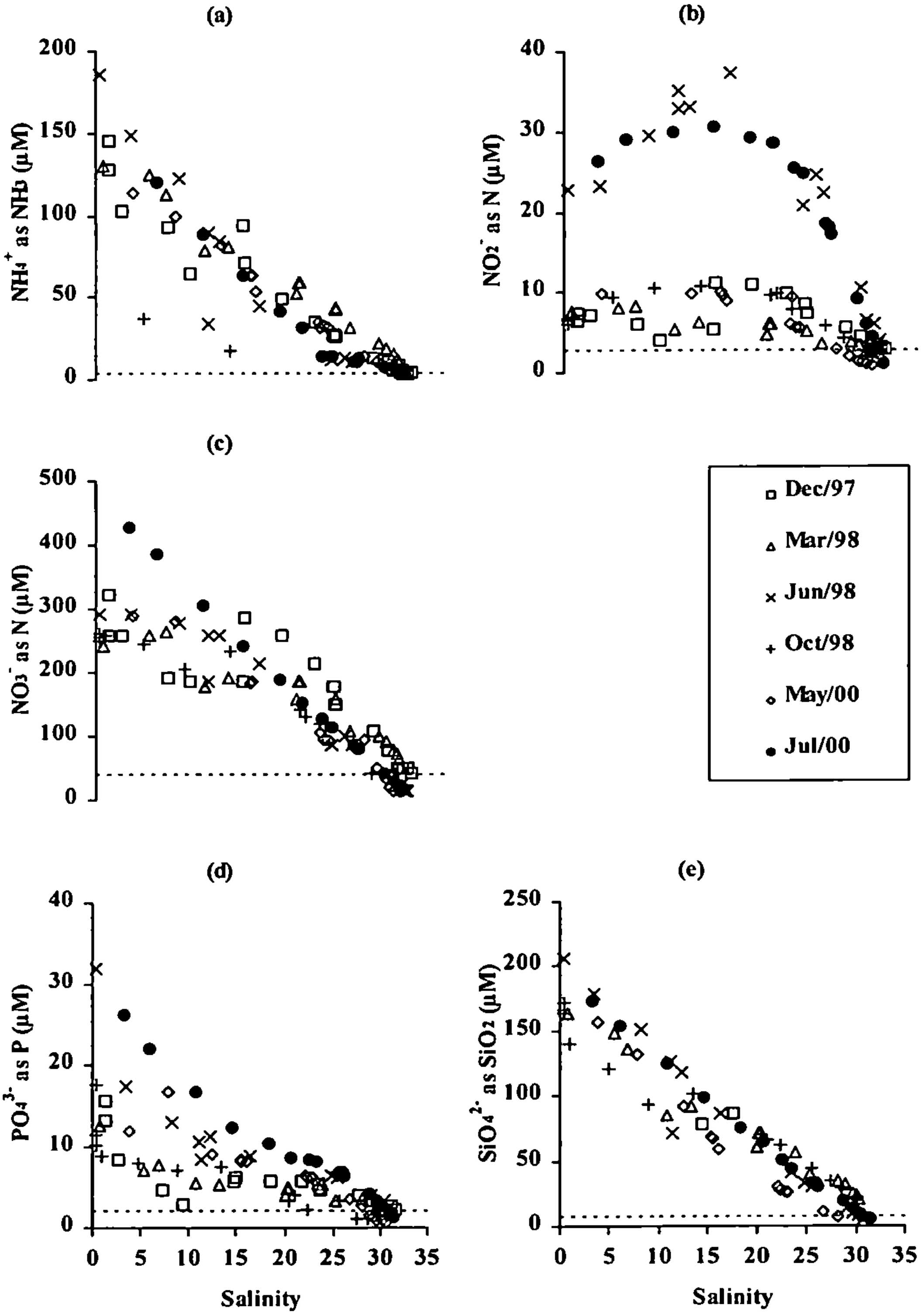


Figure 3.5 Axial concentrations of dissolved (a) ammonium, (b) nitrite, (c) nitrate, (d) phosphate and (e) silicate as a function of salinity. Source: Environment Agency. Horizontal lines indicate concentrations in Liverpool Bay in winter (16/12/1997). Data for silicate was not determined on this occasion. Instead, the mean concentration measured in Liverpool Bay by Kennington *et al.* (1998) on 01/12/1997 is shown.

Salinity-dependent distributions of the main nitrogen species (Figures 3.5a-c) exhibit little seasonal variability. Estuarine NH_4^+ concentrations (Figure 3.5a and measured as NH_3) ranged from 3.5 – 190 μM (0.060 – 3.2 mg l^{-1}) with a mean concentration at $S < 5$ of 150 μM (2.5 mg l^{-1}). This latter figure is relatively high compared to estuaries such as the Clyde, Delaware and Thames where average riverine concentrations have been reported as 1.5, 0.77 and 0.04 mg l^{-1}, respectively (Church, 1986; Muller *et al.*, 1994; Neal *et al.*, 1998). Axial profiles of NH_4^+ in the Mersey do not indicate conspicuous biological utilisation or nitrification. It is generally thought that the rate of nitrate uptake by phytoplankton is greatly diminished in the presence of ammonium and occurs either through 'inhibition' of nitrate uptake by ammonium or 'preference' for ammonium (Pennock, 1987; Dortch, 1990 and references therein). Moreover, at its most extreme, this mechanism is believed to operate such that no nitrate uptake occurs if a threshold NH_4^+ concentration of ~ 1 μM is exceeded. The in-depth study conducted by Dortch (1990) concluded that preference for ammonium would be maximal with low light and nitrogen deficiency, whereas inhibition of nitrate uptake would be favoured under conditions of nitrogen sufficiency and low light. Concentrations of nitrate, ammonium and suspended solids in the estuary are all high and it is anticipated that nitrate assimilation by phytoplankton would therefore be somewhat inhibited by ammonium. Slight removal of NH_4^+ is suggested in both June 1998 and July 2000. For other surveys, conservative behaviour is observed (ignoring the outliers for October 1998 and June 1998 which are suspected to be analytical anomalies). Nitrite concentrations (Figure 3.5b) are low compared to ammonium and nitrate and represent an intermediate between nitrate reduction and nitrification. Addition of NO_2^- occurs in June 1998 and July 2000 and it could be this rather than phytoplankton uptake which may explain the slight removal of NH_4^+ at these times. Further suggestion of nitrification in June 1998 is seen in Figure 3.5c as an overall positive deviation of NO_3^- from the theoretical dilution line but the same pattern is not apparent in July 2000, when highly conservative behaviour for NO_3^- is observed. Nitrate has previously been shown to behave conservatively with respect to salinity, particularly in small estuaries with short flushing times (Morris *et al.*, 1981, 1985; Balls, 1994). In contrast, in the tidal reaches of the Mersey and with the exception of July 2000, NO_3^- displays non-conservative behaviour for almost all surveys, tending towards alternating patterns of addition and removal throughout the salinity gradient. Nitrate concentrations at salinities < 10 are noticeably higher in July 2000 than for other surveys. Nitrate concentrations (measured as N) at salinities approaching zero appear to be independent of river flow and range from 240 – 320 μM (3.4 – 4.5 mg l^{-1}), with a mean of 280 μM (3.9 mg l^{-1}). Samples with salinities ≥ 30 are still high in nitrate and consistently contain up to 70 μM (1 mg l^{-1}) NO_3^-. Dissolved nitrate concentrations in the Mersey are of the same order of magnitude as those found in the Clyde (Muller *et al.*, 1994) and Delaware (Church, 1986) estuaries. However, they are distinctly lower than those in the Thames, which experiences considerable nitrate enrichment of up to around 30 – 50 mg l^{-1} in its upper reaches (Johnes and Burt, 1993; Neal *et al.*, 1998) and also the Humber-Ouse, which experiences a mean nitrate maxima of approximately 32 mg l^{-1} (Uncles *et al.*, 1998a).

Overall, whilst phytoplankton blooms may be present in the estuary at certain times of the year (Figure 3.3f), significant uptake of the two main nitrogen species is not readily observed. The implication of this is that concentrations of ammonium and nitrate are so high that seasonal depletion by algal populations is largely masked and that the observed deviations from conservative mixing may instead be due to other (possibly more significant) processes. Morris *et al.* (1985) measured ammonia maxima in the mid and upper estuarine regions of the Tamar, which were attributed to sediment release aided by tidal sediment disturbance. They demonstrated that the Tamar Estuary TMZ is a region of net catabolism of organic nitrogen and a source of NH_4^+, brought about by the oxidative degradation of organic detritus accumulated and trapped within the region. Thouvenin *et al.* (1994) showed that the greatest contribution to total O_2 demand in the vicinity of the Loire Estuary TMZ was associated with the amount of organic material present, whilst contributions from urban and industrial effluents were comparatively small. Owens (1986) conducted a study on nitrification in the water column of the Tamar Estuary and found a connection between nitrification and the turbidity maximum. Periodic tidal resuspension of inactive nitrifying bacteria located in anaerobic sediment horizons into oxic waters was thought to accelerate the nitrification rate. It was also postulated that if the residence time of particles in the TMZ is sufficiently long then the number of particle-associated bacteria could have adequate time to increase. Uncles *et al.* (1998a,b) showed that bacterial numbers and SPM concentration are linearly related in the Humber-Ouse and have suggested that 3.3 x 10^7 bacterial cells could be present per mg SPM. These factors were responsible for the formation of peaks in the concentration of NO_2^- observed at, or proximal to, regions of highest turbidity. The findings were also in agreement with field data for the Ems-Dollard Estuary (Helder and De Vries, 1983). Maximum turbidities recorded for the Mersey in July 1997, June 1998, May 2000 and July 2000 are associated with significant depletions of DO in the first 20 km of the estuary and range from 350 - 610 mg l^{-1}. Bacterial numbers associated with the TMZ for these surveys could reach as many as 1.2 x 10^{10} - 2.0 x 10^{10} cells. Such sizeable bacterial populations would be expected to exert a marked DO demand and produce distinct DO lags such as those shown in Figure 3.3, either through heterotrophic respiration or autotrophic ammonium oxidation. In common with the Tamar, the Mersey TMZ may possibly considered to be a 'fluidised bed reactor'. The accumulation and retention of suspended particles and organic matter would assist in the multiplication of particle-associated bacteria in the Mersey TMZ and this has important consequences for estuarine geochemical processes as particles from the turbidity maximum are advected and dispersed along the salinity gradient. Prior to the onset of the Mersey clean-up, denitrifying processes were dominant in the estuary but improved oxygenation over the last 20 years has now turned the system into one where nitrification is gradually becoming more evident over time (Wither, 2003).

Dissolved phosphate in the Mersey Estuary also shows some deviation from conservative mixing, with fairly consistent removal at salinities < 15 (Figure 3.5d). Balls (1994) showed that dissolved P is affected by adsorption onto SPM. Supporting evidence for this is the consistent loss of dissolved PO_4^{3-} at either the TMZ and/or FSI in the Mersey, a trend that has also been observed in the Humber Estuary by Uncles *et al.* (1998a). Interactions of P with freshwater sediments can include: (a) the coprecipitation of phosphate with calcite in lakes during phytoplankton blooms and with benthic algal biofilms on river sediments and (b) the formation of vivianite ($Fe_3(PO_4)_2$-$(H_2O)_8$) in anoxic bed sediments (House, 2003). Phosphate adsorbed to ferro-manganese oxides on particle surfaces may be re-dissolved when depression of dissolved oxygen causes reduction of Fe (III) to Fe (II), (Prastka *et al.*, 1998). It is debatable whether O_2 concentrations in the Mersey are low enough to support this phenomenon but the data suggest that dissolved PO_4^{3-} concentrations are lower in December 1997, March and October 1998 when there is more DO to maintain P in the particulate phase (Figure 3.5d). Similarly, higher concentrations of dissolved PO_4^{3-} were measured at salinities <10 during June 1998, May 2000 and July 2000 in response to depleted oxygen levels in the water column. At higher salinities, phosphate concentrations generally decrease in a linear fashion. These trends have also been observed in the Delaware (Church, 1986) and the Seine (Chiffoleau *et al.*, 1994). Seasonal differences between axial profiles also result from changes in the amount of fresh water entering the estuary, producing variations in riverine concentrations of the nutrient (assumed to be approximate to those measured at salinities < 5). During periods of low flow, point source inputs issuing from sewage treatment works assume more importance than diffuse sources such as runoff from agricultural land which tend to prevail during freshet conditions (Robards *et al.*, 1994). The range of concentrations encountered in the Mersey (measured as P) lie between 0.68 – 32 μM (0.021 – 0.99 mg l^{-1}). These are analogous to those in the

Delaware and both systems show phosphate enrichment compared to the Tamar (Morris *et al.*, 1981) and Seine (Chiffoleau *et al.*, 1994), where concentrations are around one and two orders of magnitude lower, respectively. However, riverine concentrations are lower than estuarine concentrations of PO_4^{3-} in both the Thames (Neal *et al.*, 1998) and Humber (Uncles *et al.*, 1998a) estuaries, which can experience maxima of 1.4 mg l^{-1} dissolved phosphate.

Diatoms require significant quantities of silica for their cell walls and Si can be limiting where diatoms are the prominent algae. Seasonal changes in silicon concentration are therefore primarily due to biological production. The dominant silicon species occurring in natural waters is reactive silica, *i.e.* soluble SiO_4^{2-} and its short chain polymers but it may also be present as longer polymers and inorganic and organic fractions of SPM. Reactive silica is probably the only form that is readily available for assimilation by diatoms. Other forms such as alumino-silicate clays and colloidal silica also play an important physicochemical role by providing sorption sites for phosphate and ammonium (Robards *et al.*, 1994). Silicate inputs into estuaries are relatively independent of anthropogenic influences but rather reflect catchment mineralogy (Conley *et al.*, 1993; Hessen, 1999; Gowen *et al.*, 2002). However, discharges of silicate from at least one point source within the Mersey catchment are known (Allen *et al.*, 1998; Kennington *et al.*, 1998).

Morris *et al.* (1981) and Uncles *et al.* (1998a) have illustrated that silicate can exhibit prominent geochemical reactivity, becoming associated with the FSI and TMZ in the Tamar and Humber estuaries, in common with NO_3^-, NO_2^-, NH_4^+ and PO_4^{3-}. Silicate data for the Mersey does not appear to agree with these findings. Dissolved silicate (Figure 3.5e) has shown no clear seasonality throughout the duration of this project and displays conservative behaviour during mixing. Concentrations (measured as SiO_2) are consistent, ranging between 5 – 170 μM (0.30 – 10.4 mg l^{-1}), and are approximately twice that measured in the Tamar Estuary by Morris *et al.* (1981). Blooms of *Phaeocystis spp.*, *Gyrodinium spp.*, *Gymnodinium spp.* and *Alexandrium tamarense* are known to occur in nearby coastal waters (EA, 1999) but there is no evidence to suggest significant uptake of SiO_4^{2-} by diatoms in the estuary. In common with the other nutrients, blooms in the estuary are seen to have little effect on the distribution of dissolved silicate.

3.3.2 Evidence of impact of nutrient inputs

Total inputs of nitrogen compounds into the estuary are largely dominated by sewage and agrochemical inputs. Low load estimates of total nitrogen received by waters of the Mersey Estuary are comparable to those of the Severn and Thames which in 1997, was around 16 000 tonnes (EA, 1999). The improved quality of industrial effluents has resulted in reductions of the direct input of ammonia to the estuary so that the major contribution is now from the non-tidal Mersey. However, due to substantial reductions in organic loads, ammoniacal nitrogen at Howley Weir has reduced from 12 mg l^{-1} in 1962 to approximately 3 mg l^{-1} in 1992 (Jones, 2000). Nedwell *et al.* (2002) have calculated an ammoniacal nitrogen load of approximately 1 000 Mmol N y^{-1} for the Mersey, the highest figure for all 93 major estuarine systems on mainland Britain. In addition, only 6% of this input is estimated to issue from sewage treatment works below the tidal limit. Anthropogenic inputs of ammonium are not apparent in the lower estuary (Figure 3.5a). Further alleviations in the ammonia load carried by the river are expected once nitrification is installed at a major sewage treatment works in Manchester (NRA, 1995). The annual fluvial load of total oxidised nitrogen, TON, (NO_3^- + NO_2^-) entering the estuary in 1995 and 1996 has been estimated at approximately 5 000 Mmol y^{-1}, with only 0.3% originating from direct discharges into the estuary from sewage treatment works (Nedwell *et al.*, 2002). Load estimates were comparable to those for the Severn, Clyde, Humber and Thames which all drain catchments with nitrate-rich soils and have high population densities.

The growing utilisation of synthetic detergents and phosphate fertilisers has resulted in increased concentrations of inorganic phosphorus in aquatic systems. Similarly, rises in organic phosphorus levels are primarily due to anthropogenic sources such as domestic sewage, plant and animal wastes and industrial effluents. The estimated PARCOM orthophosphate load to the Mersey Estuary in 1997 was of the order of 2.2 million tonnes, less than half that entering both the Humber and Thames in the same year (EA, 1999). Annual riverine phosphate loads for 1995 and 1996 have been calculated for the Mersey that are akin to those for the Clyde, Humber, Severn, Thames and Tyne estuaries (Nedwell *et al.*, 2002). Estimates of around 200 Mmol P y^{-1} are thought to be introduced by the Rivers Mersey and Weaver with a contribution of only 6.3% coming from sewage discharges into the estuarine mixing zone.

Figure 3.6 shows the atomic ratios of estuarine nutrient concentrations compared to the ratios required by algae for balanced growth, as indicated by the Redfield ratios of 106 C:16 N:1 P:16 Si (Harris, 1986). Where NO_3^- is the dominant nitrogen species, $NO_3^-:PO_4^{3-}$ ratios are commonly used (e.g. Jordan and Joint, 1998) but in areas where NH_4^+

also constitutes a significant portion of available N, it is more appropriate to compare total inorganic nitrogen (TIN, nitrate + nitrite + ammonium) and phosphate (Nedwell *et al.*, 2002). The dissolved nutrient ratios in Figure 3.6 are expressed as TIN:P, as TIN:Si and as P:Si. The full horizontal lines indicate the Redfield values for each of the ratios.

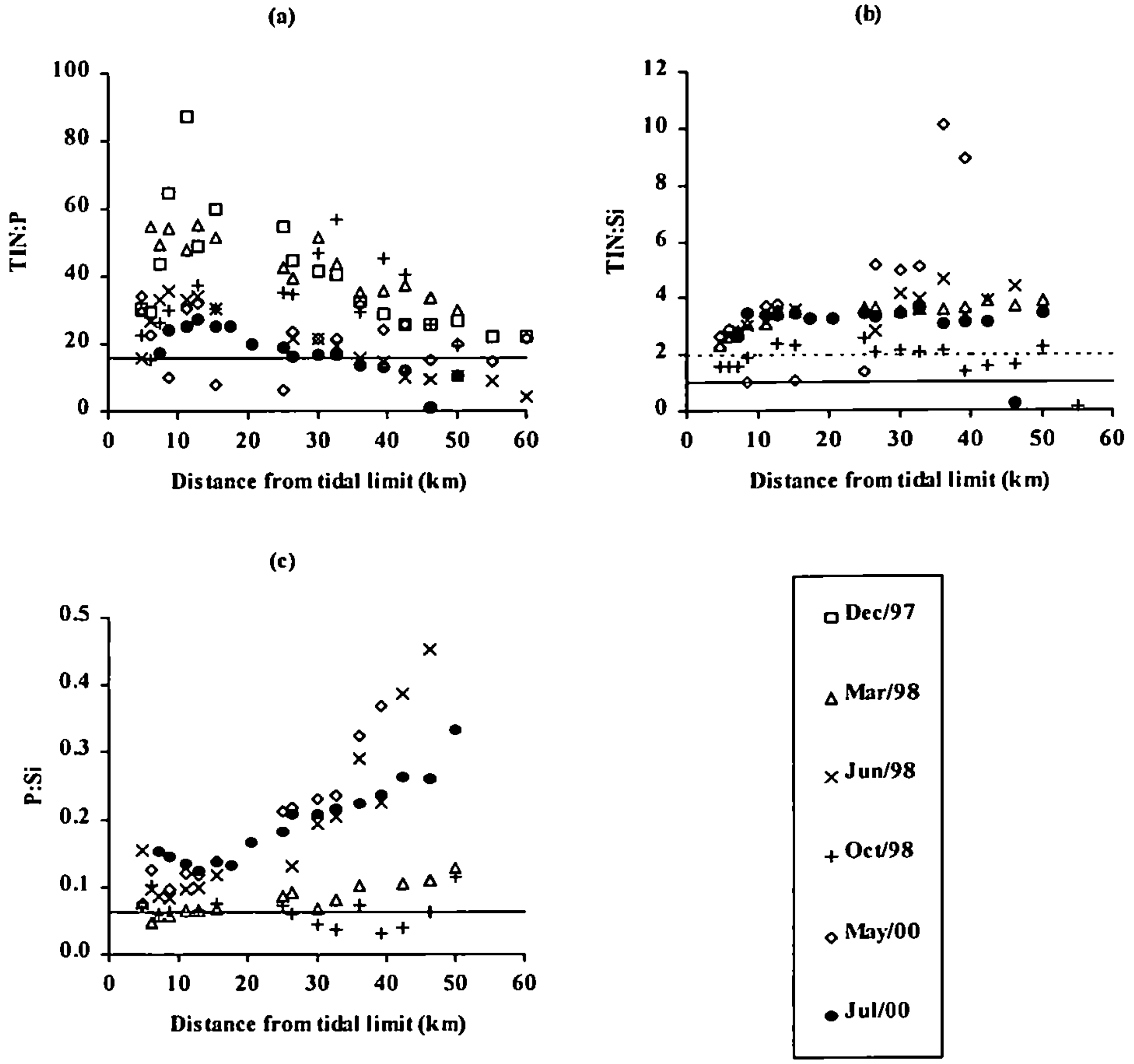


Figure 3.6 Atom ratios of (a) TIN:P, (b) TIN:Si and (c) P:Si as a function of distance along the Mersey Estuary. Full horizontal lines indicate Redfield ratios. The broken horizontal line in (b) represents the threshold ratio for TIN:Si for adverse effects in coastal waters as recommended by CSTT (1997) and NRA (1996).

Guidelines for the assessment of coastal waters with regard to the Urban Waste Water Treatment Directive are given in a Comprehensive Studies Task Team report (CSTT, 1997) which states that coastal waters are adversely affected by nutrient inputs if;

a) Winter concentrations of Dissolved Available Inorganic Nitrogen (DAIN ≡ TIN) exceed 12 μmol l^{-1} in the presence of at least 0.2 μmol l^{-1} of Dissolved Available Inorganic Phosphate (DAIP) or;

b) Summer concentrations of chlorophyll *a* exceed 10 $\mu g\ l^{-1}$.

If levels of DAIN:DAIP or summer chlorophyll *a* concentrations exceed those recommended by the CSTT then a water body is termed hypernutrified. It has also been suggested (CSTT, 1997; NRA, 1996) that a winter molar N:Si ratio > 2 is indicative of waters prone to future eutrophication. The threshold for TIN:Si is therefore also indicated on Figure 3.6b.

Combined data for dissolved NH_4^+, NO_2^- and NO_3^- in Figures 3.5a-c in December 1997 produces concentrations of TIN in the range 50 – 470 μM. Corresponding data for PO_4^{3-} in Figure 3.5d range from 2.3 – 15.5 μM. Thus the CSTT thresholds outlined above are greatly exceeded at all points along the estuary in winter. Nedwell *et al.* (2002) implied that TIN:P atomic ratios of fluvial loads into the Thames, Mersey, Severn, Clyde, Humber and Colne indicated P limitation for the production of algal biomass during the winter (TIN:P > 16:1) but N limitation during summer (TIN:P < 16:1). This is supported by data in Figure 3.6a, which shows that the greatest excess of N compared to P occurs in December 1997 (but is also quite clear during March and October 1998), whilst N is limiting at discrete points along the estuary in June 1998, May 2000 and July 2000. However, when P:Si ratios are compared throughout the seasonal cycle (Figure 3.6c), P is only potentially limiting at a few sites in March 1998 and October 1998. Increased N limitation in the summer may be significant as regulation of diffuse N sources in a catchment may be far more difficult to achieve compared to the control of point sources of P from sewage treatment works and industrial sites. It is likely that diatom growth is limited by a lack of silicate availability compared to other nutrient salts in the Mersey (Figures 3.6b,c). More significantly, TIN:Si ratios exceed the CSTT guideline of 2 for the majority of the time. Unfortunately, measurements of TIN, P and Si were not made by the EA on the same samples in December 1997 and winter TIN:Si ratios cannot be determined. Similarly, TIN:Si ratios are not available for Liverpool Bay in December 1997 (Kennington *et al.*, 1998), or for the winter period in either 1998 (Kennington *et al.*, 1999) or 2000 (Kennington *et al.*, 2001). However, it can be assumed that those recorded during March 1998 would represent near maximum ratios after some modification of the nutrient pool by any phytoplankton present. Given this assumption, it is clear that TIN:Si ratios for this survey are above that recommended by the CSTT and could only have been higher during December 1997. Allen *et al.* (1998) have demonstrated a clear increase in winter maxima of N:Si over a 25 year period and it is popularly held that this trend could lead to a shift away from diatom-dominated populations, with a possible increase in the abundance of toxic or nuisance algal species (Egge and Aksnes, 1992; Conley *et al.*, 1993).

It has already been shown (Figure 3.3f) that chlorophyll *a* concentrations surpass the CSTT maximum recommended concentration for most of the surveys in this study. This, and the fact that winter TIN and PO_4^{3-} concentrations and winter TIN:Si ratios also exceed CSTT guidelines indicate that the Mersey is hypernutrified and could be liable to future eutrophication.

The classification of nutrients according to the EA's GQA scheme is provided in Table 3.2. Data for the Mersey (Figures 3.5c,d) indicates that in July 2000, Grade 2 classification was produced for NO_3^- at salinities ≤ 5, but at other times, Grade 1 applied to waters in the estuary. In contrast, relatively high concentrations of dissolved PO_4^{3-} in waters of low salinity would produce a classification of Grade 5 in June 1998 and July 2000. At other times of year and with progressive movement downestuary, dissolved PO_4^{3-} concentrations decline but are still high enough to warrant GQA grades of 4-5. Thus, based on this evidence it would seem that high phosphate concentrations are certainly implicated in reducing GQA status in the Mersey whilst nitrate is not.

Table 3.2 GQA nutrient classifications. Source: Environment Agency.

Classification for PO_4^{3-}	**Grade limit (μmol P l^{-1}) Average**	**Description**	**Classification for NO_3^-**	**Grade limit (μmol N l^{-1}) Average**	**Description**
1	0.6	Very low	1	~ 360	Very low
2	1.9	Low	2	~ 710	Low
3	3.2	Moderate	3	~ 1430	Moderately low
4	6.5	High	4	~ 2140	Moderate
5	32	Very high	5	~ 2860	High
6	> 32	Excessively high	6	> 2860	Very high

Despite tighter control of sewage discharges, nitrate concentrations have increased in 11% of English rivers in the period 1995-2000 (Wither, 2003) and 80% of NO_3^- is now believed to originate from agricultural sources (Gaskell, 2003). This demonstrates the importance of tackling the problem of diffuse sources of nutrients to the aquatic environment and especially in the North West of England, as the Irish Sea is likely to be officially designated as a nitrate-sensitive area in the near future (Wither, 2003). The issue is additionally complicated by the fact that episodic pulses of NO_3^- and PO_4^{3-} from high flow events are not necessarily captured in the EA's routine surveys and load estimates to Britain's estuaries may therefore be significantly underestimated (Gaskell, 2003). The effects of global climate change therefore need evaluating in this regard.

3.4 Particulate carbon

Axial transects were undertaken in order to collect SPM, some of which was settled prior to the determination of particulate carbon species. Bed sediments taken from the estuary in July 1999 were also subjected to the same protocols as the settled SPM (Figure 2.1). This section presents a discussion on the distribution and possible origins of POC in the estuary.

3.4.1 Sediments

Sediment grain size is a controlling factor in the distribution of trace metals and it is generally accepted that trace metals are mainly concentrated in the clay/silt fraction, *i.e.* particles < 63 μm in diameter (Araujo *et al.*, 1988). Smaller particles possessing a larger surface area will necessarily have the ability to sequester trace metals more effectively than coarser grained material with lower surface areas. It is of prime importance therefore, to have knowledge of the grain size distribution of sediments as this reflects the overall adsorption capability of sediment particles at any one locality.

Significant dredging operations have been carried out regularly over the last century in order to keep the main channel navigable and an average of $5 \times 10^6\ m^3\ a^{-1}$ of sediment have been removed from the Mersey (Prandle *et al.*, 1990). This figure is around 100 times greater than the calculated sediment yield for the estuary (see Table 1.7) and based on this information alone, siltation would not be anticipated to be a problem. Despite this, the total volume of the estuary ($650 \times 10^6\ m^3$) is reducing at a rate of approximately $10^6\ m^3\ a^{-1}$ with a large percentage of fine-grained dredged material being returned relatively quickly directly back into the estuary (O'Connor, 1987). In common with other macrotidal estuaries such as the Ribble, Thames, Humber and Tees, the Mersey is therefore a zone of net sediment accretion.

The percentage mass of the fine (< 63 μm grain size) fraction of surficial sediments were determined and the results are plotted against distance from the tidal limit in Figure 3.7. A relatively stable interannual sediment grain size distribution is observed. Around 40% of freshwater sediment is composed of fine materials such as clays and silts. This proportion increases to around 60-80% in the first 12 km downstream of the weir, covering the sector where the TMZ is usually situated during spring tides. Silt/clay content declines progressively over the next 25 km, approaching ~0 - 10%, confirming the presence of a large sandbank 28 km from the weir. After this point there is a substantial increase in silt content which is likely to be connected to the mobilisation of material from intertidal mud banks and saltmarshes along the inner estuary shoreline (Harland *et al.*, 2000). With progression towards the estuary mouth, sandy material originating offshore begins to influence sediment composition and the proportion of fine-grained material present falls. These findings tend to agree with the description of sediment distributions given by Harland and Riddle (1997).

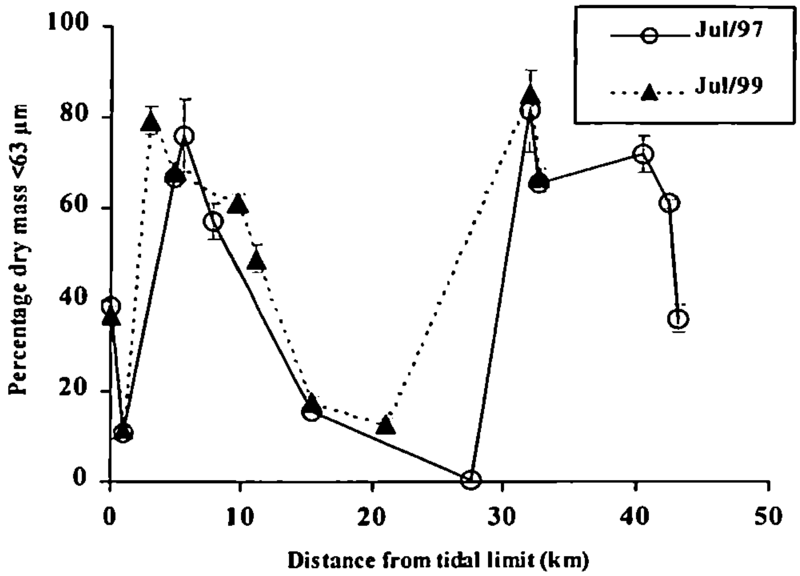


Figure 3.7 Distribution of fine-grained sediment along the Mersey Estuary.

Sediments from July 1999 were subjected to a sequential leach as described in Section 2.1.6 and the results of CHN analyses are presented for both fine- and coarse-grained components in Figure 3.8. Total carbon allied with fine-grained bed sediments indicates effective mixing of carbon-rich river water with carbon-depleted marine particles in the uppermost 2-5 km of the estuary (Figure 3.8a). Further downestuary, total C initially reaches a plateau and then peaks slightly in the vicinity of Runcorn (15.4 km from the weir) and also in the Manchester Ship Canal/Eastham Locks area (~ 32 km). Total and organic C content generally declines in > 63 µm sediments sampled from the first 22 km of the estuary, but remains relatively unchanged over the same distance in the fine-grained material. Up to half of the carbon associated with < 63 µm sediment is removed by the partial digest ($NH_2OH.HCl$ + CH_3COOH). The same spatial variation for total carbon is repeated for POC, indicating that the percentage contributions made by inorganic C and that associated with surface deposited ferromanganese oxides are quite consistent throughout the upper and inner estuary. Largest differences in the total and organic C contents of > 63 µm fractions are probably due to the dissolution of calcareous shell fragments, the presence of which was noted during sample manipulation. Further digestion of the particles to remove organic matter reveals that a small amount of C (typically up to

2%) is composed of a highly resilient 'residual' fraction, which is only detectable in sediments obtained from the upper 10-15 km of the estuary. This highly resistant POC is assumed to be locked deep within particle matrices and therefore held in a relatively unavailable form.

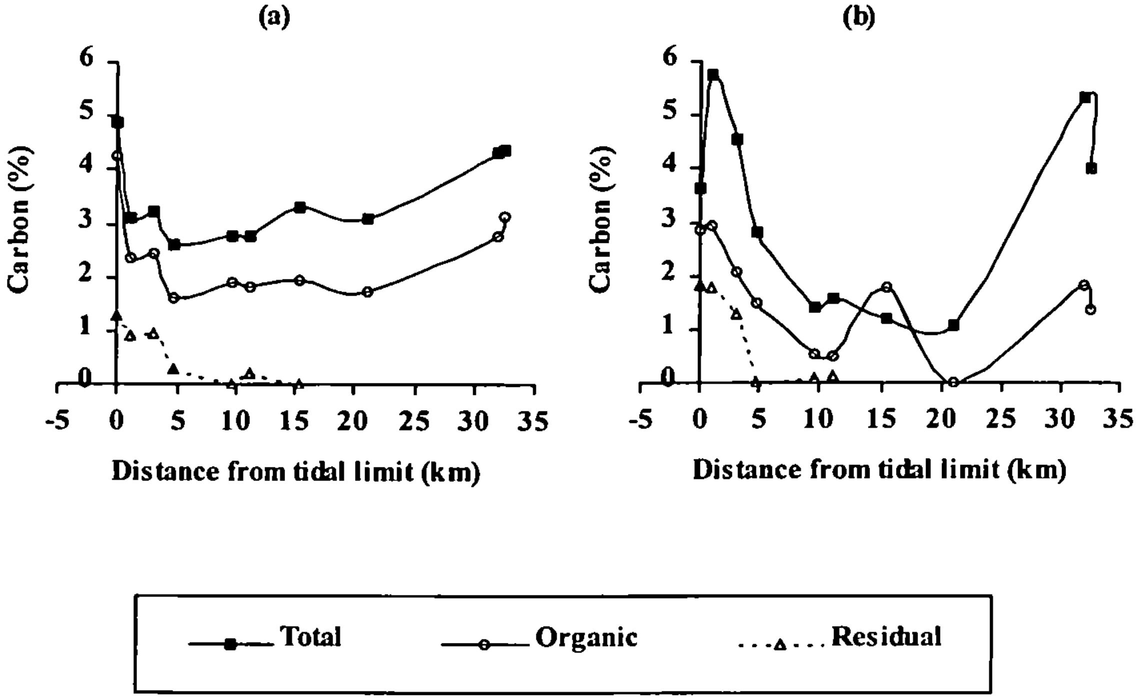


Figure 3.8 Total, organic and residual carbon contents (as percentage contribution to dry mass) of (a) < 63 μm and (b) > 63 μm sediment fractions as a function of distance along the estuary in July 1999.

As the Mersey basin is not an organic-rich catchment (the underlying geology being dominated by limestone grit), the majority of carbon present in the estuary is thought to derive from allochthonous plant material and/or have anthropogenic sources such as industrial effluents and partially treated domestic sewage (e.g. Norton *et al.*, 1984; Campbell *et al.*, 1988; Turner *et al.*, 2001b, 2002; Martino *et al.*, 2002). Partial identification of organic compounds includes surfactants (Blackburn *et al.*, 1999) including linear alkyl benzenes (Preston and Raymundo, 1993), phthalate esters (Preston and Al-Omran, 1986), volatile organohalogen compounds (Rogers *et al.*, 1992), polycyclic aromatic hydrocarbons (PAHs), polycyclic aromatic ketones, nitro polycyclic aromatic compounds, 'Triclosan' found in health and beauty products and the hospital disinfectant 'Clorophene' (Thomas *et al.*, 2002). However, with a significant proportion of organic contaminants in the Mersey remaining unresolved and the majority of studies only providing qualitative results, it is not possible at present to estimate what fraction of the sedimentary organic carbon pool is comprised of compounds such as these.

The use of elemental ratios as indicators of organic matter source is a common approach in estuarine biogeochemical studies. This typically involves the derivation of C:N ratios (Müller, 1977; Hedges *et al.*, 1986; Meyers, 1994) whilst the use of C:P ratios is less common (Ruttenberg and Goñi, 1997). Atomic C:N ratios (as C_{org}:N) of fine-grained sedimentary material from July 1999 have been investigated, and the findings are presented in Figure 3.9. Lines have been superimposed to indicate atomic C:N ratios of ≥ 20 for vascular terrestrial plants (Meyers, 1994), which coincides with that for well humified material (C:N = 21, Ferreira *et al.*, 1997) and 12.6 for sewage effluent from Invergowrie Bay determined by Thornton and McManus (1994). The C:N ratio for phytoplankton of 6.63 has also been included and is derived from the Redfield atomic ratio (106 C: 16 N: 1 P: 16 Si).

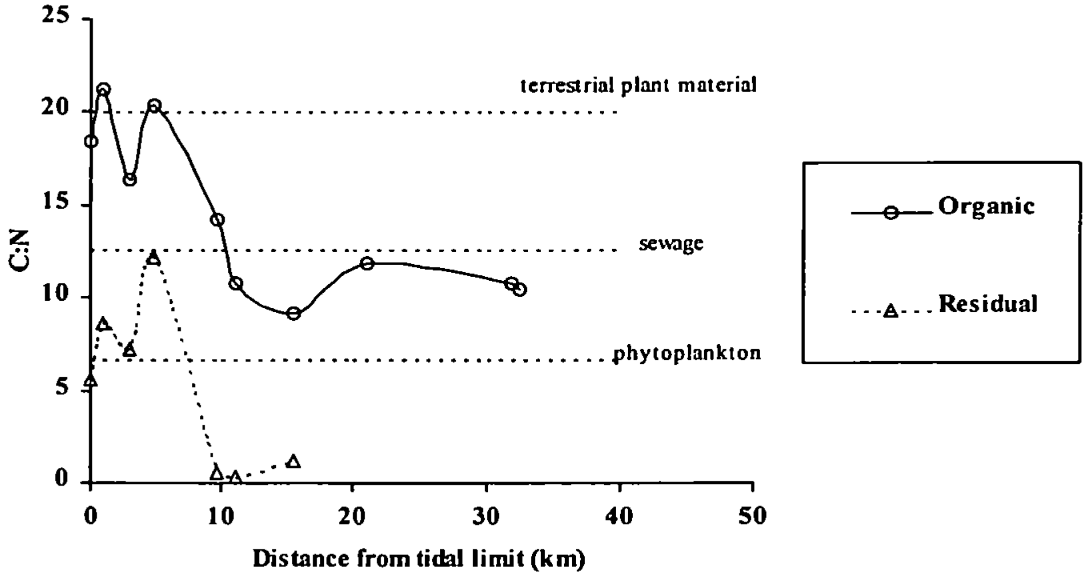


Figure 3.9 Atomic C:N ratios in <63 μm sediments from July 1999 after sequential digestion. Also shown are the mean atomic C:N ratios for phytoplankton, sewage and terrestrial plant material.

With removal of organic C by H_2O_2, C:N ratios decrease and increasingly nitrogenous material remains. The mean C:N ratio for samples taken from the REM and uppermost 5 km of the estuary was found to be 19.1. This value approaches that of well-humified organic matter (C:N = 21.5) and has been identified for Ouse Estuary SPM (Ferreira *et al.*, 1997) and it has previously been suggested (Millward *et al.*, 1990) that a large portion of the Mersey sedimentary carbon pool is either humic or humin in nature. Further away (> 10 km) from the tidal limit, the presence of sewage may be indicated as C:N approaches 12.6. Data for POC suggest that determinations have been made on samples containing carbon that may principally originate from a mixture of natural and anthropogenic sources. It is notable, however, that certain signatures can become obscured over time. For example, there is a tendency for vascular plant tissues to preferentially gain N during microbial decay and for degrading marine plankton to lose N in preference to C (Meyers, 1994). The additional use of carbon and nitrogen isotopic compositions is therefore required if organic matter sources are to be more effectively distinguished from one another (Prahl *et al.*, 1994; Hedges *et al.*, 1997). The mean ratio of C_{res}:N in freshwater sediment approximates to that of bacterial C:N (4-6) and labile organic matter (Goñi and Hedges, 1995; Hedges *et al.*, 1997) whilst algal and sewage signatures are visible in the first 5 km of the estuary. After the first 5 km, C_{res}:N ratios rapidly decrease to fall below Redfield values. Such low values tend to be attributed to high inorganic ammonium content, but may also be due to organic nitrogen compounds sorbed to clay particles (Müller, 1977). Whilst ammonium concentrations have not been measured in Mersey sediments, surface waters do contain high concentrations of NH_4^+ and clays/silts account for up to ~ 80% of surface sediment mass and together, would lend support to this idea.

3.4.2 Suspended particles

As with bed sediments sampled in July 1999, some of the SPM from the May 2000 and July 2000 campaigns were treated with a sequential leach (after bulk water samples were allowed to settle for 3 hours). Variations in the total, organic and inorganic carbon contents of the suspended solids with changes in turbidity during both surveys in 2000 are combined in Figure 3.10. Corresponding data for the Tamar Estuary in August 1980 (Morris *et al.*, 1982a) are also provided for comparison. Morris *et al.* (1982a) proposed that a sub-population of PSPM persisting within the TMZ of the Tamar had an organic carbon content which was intermediate between the high concentrations characteristic of the inputs and the low values shown by TSPM. In contrast, the inorganic carbon content of PSPM was lower than that in resuspended particles and those originating from the marine and freshwater end-members. It was suggested therefore that organic carbon remained associated with PSPM whilst inorganic carbon was preferentially lost from suspension to become allied with recycled TSPM. Oxygen demand exerted by particles remaining in suspension may therefore produce a reduction in DO concentrations seaward of the limit of saline intrusion due to the slow degradation of organic matter trapped within the turbidity maximum. Suspended particles from the two estuaries contain similar amounts of carbon, but those in freshwater and waters of low (< 50 mg l^{-1}) turbidity are higher in the Tamar than the Mersey. Fractional contributions made by organic and inorganic carbon to the suspended load are just as variable in both estuaries. Organic carbon in Mersey SPM remains relatively constant throughout the turbidity range but the inorganic carbon content increases. This implies that whilst PSPM and TSPM in the Mersey are not as dissimilar in composition in terms of organic carbon as they are in the Tamar, the two populations do however contain different proportions of inorganic carbon.

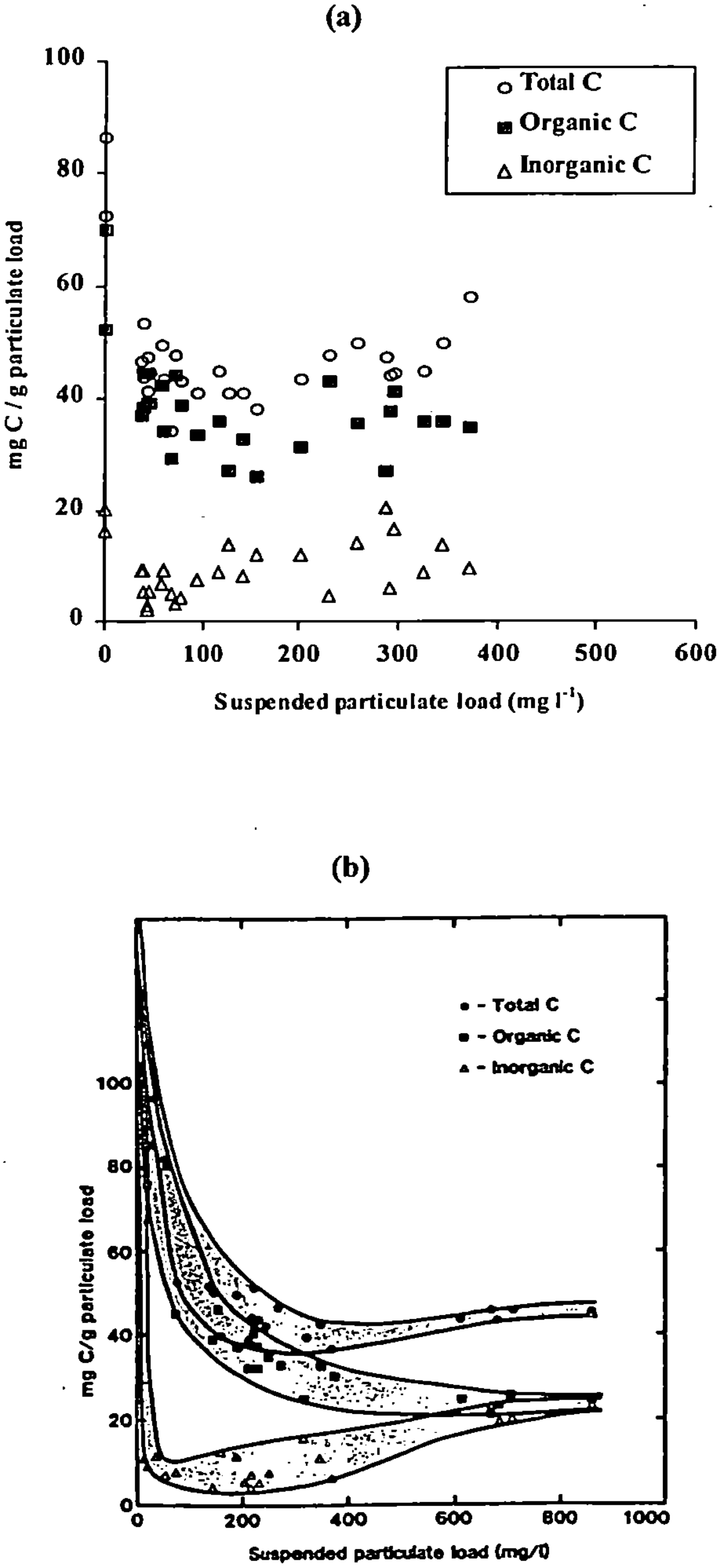


Figure 3.10 Total, organic and inorganic carbon contents of suspended particles in (a) the Mersey Estuary and (b) the Tamar Estuary (from Morris *et al.*, 1982) as a function of total suspended load.

Quantification of total particulate carbon associated with filtered SPM from the March 1998, June 1998 and October 1998 surveys were also made on unfumed filters. Comparison of total carbon data with that reported by Millward *et al.* (1990) indicates that the amount of total carbon (as % composition by weight) in Mersey Estuary SPM has reduced from 6.4 ± 1.6% in November 1987 (range = 4.7 – 9.4%) to 1.5 ± 0.7% (range = 0.2 – 3.3%) in this study. Ongoing measures to improve water quality therefore appear to include substantial reductions in, or improved treatment of, organic effluents discharged into the estuary and its rivers.

Pooled estuarine POC data in Figure 3.10 in May and July 2000 reveal that a mean of approximately 81% of C is present in organic form (80.7 ± 7.4, rsd = 9.2%, n = 27) and it is proposed that this could be used as a proxy to estimate the POC content of SPM collected in other surveys. The results of this conversion are presented graphically in Figure 3.11. It can be seen in Figure 3.11a that with procession down the estuary, patterns in the axial distribution of POC are fairly consistent between surveys and tend to mirror turbidity (Figure 3.3b) and the distribution of fines in surface bed sediments (Figure 3.7).

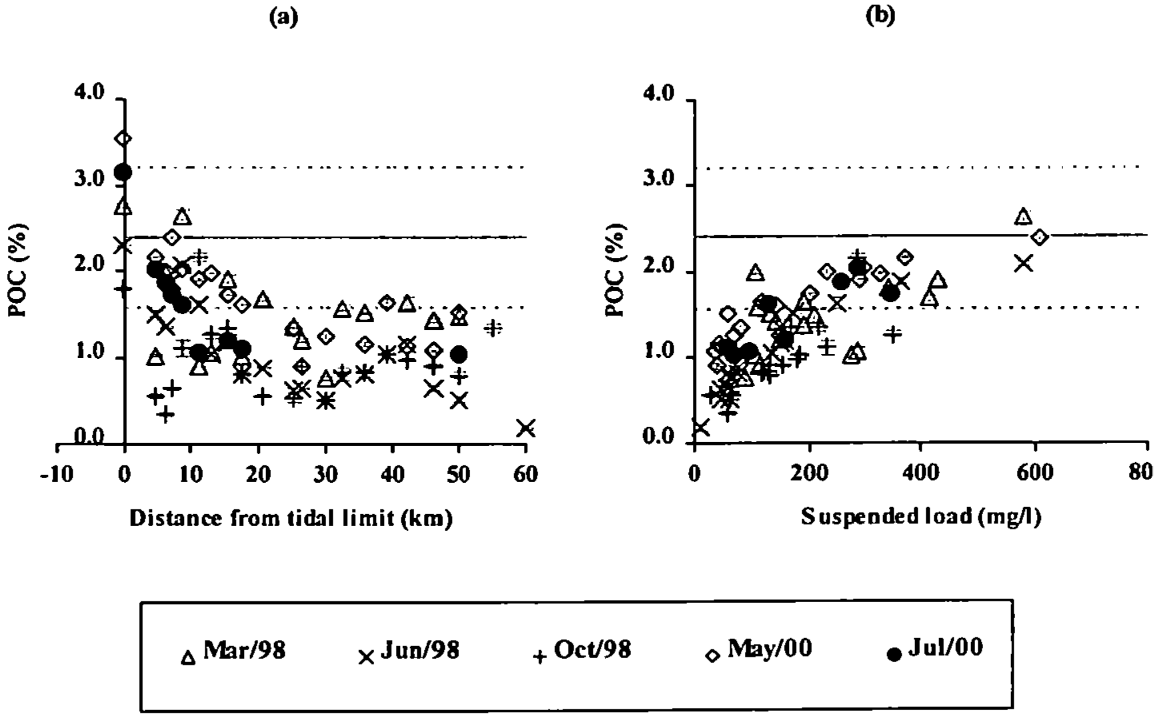


Figure 3.11 Variation of POC in SPM with (a) distance along the estuary and (b) suspended load (riverine data excluded in (b)). The lines represent the mean ± 1 σ of POC content in < 63 μm sediment samples from July 1999.

Persistent carbon peaks associated with SPM in the first 10 km below the weir are thought to correspond with the position of the estuarine null point where tidally pumped organic-rich sediments undergo accelerated decomposition (Abril *et al.*, 1999). Less significant peaks in SPM carbon also occur near sites where freshwater enters the estuary, namely in the vicinity of the Weaver Sluices just below Runcorn (16 km) and Eastham Locks at the entrance to the Manchester Ship Canal (~ 30 km), a trend which follows that already observed in bed sediments (Figure 3.8). The overall downestuary decrease in POC may be related to: (1) differences in the distribution and geochemical composition of SPM; (2) siting of natural and anthropogenic inputs in the non-tidal rivers and upper tidal estuary; and (3) spatial variability in the biological utilisation of POC. The highest levels of POC are encountered where turbidity is greatest when POC in SPM approaches that observed in < 63 μm sediments (Figure 3.11a,b). Highly significant correlations (where $P \leq 0.005$ or better, n = 8 - 19) are consistently found between SPM load and estuarine POC (March $R^2 = 0.37$, June $R^2 = 0.83$, October $R^2 = 0.71$, May $R^2 = 0.85$ and July $R^2 = 0.72$) and is consistent with the findings of other authors (e.g. Tipping *et al.*, 1997).

Axial trends are comparable between seasons but SPM POC at some sites in the first 20 km of the estuary during June 1998, May 2000 and July 2000 are slightly higher overall than those measured in March and October 1998. It is possible that phytoplankton blooms may be contributing to the higher POC values observed in June 1998 and May and July 2000 and this can be assessed by obtaining POC:Chl *a* ratios (Wienke and Cloern, 1987; Cifuentes *et al.*, 1988; Taylor *et al.*, 1997; Abril *et al.*, 2002; Bouillon *et al.*, 2003). The POC:Chl *a* ratio varies from about 12 – 200 g g^{-1} in phytoplankton (Parsons *et al.*, 1977; Cifuentes *et al.*, 1988, Taylor *et al.*, 1997). This ratio is minimal at high temperatures and low irradiances in a nutrient replete environment and increases at high irradiances, especially at low temperature and under nutrient-limiting conditions (Geider *et al.*, 1997). POC:Chl *a* ratios have been determined and are plotted as a function of distance along the estuary in Figure 3.12 (a). The lowest POC:Chl *a* ratio was found to be 24, occurring in May 2000 near the estuary mouth (46 km) in water of relatively low turbidity (36 mg l^{-1}) and moderate chlorophyll *a* concentration (16 μg l^{-1}). Multiplying observed concentrations of chlorophyll *a* at each site by the minimal ratio of 24 (after Abril *et al.*, 2002) then provides an estimation of the amount of POC that could be due to the presence of algae. Finally, the percentage contribution of algal POC to known values of total POC was calculated for each sample and these data are also given in Figure 3.12 (b).

Ratios of POC:Chl *a* (Figure 3.12a) ranged from 24 - 734 (mean = 142) and as the majority of values are < 200, phytoplankton predominance is suggested in May and July 2000.

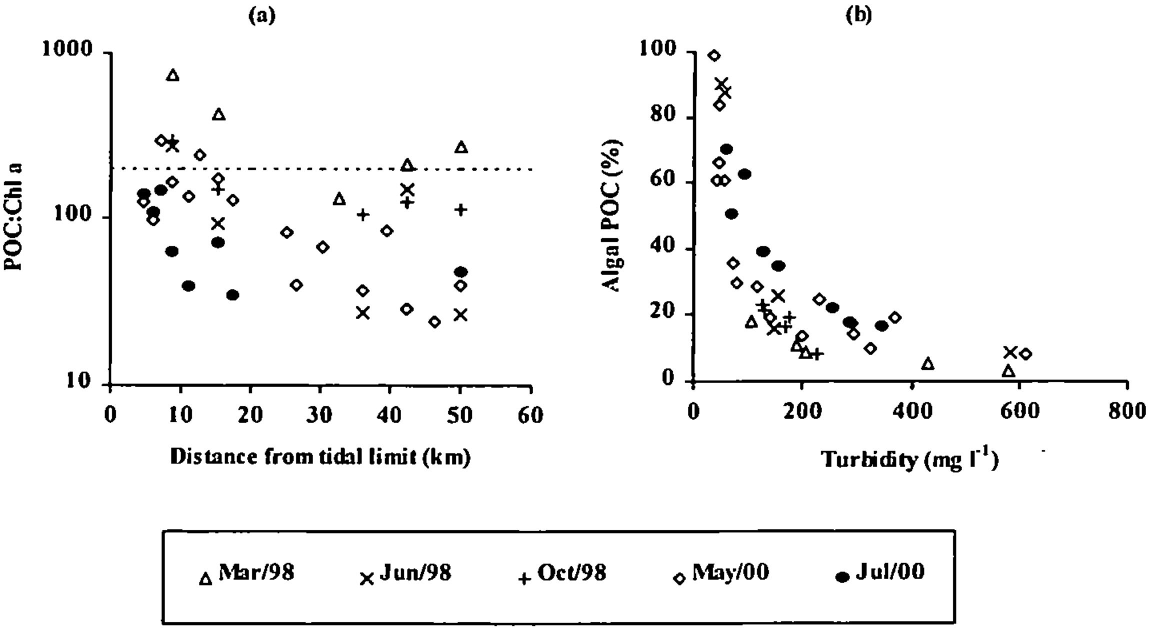


Figure 3.12 (a) POC:Chl *a* as a function of distance along the estuary, and (b) algal POC as a percentage of total POC against SPM load. The broken line in (a) represents the maximum ratio (200) of POC:Chl *a* exhibited by phytoplankton.

Detrital material, having POC:Chl *a* ratios of > 200 are only identified for a few samples. However, chlorophyll *a* data are more limited than that for POC (particularly in March, June and October 1998) so relatively little can be inferred from this interpretation. Algal POC (Figure 3.12b) is estimated to constitute between 3 – 99% of seston POC and declines markedly with increases in suspended load. This pattern is to be expected in a highly turbid system such as the Mersey where low light levels would somewhat inhibit primary productivity even when nutrient concentrations are usually more than adequate to support phytoplankton growth. Despite the scarcity of actual chlorophyll *a* data, highest contributions to total POC by algae occur in June 1998, May 2000 and July 2000. Along with the POC:Chl *a* data it would appear that the aforementioned slight increases in POC measured during these surveys may be linked to phytoplankton blooms, although the evidence is not unequivocal and another means of assessing SPM organic carbon provenance, such as the use of C:N ratios is also required.

Atomic C_{org}:N ratios in SPM have therefore been investigated and the results are presented in Figure 3.13. Samples of SPM from March 1998 have C:N ratios of 5.6 – 18.4 and those from May 2000 range from 4.2 – 8.2. As explained earlier (Section 3.4.1) lower than Redfield values may indicate the presence of bacteria, labile organic matter, inorganic ammonium or organic nitrogen sorbed to particles. These low values tend to be restricted to the upper estuary up to a distance of 18 km from the tidal limit. Elsewhere in May 2000, and at certain sampling sites in July 2000 (and less so in June 1998), samples demonstrate ratios approximating to that of the Redfield ratio and this reinforces some of the earlier discussions regarding the presence of phytoplankton blooms and their contribution to total POC in SPM. At various locations during March 1998, June 1998, October 1998 and July 2000, ratios are elevated to different extents above the Redfield value. These samples imply mixed composition along the transects of possibly sewage-related and terrestrially-derived organic matter from either C3 or C4 plants (which may also include humic acids).

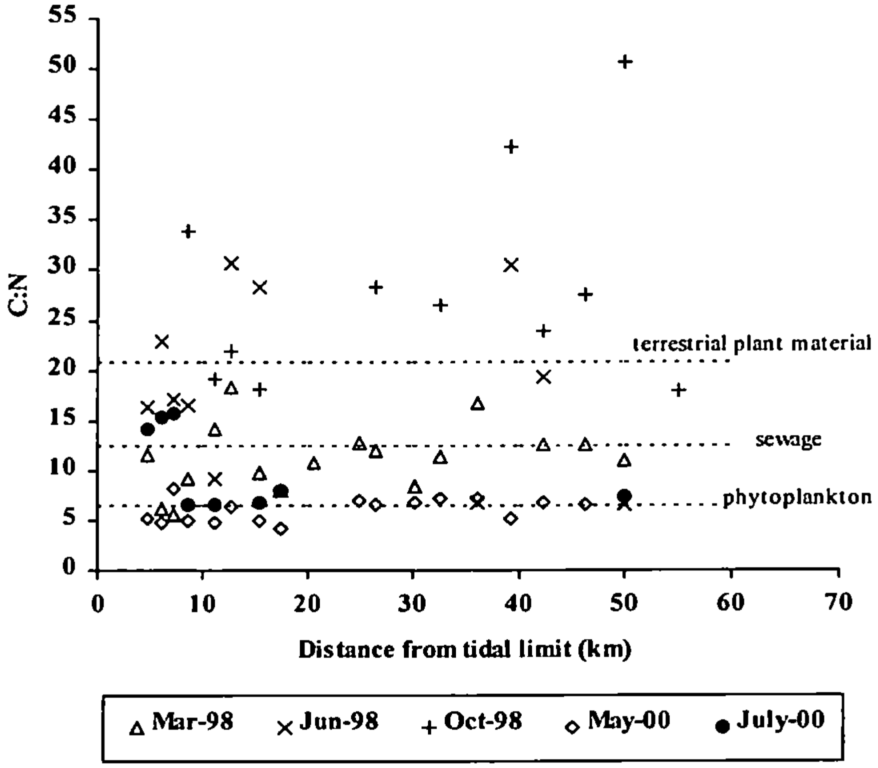


Figure 3.13 Variation of atomic C:N ratios in suspended particles as a function of distance along the estuary. Also shown are mean atomic C:N ratios for phytoplankton, sewage and terrestrial plant material.

Tipping *et al.* (1997) observed major POC peaks associated with the first increase in freshwater discharge following the low-flow summer period in the Humber rivers. Autumnal peaks were thought to arise from enhanced catchment erosion and re-entrainment of particulate material accumulated in the riverbed over the preceding months (Tipping *et al.*, 1993). Veyssy *et al.* (1999) proposed that the greatest seasonal variation in riverine POC is due to the increased flux of riparian litter entering rivers and streams after vegetation die-off in late summer and early autumn. This has also been indicated in the Humber Estuary where POC generally varies by just a factor of 2, but where the most marked increases relate to inflows of poor quality terrestrial POC later in the year (Uncles *et al.*, 2000). In the Mersey, this same effect may explain the high C:N ratios measured in

October 1998, as during that month, the mean monthly freshwater discharge was 68 m^3 s^{-1}, approximately double that for September 1998 (32 m^3 s^{-1}) even though an overall increase in POC was not observed at the time (Figure 3.11a). Some C:N ratios measured in June 1998 were also high and could have occurred for the same reason because on average, river flows in June, rather than declining from those in May (monthly average = 20 m^3 s^{-1}) actually rose to a monthly mean of 45 m^3 s^{-1}.

The POC content of suspended particles from a number of riverine and estuarine sources are compared to those from the Mersey from the five surveys conducted between March 1998 and July 2000 (combined data) in Table 3.3. Mersey Estuary SPM has comparable POC concentrations to those from the Delaware, Ems, Garonne, Gironde Humber and Sado estuaries, San Francisco Bay and Tolo Harbour. As previously exemplified in Figure 3.11, POC varies by only 2.5% throughout the mixing zone in the Mersey, reflecting that SPM in this system is more chemically homogeneous with respect to organic carbon than suspended particles from the Douro, Rhine, Scheldt and Thames. Seasonal independence of POC% of SPM in the TMZs of the Gironde, Loire, Elbe and Ems was explained by Abril *et al.* (2002) as being due to the POC being almost refractory. In contrast, data for POC% in the Mersey TMZ varies by approximately 2% throughout the sampling programme and ratios of POC:Chl *a* and C:N have already indicated that for the majority of samples analysed, POC is mostly dominated by forms that would be prone to more complete microbial degradation (algal, sewage, other labile organic matter) than poor quality terrestrial detritus.

For the majority of estuaries in Table 3.3, including the Mersey, riverine POC exceeds that in the turbidity maximum. This is due to mineralisation of labile riverine POC with simultaneous dilution of POC-rich riverine SPM by a pool of relatively POC-impoverished particles in the TMZ. The loss of POC in the river-estuary transition zone was investigated by Abril *et al.* (2002) for a number of estuaries and the results from that study are presented with corresponding data for the Mersey in March 1998, June 1998, October 1998, May 2000 and July 2000 in Table 3.4. The same order of loss of POC for estuaries other than the Mersey in Table 3.4 has also been reported for pCO_2 in inner estuarine zones. This is believed to correlate with differences in the buffering capacities of those estuaries with respect to dissolved inorganic carbon and the degree of nitrification affecting pCO_2 in those systems (Frankignoulle *et al.*, 1996, 1998). Abril *et al.* (2002) also showed that mineralisation efficiency is a function of flushing time and that a flushing time in excess of 20 days provides sufficient time for the mineralisation of the majority of labile

Table 3.3 Suspended particulate organic carbon (as percentage dry mass SPM) in a variety of estuarine systems.

Estuary	Riverine	TMZ	POC (%) Estuarine range	Estuarine mean	Reference
Cochin Backwater Estuary			0.7 – 3.8	1.6	Sankaranarayanan and Panampunnayil (1979)
			0.2 – 6.2	3.6	Seralathan *et al.* (1993)
Delaware Estuary	9.0	2.3			Biggs *et al.* (1983)
Douro Estuary	11.9	7 – 17	7 – 20		Abril *et al.* (2002)
Elbe Estuary	10.5	4.0	4.0 – 8.3		Abril *et al.* (2002)
Ems Estuary	6.1	2.8			Eisma *et al.* (1982a)
	7.0				Cadée (1987)
	4.5	3.5	3.5 – 5.1		Abril *et al.* (2002)
Garonne Estuary	1.5 – 14.6	1.5			Etcheber (1983)
Gironde Estuary	3.0	1.4 – 1.5	1.4 – 2.9		Veyssy *et al.* (1999)
Humber Estuary	~ 5.0	~ 2.0	~ 2.0 – 5.0	2.6 ± 0.6	Uncles *et al.* (2000)
Loire Estuary	7.9	3.0			Meybeck *et al.* (1988)
	20.1	3.8	3.8 – 4.6		Abril *et al.* (2002)
Mersey Estuary	1.79 – 3.54	0.92 – 2.85	0.19 – 2.85	1.35 ± 0.53	This study
Mississippi River Estuary				1.8	Trefry *et al.* (1994)
Rhine Estuary	5.7	5.0 – 5.7	5.0 – 12.2		Abril *et al.* (2002)
	5.6				Eisma *et al.* (1982b)
Sado Estuary	2.9 – 3.8	2.0 – 2.6	2.0 – 3.3		Abril *et al.* (2002)
San Francisco Bay			1.0 – 4.0		Schemel *et al.* (1996)
Scheldt Estuary	11.2	4.0 – 11.2	2.6 – 11.2		Abril *et al.* (2000)
Tamar Estuary	5.0	2.5			Morris *et al.* (1982a)
Thames Estuary	6.0	3.5 – 7.5	1.6 – 7.5		Abril *et al.* (2002)
Tolo Harbour, Hong Kong			≤ 2.0		Thompson and Yeung (1982)

Table 3.4 Calculation of POC loss in the river > estuary transition.

Estuary	River POC% (%SPM)	Estuarine POC% (%SPM)	POC% loss (%SPM)	Percentage of riverine POC mineralised
Scheldt	11.2	2.1	9.1	82
Thames	6.0	1.7	4.3	72
Sado	3.7	2.0	1.7	59
Mersey July 2000	3.14	1.32	1.82	58
Ems	7.0	3.0	4.0	57
Mersey June 1998	2.29	1.02	1.27	56
Loire	7.9	3.8	4.1	52
Mersey May 2000	3.54	1.79	1.75	49
Gironde	3.0	1.5	1.5	49
Mersey March 1998	2.75	1.51	1.24	45
Elbe	6.5	4.0	2.5	38
Mersey October 1998	1.79	1.15	0.64	36
Rhine	5.5	5.3	0.2	4
Douro	11.9	11.9	0.0	0

POC to occur. The flushing time of the Mersey ranges from 20-50$^+$ days, with a mean of 32 days (Jones, 1978) and this, combined with possible evidence for nitrification in the Mersey may also assist in explaining why mineralisation of POC increases by more than 20% between surveys. Mineralisation is lowest in October 1998 when the POC content of riverine and estuarine SPM are most similar and POC largely arises from inputs of detrital material during high run-off. In the warmer months, mineralisation of POC steadily increases as water temperatures increase, freshwater discharge is progressively lessened and riverine and estuarine SPM have more distinct compositions in terms of their organic carbon content. This is due to changes in the type and biodegradability of carbon present, with phytoplankton and sewage accounting for more of the POC entering the estuary in other surveys. For example, algal contributions to POC are high at some locations in the estuary in June 1998, May 2000 and July 2000 and sewage inputs are noticeable during March 1998, June 1998 and July 2000. Both types of material would be rapidly remineralised, thereby contributing to the higher mineralisation efficiencies reported in Table 3.4.

Values for riverine DOC and POC for the five surveys between March 1998 and July 2000 have been combined and plotted against inhabitants/discharge ratios (Figure 3.14). Data from Abril *et al.* (2002) are provided for comparison. The estuaries fall into four distinct categories. Concentrations of TOC in the Gironde and Douro are at or close to natural

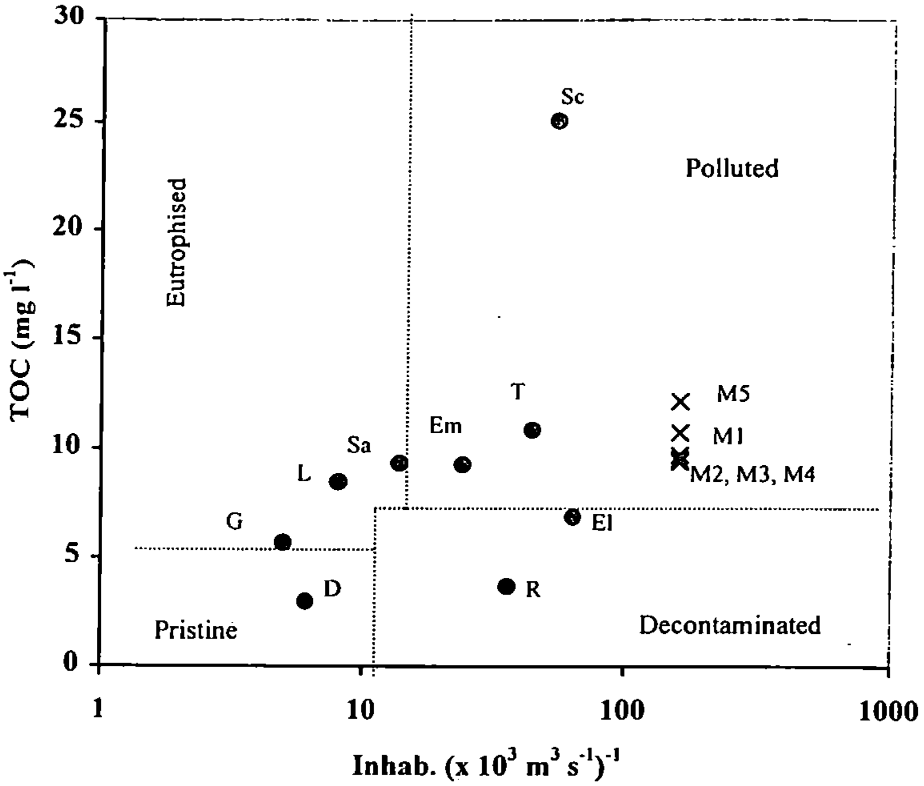


Figure 3.14 Classification of estuarine systems by TOC as a function of the number of inhabitants (normalised with freshwater discharge). D = Douro, El = Elbe, Em = Ems, G = Gironde, L = Loire, M1 = Mersey March 1998, M2 = Mersey June 1998, M3 = Mersey October 1998, M4 = Mersey May 2000, M5 = Mersey July 2000, R = Rhine, Sa = Sado, Sc = Scheldt and T = Thames. Adapted from Abril *et al.* (2002).

levels, TOC in the Gironde being elevated due to soil erosion in the Pyrenees. Population density is low around the Sado but the region has low sewage treatment. The Loire is eutrophised and consequently experiences high algal POC contributions in the summer. Increased population density in the Thames region and the presence of food processing plants in the vicinity of the Ems means that a large fraction of the TOC is likely to come from sewage inputs. Like the Mersey, Scheldt and Thames, the Elbe and Rhine basins are highly populated. The latter two estuaries have essentially become decontaminated due to recent improvements in sewage treatment. Consequently, TOC concentrations are approaching natural levels, as exemplified by the Douro. The Mersey has the highest population density and despite a factor of eight difference in freshwater discharge between the five surveys, riverine TOC concentrations are very similar. Results from this study have already shown that the amount of total carbon associated with SPM in the Mersey has reduced in the last decade. In time, it is anticipated that if the quality of effluents entering the tidal and non-tidal reaches of the Mersey continues to improve, then TOC concentrations will approach those currently seen in the Elbe and Rhine.

3.5 Specific surface areas of estuarine particles

3.5.1 Sediments

Specific surface areas of July 1999 sediments are given as a function of distance along the estuary in Figure 3.15. The term 'natural' refers to samples that were measured prior to digestion with $NH_2OH.HCl$ in 25% CH_3COOH, *i.e.* containing total carbon, whilst 'organic + residual' describes the particulate fraction remaining after inorganic carbon and ferromanganese oxides have been removed. The SSAs of unaltered < 63 μm grain size sediments (Figure 3.15a) are consistently around 2–3 times greater than that of the > 63 μm material (Figure 3.15b). The SSA in finer particles remains consistent throughout the very low salinity region despite a rapid decrease in POC content in the first km from the tidal limit (Figure 3.8). This suggests that riverine sediment particles are 'saturated' with POC and that the loss of two thirds of the carbon does not therefore affect the SSAs of those particles. The same patterns of changing SSA with distance are exhibited for natural and altered particles. Thus, SSA appears to be largely a reflection of C_{org} and C_{res} content.

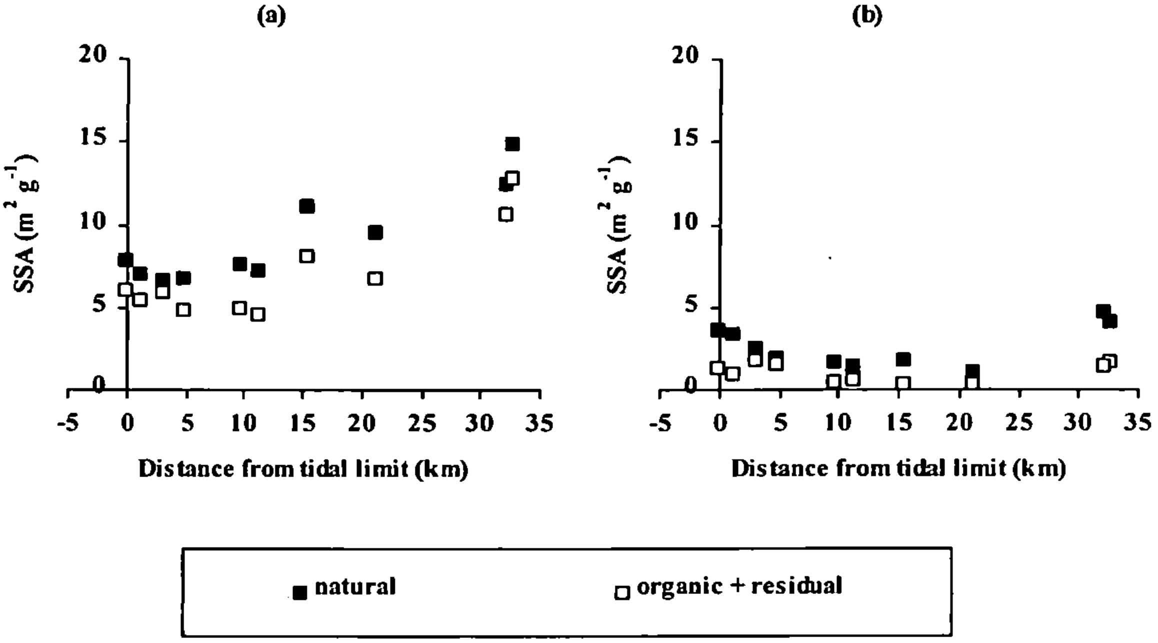


Figure 3.15 Specific surface areas of (a) < 63 μm grain size and (b) > 63 μm grain size sediments before and after digestion with hydroxylammonium chloride in acetic acid.

3.5.2 Suspended particles

Settled SPM samples from the May 2000 and July 2000 transects, were treated in the same manner and the resulting measurements are similarly displayed in Figure 3.16. The SSAs of suspended particles are approximately twice that of fine-grained sediment particles. Surface areas of SPM are more consistent than for the sediment and remain almost unchanged over distance, a feature noted by Millward *et al.* (1990). Smaller SSA peaks exist for SPM than for the < 63 µm sediment at the same locations in the upper estuary. However, SSA in SPM falls by the same proportion as seen in the fine sediments following

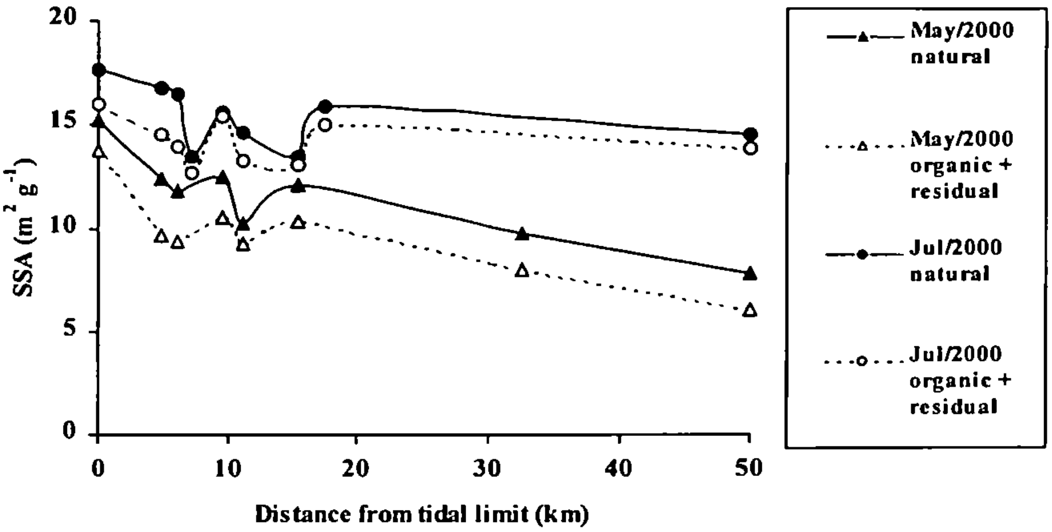


Figure 3.16 Specific surface areas of bulk settled SPM from May 2000 and July 2000 before and after digestion with hydroxylammonium chloride in acetic acid.

digestion. This implies that both bed sediment and suspended particle surfaces have very similar compositions in terms of the amounts of Fe-Mn oxide and inorganic carbon present. Again, as for bed sediments, the results infer that organic and residual forms of particulate carbon are essentially determining the SSA of SPM and that other surface sorbent phases may play a comparatively minor role in determining the amount of active surface available for contaminant binding.

The mean specific surface area of May 2000 SPM and July 2000 SPM are 11.0 ± 1.6 m^2 g^{-1} and 15.1 ± 1.3 m^2 g^{-1}, respectively (Table 3.5). Both mean values exceed that previously reported for Mersey SPM (9.6 ± 2.4 m^2 g^{-1}) by Millward *et al.* (1990). Thus, the reductions in SPM carbon may have resulted in less pore-blocking (Vdović *et al.*, 1991), producing a consequent overall rise in specific surface areas of Mersey Estuary suspended particles compared to those determined in 1987. The SSA of Mersey Estuary SPM is low compared to that of suspended particles from some other major European estuaries (Table 3.5). Anthropogenic Fe in the Humber and elevated Mn in the relatively clean Weser and Elbe (refer to Figure 3.14) promote an increase in SSA, but in the moderately polluted Thames

Table 3.5 Specific surface areas of suspended sediments in a selection of European estuaries. Mean ± one standard deviation and range, R, of n sample analyses are given.

Estuary	Sampling date	Statistical parameters	SSA (m^2 g^{-1})	Reference
Dee, upper	Dec 1991	n	4	Turner *et al.* (1994)
		Mean ± σ	4.4 ± 4.1	
		R	(0.5 – 9.3)	
Dee, lower	Dec 1991	n	3	Turner *et al.* (1994)
		Mean ± σ	8.3 ± 1.7	
		R	(6.4 - 9.5)	
Elbe	Jun 1988	n	10	Turner *et al.* (1991)
		Mean ± σ	25.6 ± 8.6	
		R	(7.2 - 35.5)	
Humber	Jan 1988	n	18	Turner *et al.* (1991)
		Mean ± σ	24.0 ± 6.5	
		R	(9.8 – 38.3)	
Humber	Jul 1989	n	11	Turner *et al.* (1991)
		Mean ± σ	25.2 ± 3.9	
		R	(16.3 – 29.5)	
Mersey	Nov 1987	n	10	Millward *et al.* (1990)
		Mean ± σ	9.6 ± 2.4	
		R	(6.0 – 14.9)	
Mersey	May 2000	n	7	This study
		Mean ± σ	11.0 ± 1.6	
		R	(7.8 – 12.5)	
Mersey	Jul 2000	n	8	This study
		Mean ± σ	15.1 ± 1.3	
		R	(13.4 – 16.8)	
Scheldt	Feb 1987	n	12	Turner *et al.* (1991)
		Mean ± σ	9.7 ± 1.5	
		R	(7.3 - 11.6)	
Scheldt	May 1987	n	13	Turner *et al.* (1991)
		Mean ± σ	6.2 ± 2.9	
		R	(< 1 – 10.3)	
Scheldt	Aug 1987	n	12	Turner *et al.* (1991)
		Mean ± σ	10.5 ± 2.2	
		R	(6.8 - 13.7)	
Thames	Feb-Mar 1989	n	14	Turner *et al.* (1991)
		Mean ± σ	12.3 ± 4.0	
		R	(< 5 – 19.2)	
Weser	Aug 1989	n	15	Turner *et al.* (1991)
		Mean ± σ	18.8 ± 6.3	
		R	(9.3 – 28.2)	

and severely polluted Scheldt, which have both received high organic loadings and where Fe and Mn are relatively low due to reduced oxygenation (Section 1.3.2), SSAs are lowered. Data for Mersey SPM tend to resemble those from the Thames Estuary rather than the more impacted Scheldt.

3.6 Summary

Waters in this tidally dominated energetic system tend to be well mixed apart from when increased freshwater runoff produces only partial mixing in the upper estuary. On spring tides, a turbidity maximum is formed at around a distance of 9 km from the tidal limit but this becomes broader and is shifted seawards in response to higher river flows. Seasonal variations in temperature, DO and pH are apparent and chlorophyll *a* concentrations were highest in the TMZ. A persistent broad oxygen sag corresponds with a reduction in pH and arises from CO_2 production due to the respiration of organic-rich bed sediments by what is believed to be an extensive bacterial population.

Evidence for nutrient cycling is restricted and no clear pattern emerges to suggest obvious seasonal nutrient uptake by phytoplankton, largely because nutrient inputs are very high. As a result of improved oxygenation and reduced ammonia loads, former evidence of substantial denitrification in the Mersey has since been replaced by partial nitrification but estuarine NO_3^- concentrations do not appear to pose any concern to the regulators. In contrast, dissolved phosphate concentrations are high, particularly in the summer months, and along with low DO, contribute to the EA's classification of poor water quality in the estuary. The use of nutrient ratios gives some indication that N may become limiting in the spring and summer, whilst P could be limiting in autumn and winter. Silicate is likely to limit diatom growth unless river runoff is sufficient ($\geq \sim 40$ m^3 s^{-1}) to recharge estuarine waters with the nutrient though enhanced catchment erosion. CSTT (1997) guidelines are exceeded for winter concentrations of DAIN (12 μM) and DAIP (0.2 μM) and, apart from in December 1997, chlorophyll concentrations also transcend the recommended value of 10 μg l^{-1} as set down under the EC Urban Waste Water Treatment Directive. In addition, winter molar N:Si ratios > 2 are produced for the majority of sites along the estuary at different times of year and together, these facts point to hypernutrification in the Mersey.

Concentrations of DOC are relatively high and CHN analyses of suspended and bed sediment particles has revealed that the organic carbon pool is derived from a mixture of anthropogenic and natural sources. The amount and type of POC present in the estuary varies throughout the year in response to changes in freshwater runoff, vegetative die-off, the relative magnitude of wastewater inputs compared to the dilution capacity of the estuary as well as the incidence of bacterial and photosynthetic activity. Phytoplankton blooms occurred, the most prominent of which were in May and July 2000, although some evidence of heightened photosynthetic activity was also produced at discrete locations in March and June 1998. It is likely that the blooms originated in Liverpool Bay and were advected into the estuary by strong tides. Once in the estuary, bloom activity increased due to high nutrient availability and algal POC contributed from 20 – 99 % of total POC in SPM, but became progressively reduced due to poor light availability at turbidities greater than ~ 100 mg l^{-1}.

Carbon in bed sediments is largely a function of sediment granulometry, which itself reflects the hydraulic sorting and energetic dispersal of bed sediment particles within the system. Carbon associated with SPM tends to follow the same spatial trends as that in bed sediments and reflects the position of freshwater inputs and the regeneration of labile organic matter at the estuarine null point. A long average flushing time and partial nitrification alter the buffering capacity of the estuary and consequently, around 35 – 60% of seston POC is rapidly mineralised. Analysis of POC:Chl *a* and atomic C:N ratios indicates that this is dependent on the type of POC predominating in the estuary at the time of sampling. Reduced mineralisation occurred in October 1998 when high river discharge lead to significant inputs of terrestrial organic matter but increased when more labile POC sources such as phytoplankton, bacteria and sewage inputs became more prominent.

Mersey SPM is fairly chemically homogeneous with respect to organic carbon and cleansing of the estuary with respect to organic contaminants is strongly suggested as the total carbon content of SPM has reduced by approximately 75% between 1987 and 1998 due to improved treatment of sewage and organic industrial effluents. This has assisted in producing an increase of up to 57% in the average SSA of SPM over the same period, although SSAs are still lower than those in less impacted systems.

Hence, the underlying chemical conditions in the Mersey Estuary have been identified. These observations will facilitate the holistic interpretation of spatial and temporal alterations in the distributions, reactivity, cycling and particle-water interactions of trace metals in the Mersey, which will be described in subsequent chapters.

Chapter 4

Trace Metal Distribution and Reactivity in the Mersey Estuary

4 Trace metal distribution and reactivity in the Mersey Estuary

This chapter reports the seasonal distributions of trace metals associated with bed sediments and suspended particles in the Mersey Estuary. The discussion covers an interpretation of physical and geochemical processes affecting the transport and behaviour of a number of trace metals which have been selected for their differences in geochemical interaction with particulate matter. The advances made to date of metal decontamination in the estuary will be evaluated using data from this work and those from previous studies.

4.1 Particulate trace metals

4.1.1 Axial trace metal distributions in bed sediments

Estimates of non-detrital trace metal concentrations (available to 1M HCl) have been determined for fine- (< 63 μm) and coarse-grained (> 63 μm) surficial sediment fractions sampled during July 1997 and July 1999. In July 1997, bed sediments were collected from almost the entire length of the estuary (Figure 2.3), at locations of net sediment accretion that were assumed to represent a range of contaminant sources and sediment granulometries. By way of contrast, the July 1999 survey focussed primarily on sampling within the upper estuary (Figure 2.3). This was done: (a) because the first survey had identified an accumulation of fine-grained material backed up against the mechanical weir in the uppermost 10 km of the estuary resulting from the winnowing and upestuary advection of fines by strong tidal action and (b) because previous work on sediment metal concentrations has focussed on sampling in the mid and lower estuary (Taylor, 1986; Harland and Riddle, 1997; Harland *et al.*, 2000), leaving the upper estuary largely unaccounted for. Sampling for trace metals in July 1999 therefore concentrated on collecting sediments in the 5 km labyrinth between the tidal limit and EA station 22 (refer to Figure 2.2 for EA station locations).

Trace metal distributions in sediments sampled in both surveys are plotted together against distance from the normal tidal limit in Figure 4.1. Each metal shows variable affinity for the two grain size fractions. Highest metal concentrations tend to occur in freshwater sediments and those from locations where sediment composition is dominated by silts and clays (see Figure 3.7). Conversely, the lowest concentrations of trace metals were found at stations where surface bed sediments were largely composed of sandier material (Figure 3.7). Metal distributions are therefore reflecting physical sediment characteristics and this confirms the findings of other researchers (Taylor, 1986; Harland *et al.*, 2000; Turner, 2000).

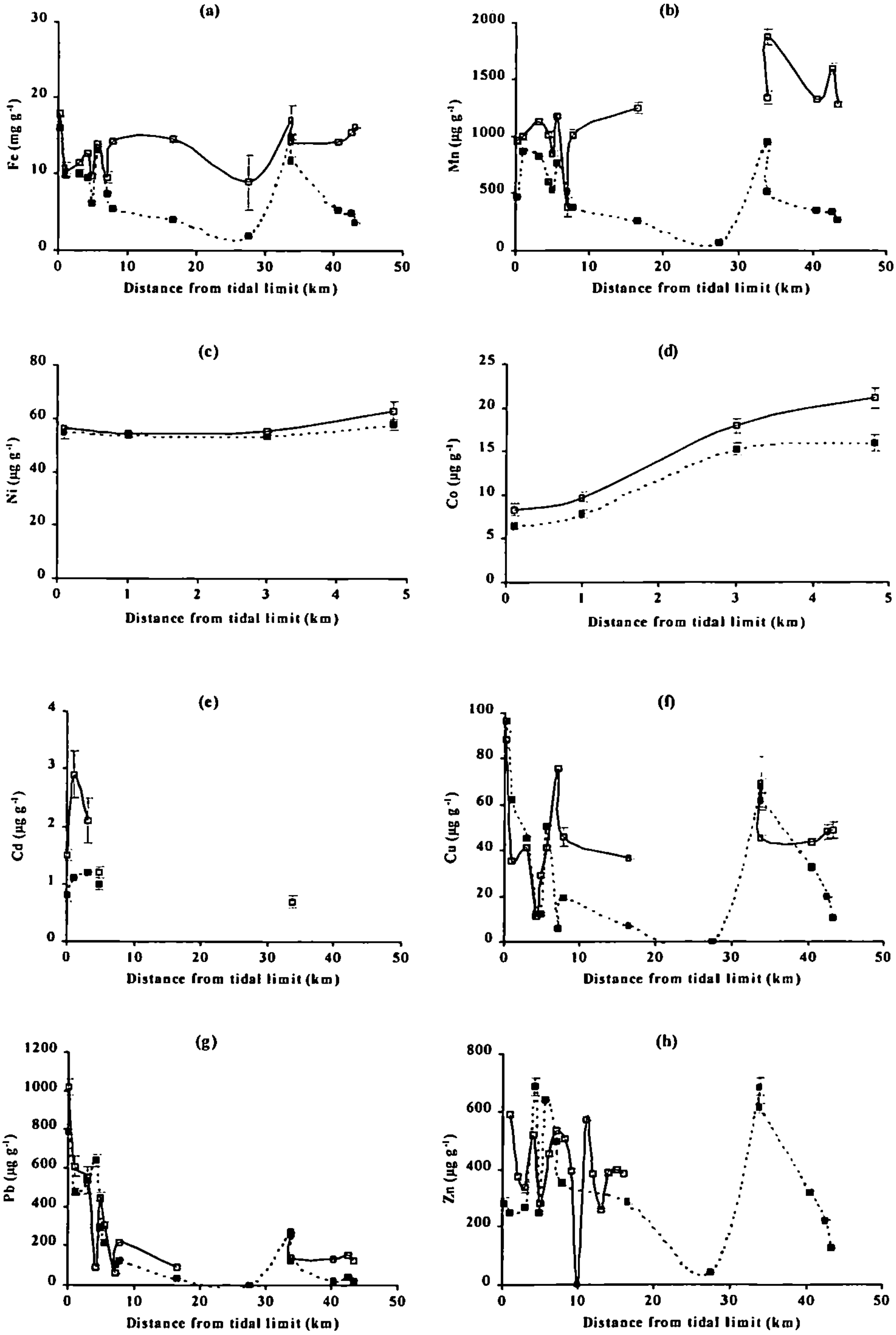


Figure 4.1 Concentrations of non-detrital (available to 1M HCl) (a) Fe, (b) Mn, (c) Ni, (d) Co, (e) Cd, (f) Pb and (g) Zn in fine (□) and coarse (■) sediment fractions from July 1997 and July 1999 as a function of distance along the Mersey Estuary. Missing data points indicate concentrations that were below the limits of detection, rather than a lack of analysis at that location.

Iron and Mn affect particle properties and are commonly used to geochemically characterise particulate matter in estuarine systems (Turner *et al.*, 1991; Turner, 2000). The amount of Fe in the < 63 μm fraction (Figure 4.1a) is relatively uniform overall, with sediments exhibiting common geochemical composition throughout the estuary. Iron concentrations are fairly low in the labyrinth, are generally the same in both size fractions and only show a difference 5 km from the weir. Here, concentrations have fallen by around 30% compared to those in riverine sediment. The largest differences in concentrations between the two fractions are observed at locations where silt content is reduced.

Manganese is a redox sensitive element and is transferable between the dissolved and particulate phase in response to physicochemical changes. Even though Mn is particle reactive, the concentration of Mn in sediments is relatively low in the region of the TMZ (Figure 4.1b), which on spring tides is usually located at a distance of around 8-9 km from the tidal limit. Here, depressed oxygen levels could cause the dissolution of Mn from particle surfaces (Duinker *et al.*, 1979). Particulate Mn increases in the middle and lower regions of the estuary as oxygenation of the water improves, causing the re-precipitation of manganese oxides although the oxidation of Mn^{2+} slows in seawater (Morris *et al.*, 1982b). Turner *et al.* (1993) also showed that the partition coefficient of Mn increases with increasing salinity. Additionally, strong tidal disturbance of surface sediments leads to porewater infusion of Mn and subsequent oxidation to Mn (IV) on particle surfaces. The autocatalytic reaction ensues whereby the presence of Mn on particle surfaces promotes the adsorption of dissolved Mn. Manganese concentrations in the < 63 μm fraction almost exclusively exceed those in the > 63 μm fraction. The only exceptions to this are at the TMZ where the concentration is higher in the coarse-grained material and midway along the estuary where Mn in undetectable in the fine-grained fraction.

Nickel and Co concentrations have only been determined in sediments from the top of the upper estuary (Figure 4.1c and Figure 4.1d, respectively) in 1999. Particulate Ni rises slightly in the first 5 km from the tidal limit and correlates well with independent measurements of dissolved Ni which have shown maximum concentrations in this area (Martino, 2000). Other researchers have cited industrial inputs as the main source of Ni in this region (Jones, 1978; Campbell *et al.*, 1988; Comber *et al.*, 1995). Although discharges of Ni into the estuary have been reduced and the major manufacturer responsible for the production of Ni catalysts is no longer operating, the sediments at this location do appear to be retaining an historical accumulation of the metal. The fact that both size fractions contain equivalent Ni concentrations may indicate that past Ni inputs were so large that any grain size effects are overcome. This could be achieved either through: (a) strong binding of Ni with organic carbon including residual POC, which was only detected in sediments from the top of the estuary (Figure 3.8), or (b) through the co-association of Ni with Fe as the latter also occurs in almost equal proportions in both size fractions in the first 5 km of the estuary (Figure 4.1a).

Particulate Co (Figure 4.1d) shows the same trend as Ni, but is more exaggerated, with concentrations in the silt fraction experiencing a 3-fold increase a short distance from the weir. However, concentrations in the two fractions diverge as distance increases, suggesting that inputs of Co may not be as large as those for Ni.

Concentrations of Cd in < 63 μm sediment (Figures 4.1e) at distances of 1-5 km from the weir increase above those found in the corresponding riverine sample. It was originally thought that this could be attributed to the close proximity of a sewage treatment works and associated outfalls in the extreme upper estuary. Supporting evidence is somewhat limited (Figure 3.8); whilst a clear signature for sewage is demonstrated for residual POC at a distance of 5 km, C:N ratios tend to suggest that humic substances are the dominant source of organic carbon in bed sediments in this region. Cadmium concentrations are below the limits of detection throughout most of the tidal estuary, the exception to this occurring some 35 km from the tidal limit. Here, the ratio of C:N again approaches that for sewage derived material (Figure 3.8).

The trend for Cu shows an equal or greater tendency toward the coarser sediment (Figure 4.1f) at locations where silt content is high. This again could imply that past inputs of Cu were substantial enough to reduce the normal effects of sediment granulometry. Elevated concentrations of Cu occur in < 63 μm sediment at around 8 km from the tidal limit. Here, there could be significant binding of Cu with labile organic carbon generated through the decomposition of organic matter at the estuarine null point, the location around which highest SPM POC is observed (Figure 3.11).

Estuarine Pb and Zn concentrations are high (Figure 4.1g and Figure 4.1h, respectively) and once more seem to be preferentially associated with the coarser sediment in the upper estuary and at a distance of 35 km. Common (and large) sources may therefore exist between these two metals as well as Cu. Riverine sediment, sampled from above the weir is shown to contain exceptionally high concentrations of Pb which are assumed to originate from both diffuse and point sources further up the river, although the exact nature of inputs giving rise to these levels are at present unknown. It may be that the relatively minor river flow passing through such an extensive catchment is insufficient to adequately dilute the load and this leads to a gradual accumulation of the metal from several large conurbations.

As mentioned already, in addition to the magnitude of inputs and grain size distributions, another contributory factor affecting trace metal contents in sediments is thought to result from the amount of organic carbon present (see Figure 3.8). Maximum estuarine concentrations of metals and carbon generally occurred at both the TMZ and near the entrance to the Manchester Ship Canal at Eastham some 35 km downstream from the tidal limit. Elevated concentrations at Eastham may be due to the flux of metal- and organic carbon-laden sediments from the canal being flushed into the estuary upon operation of the lock gates. Away from the upper estuary, it is at this station alone that Cd was detected in the sediments at a concentration of 0.7 $\mu g\ g^{-1}$. Apart from these two locations, it appears that metals in both sediment fractions are tending towards a gradual decline in concentration as distance from the head increases. It appears therefore, that a mixture of geochemical and physical processes influence trace metal distributions in Mersey sediments.

Mean trace metal concentrations in fine-grained sediments from a number of UK estuaries are provided in Table 4.1. Comparisons of data from this study with those from Williams (1995) reveal that, except for Fe, Humber and Mersey sediments show similar degrees of

Table 4.1 Mean trace metal concentrations in fine-grained surface sediments from a variety of UK estuaries. Concentrations are in $\mu g\ g^{-1}$ (dry wt.) except for Fe ($mg\ g^{-1}$).

Site	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Humber Estuary[a]	0.5	16	50	35	1000	39	110	250
Humber Estuary[b]	1-2	> 6	20-40	> 20	> 1500	-	> 150	> 200
Liverpool Bay[b]	> 5	< 2.5	20-40	10-12.5	> 1000	-	> 100	> 150
Mersey Estuary[c]	1.7	16	40	13	1200	57	250	380
Severn Estuary[a]	0.6	15	40	28	700	33	89	260
Solway Firth[a]	0.2	6	7	15	600	17	25	59
Tamar Estuary[a]	1.0	21	330	35	600	44	240	450
Tyne Estuary[a]	2.2	11	90	28	400	34	190	420
Wyre Estuary[a]	0.4	8	20	17	600	17	44	120

[a] < 100 µm fraction, conc. HNO_3 digest (Bryan and Langston, 1992); [b] < 63 µm fraction, 1M HCl digest (Williams, 1995); [c] This study, < 63 µm fraction, 1M HCl digest.

contamination for all the trace metals studied. Humber sediments possess higher non-detrital Fe due to inputs into the estuary from titanium dioxide processing plants (Grant and Middleton, 1990, 1993). Data for the Mersey are also largely in accord with that of sediments originating from the adjoining coastal area. Metal concentrations offshore may be attenuated (or even augmented in the case of Cd), by high trace metal contents in dredge spoil, sewage sludge and industrial waste deposits dumped at various sites in Liverpool Bay (Norton *et al.*, 1984). Mersey surface sediments are similarly contaminated, for different metals, as sediments in the Tamar, Severn, Tyne and Humber estuaries but show considerable metal enrichment compared to sediments from the Wyre and Solway.

4.1.2 Axial trace metal distributions in bulk and settled SPM

Axial distributions of non-detrital metals available to 1M HCl in bulk SPM, and PSPM and TSPM components separated from bulk SPM by settling are reported in Figure 4.2. Total metal concentrations determined by extraction of bulk SPM with HF are also provided in Figure 4.2. It should be noted that the removal of riverine concentrations from plots (i) and (ii) in Figure 4.2 produces no appreciable change in the shape of the profile for any of the metals studied.

Apart from its concentration in riverine particles, non-detrital suspended particulate Fe does not appear to exhibit seasonal variability, but instead gives relatively uniform trends along the estuary (Figure 4.2a). This indicates that these particles are homogeneous in terms of Fe content and therefore also, to a certain extent, their reactivity is also invariable. Around 50% of total Fe is released from bulk SPM by HCl. Results demonstrate that PSPM consistently possesses slightly higher concentrations of Fe than TSPM, which is important in terms of the longer-range transport of metals by those particles 'permanently' in suspension, especially for any metals that may bind strongly with Fe oxyhydroxides. Williams and Millward (1998) demonstrated that the same trend exists for 1M HCl-leachable Fe in PSPM and TSPM from the tidal reaches of the Ouse and Trent rivers.

Non-detrital particulate Ni concentrations (Figure 4.2b) are highest in the upper 2 km of the estuary followed by relatively constant concentrations further downstream. This profile is analogous to that given by Fe. Nickel may therefore be closely associated with iron oxyhydroxides (and possibly organic phases) at the particle surface. The concurrence of Ni with Fe in estuarine SPM has also been reported for the Humber and Mersey estuaries by Comber *et al.* (1995) and for SPM from the Humber mouth and plume by Sands (1997).

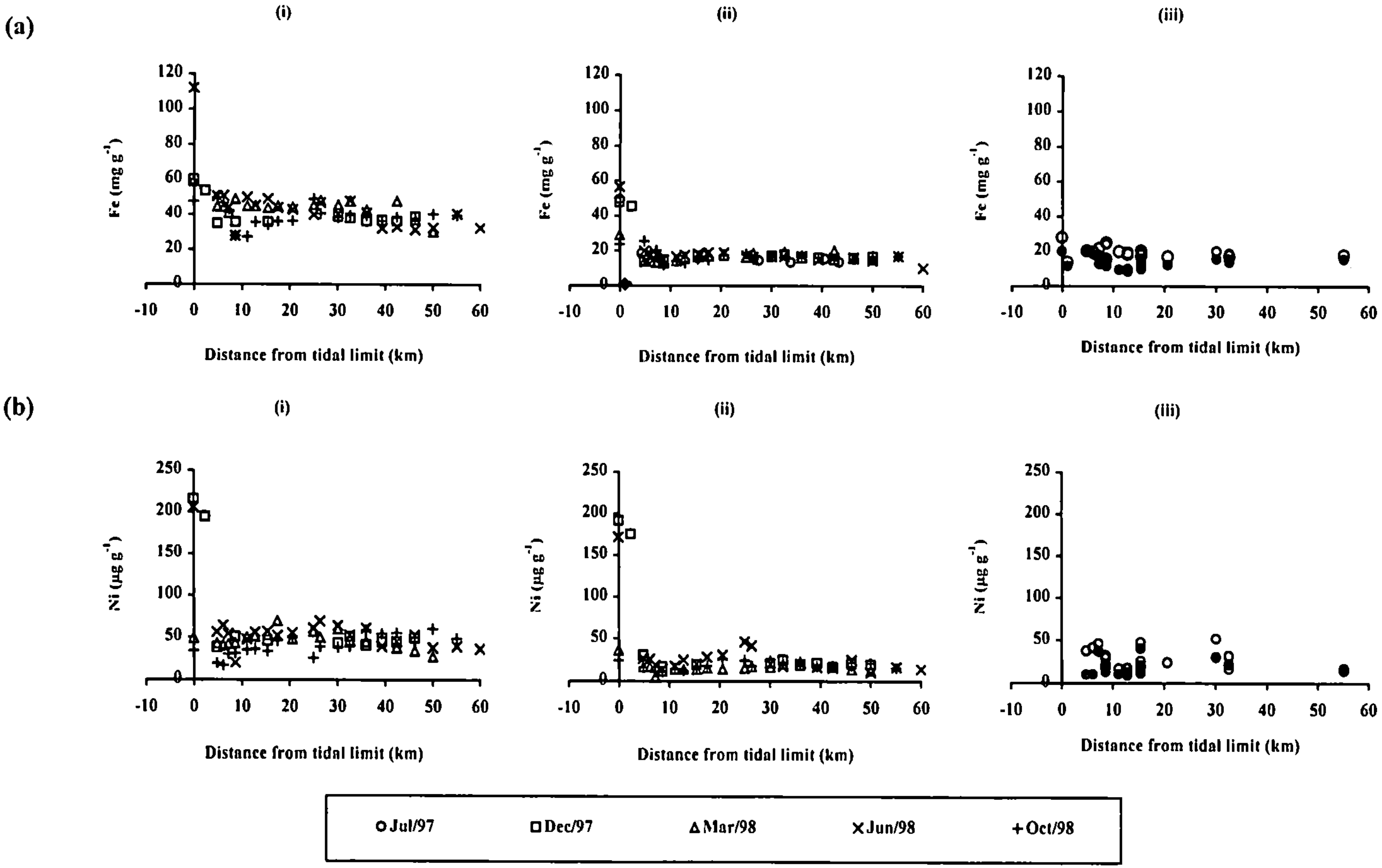


Figure 4.2 Concentrations of (a) Fe and (b) Ni available to (i) HF in bulk SPM, (ii) 1M HCl in bulk SPM and (iii) 1M HCl in PSPM (○) and TSPM (●) as a function of distance along the Mersey Estuary.

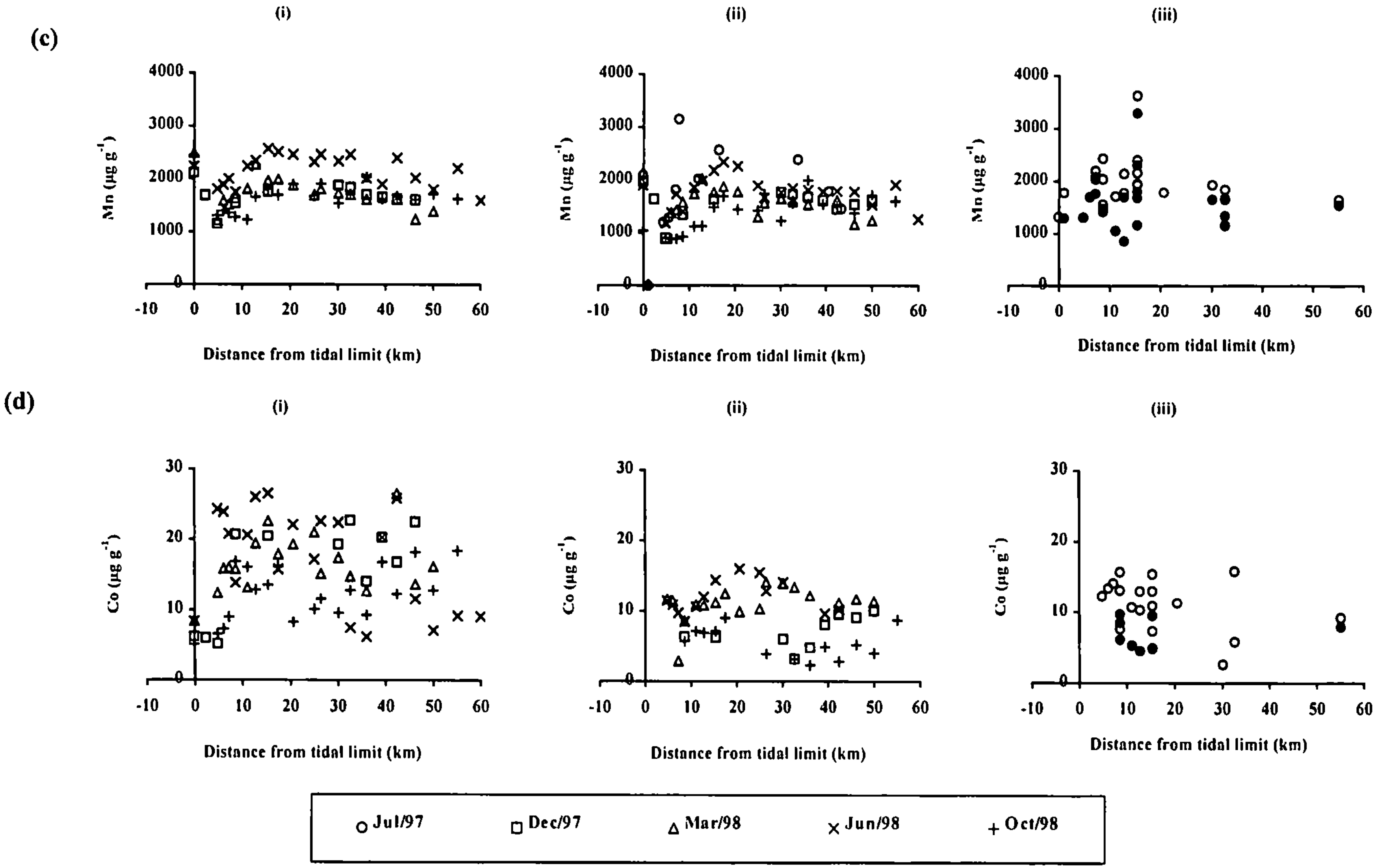


Figure 4.2 Concentrations of (c) Mn and (d) Co available to (i) HF in bulk SPM, (ii) 1M HCl in bulk SPM and (iii) 1M HCl in PSPM (○) and TSPM (●) as a function of distance along the Mersey Estuary.

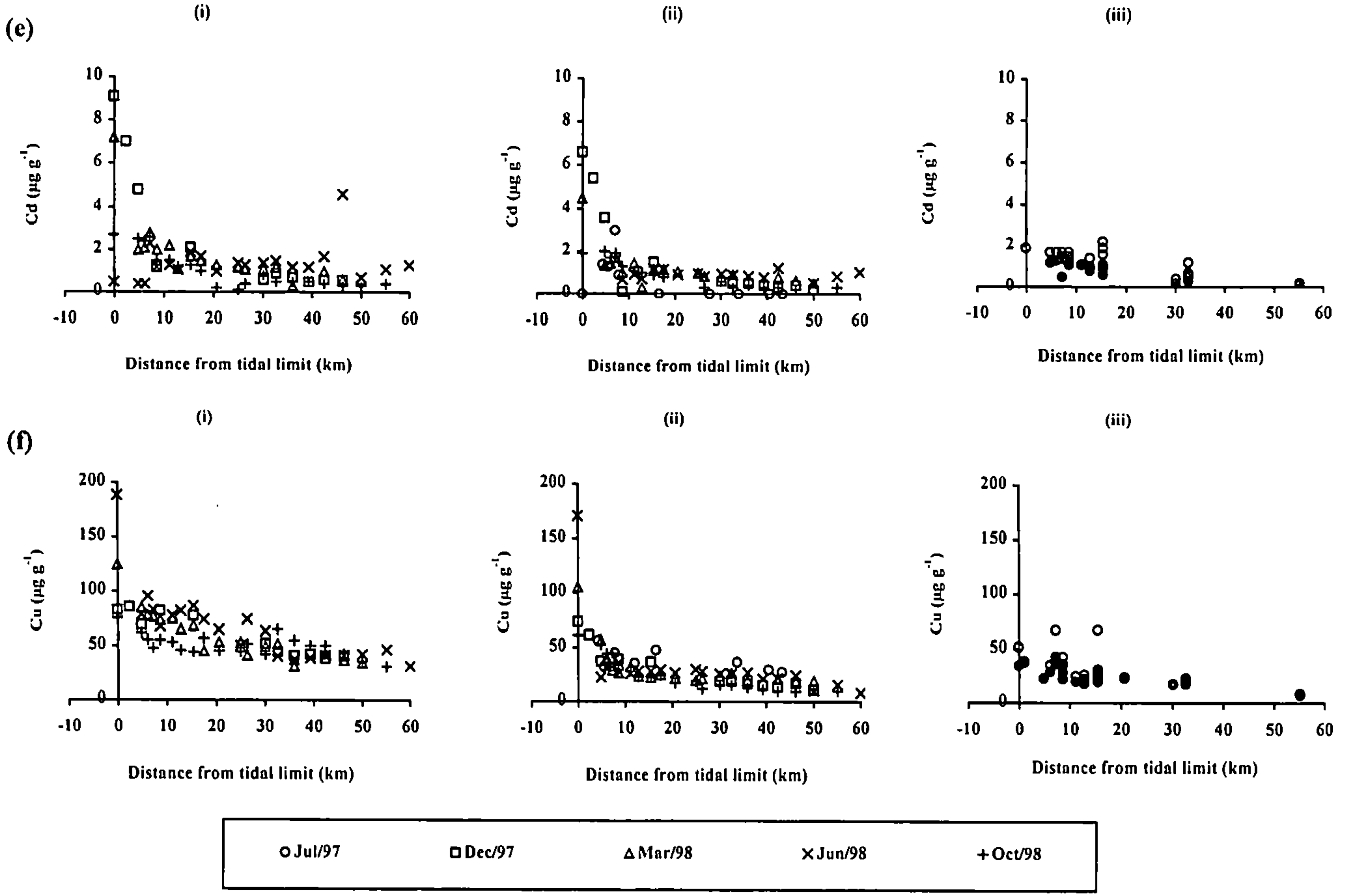


Figure 4.2 Concentrations of (e) Cd and (f) Cu available to (i) HF in bulk SPM, (ii) 1M HCl in bulk SPM and (iii) 1M HCl in PSPM (○) and TSPM (●) as a function of distance along the Mersey Estuary.

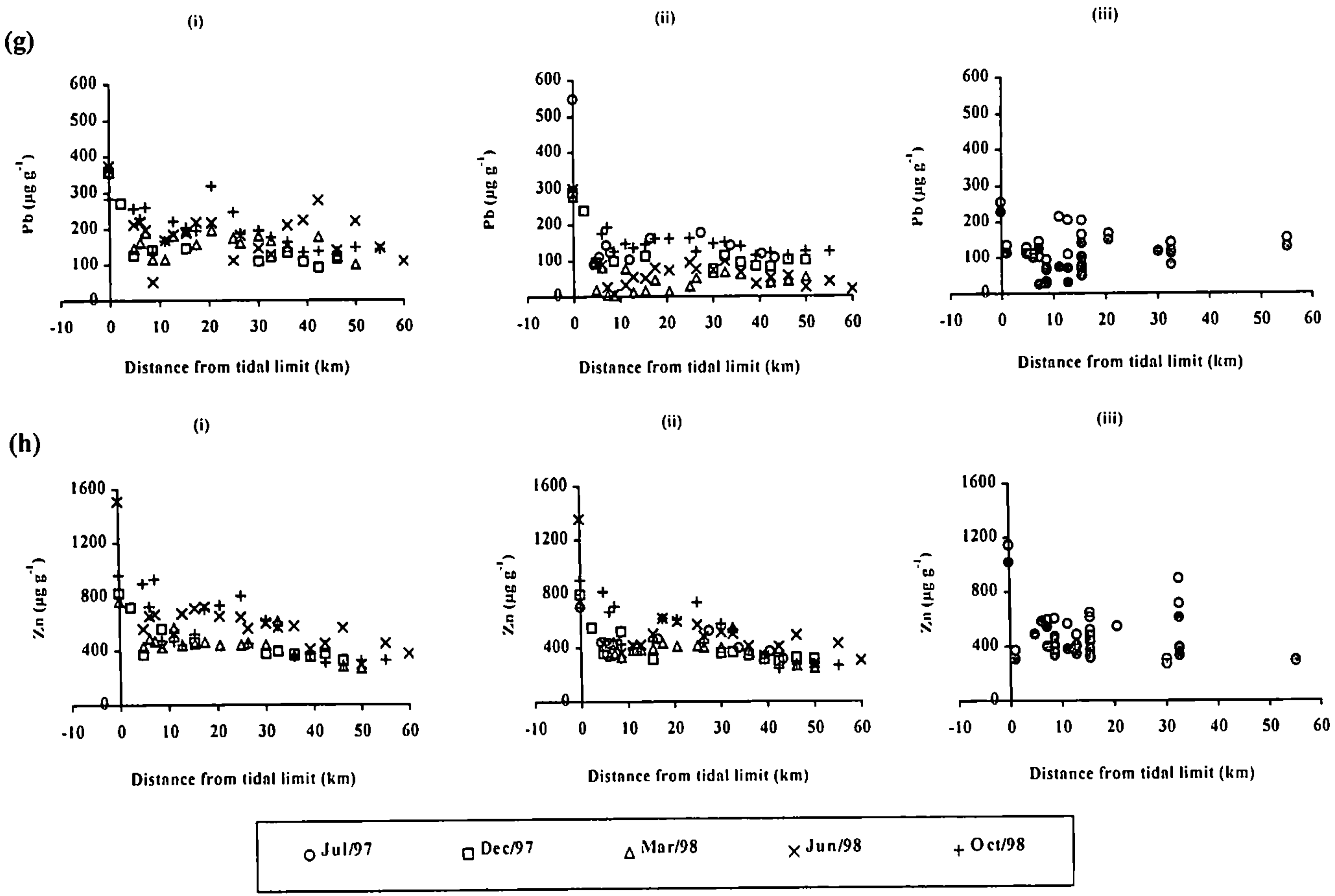


Figure 4.2 Concentrations of (g) Pb and (h) Zn available to (i) HF in bulk SPM, (ii) 1M HCl in bulk SPM and (iii) 1M HCl in PSPM (○) and TSPM (⊙) as a function of distance along the Mersey Estuary.

Approximately 35% of total Ni is removed from estuarine SPM by the HCl digest. Some seasonality is observed with total particulate Ni, as concentrations are elevated in the upper-mid estuary region in June 1998. Non-detrital Ni in settled SPM varies throughout the estuary, with concentrations in PSPM and TSPM generally becoming closer at higher turbidities and diverging when suspended solids loads are below around 300 mg l^{-1}. Nickel is undetectable in TSPM samples from low turbidity ($\leq$ 100 mg l^{-1}) water samples. Equivalence of Ni concentrations in the two settling fractions may imply that bed sediment concentrations of Ni are highest at these locations. Riverine concentrations of total particulate Ni range from 30-220 μg g^{-1} depending on flow conditions and variations in anthropogenic inputs into the River Mersey. As for Fe, an inverse relationship exists between river flow and particulate Ni concentrations, as dilution of point source Ni inputs becomes more effective with an increase in freshwater discharge. Inputs of nickel in the estuary originate from industrial sources (Campbell *et al.*, 1988) and are thought to be due to continuous and pulsed discharges occurring both above and below the weir in Warrington. One of the major inputs into the upper estuary located approximately 1.6 km from the tidal limit ceased in 1996 and other Ni-containing industrial effluents are now treated (P. Jones, Environment Agency, pers. comm.). Historic loading of Ni in upper estuary sediments may now be more important than direct anthropogenic loads of the metal, representing a reversal of the conclusions of previous studies conducted when industrial inputs were considerable (Campbell *et al.*, 1988).

In contrast, the particulate Mn profiles in Figure 4.2c do not show the same degree of uniformity as those observed for Fe and Ni. Concentrations of non-detrital Mn in SPM account for around 75% of the total concentration. Manganese is not usually regarded as a contaminant metal and the fact that three quarters are present in the non-detrital fraction infers that Mn in the Mersey is dominated by natural sources (Zhou *et al.*, 2003). In the vicinity of the TMZ, where DO levels are lower, some resuspension of slightly oxygen depleted bed sediments may cause reduction of Mn (IV) to Mn (II) which then enters the dissolved phase. As salinity increases and oxygenation increases, so suspended particulate Mn concentrations in bulk and settled SPM populations rise to form broad mid-estuarine maxima in waters of intermediate turbidity before declining again to those observed at the TMZ at stations in the lower estuary and beyond, into Liverpool Bay. This trend appears to be enhanced in July 1997 and June 1998 and is likely to be linked to the broad oxygen sag, which begins only a short distance in from the mouth (Figure 3.1d). Higher concentrations in mid-estuary could be due to tidal resuspension of bed sediments releasing Mn from porewaters which is then subject to oxidative precipitation onto the surface of SPM.

Cobalt is not included in the suite of metals routinely monitored by the Environment Agency and this study is the first known investigation of suspended particulate distributions of this element in the Mersey. Particulate Co (Figure 4.2d) appears to follow the same distribution patterns as those shown for Mn. Positive relationships have previously been established between the two metals in the Scheldt and Weser by Turner *et al.* (1991). Scavenging of Co with insoluble Mn (IV) under oxic conditions is released into sediment pore waters during reductive solubilisation of Mn (IV). Disturbance of sediments by strong tides encourages the injection of Co and Mn (II) into the water column, which are then concomitantly oxidised and adsorbed onto suspended particles. This phenomenon has also been implied in the distribution of suspended particulate Co in the Seine Estuary (Chiffoleau *et al.*, 1994). Concentrations of dissolved Co in the Mersey REM are an order of magnitude higher than those for other estuaries with a similar pollution history such as the Scheldt, which strongly suggests an anthropogenic source for Co in the tidal and non-tidal reaches of the Mersey (Martino, 2000). Particulate Co was only detected in REM suspended particles when these were digested with HF. Generally around 50% of total Co is removed by the weaker leach. A persistent and localised input occurs which is coincident with the TMZ and moves with the TMZ in response to variations in the volume of freshwater entering the estuary at Howley Weir. The highly variable Co concentrations observed in bulk SPM are repeated in the data for settled SPM. Differences in non-detrital concentrations in the separated populations were more apparent for this metal than all the others studied. Cobalt in PSPM was consistently greater than that in TSPM, which often contained undetected concentrations of non-detrital Co. However, at sites where bed sediments were dominated by fine-grained material and in the TMZ, Co concentrations in PSPM and TSPM are considerably closer.

Particulate Cd (Figure 4.2e) and Cu (Figure 4.2f) available to 1M HCl show significant declines in concentrations in suspended particles in the region of the TMZ. Turner *et al.* (1991) also noted co-distribution of the two metals in the Scheldt and Weser estuaries. Reduction in particulate Cd is most likely caused by complexation with chloride anions in seawater. As salinity increases, desorption of Cd is enhanced due to the formation of thermodynamically stable chloro-complexes with competing chloride ions from seawater. Peaks in the lower estuary may be due to contaminated particles entering from the Manchester Ship Canal. Chlorocomplexation also occurs as salinity rises for Cu and this is coupled with competition from Ca^{2+} and Mg^{2+} for active surface sites (Comans and Van Dijk, 1988) and this has previously been observed in the Mersey by Comber *et al.* (1995). The ability of both metals to form strong complexes with chloride ions is reflected in the fact that HCl is shown to remove the majority of apparently largely surface-bound Cd and Cu (up to 75% of the total metal content). After reaching waters of increasing salinity, the distributions of both metals generally become more uniform throughout the rest of the estuary. However, freshwater concentrations do change considerably with season and corresponding changes in river flow. For example, variations are seen for Cu, with higher concentrations occurring, especially for REM SPM, in July 1997 and March and June 1998. Copper has a high affinity for surface organic ligands (e.g. Paulson *et al.*, 1994). Changes in particulate Cu distributions along the salinity gradient may also result from solubilisation and pore water infusion due to the degradation and recycling of particulate organic matter (Church, 1986) and/or desorption from seaward-advected particles (Chiffoleau *et al.*, 1994).

Pb concentrations in SPM (Figure 4.2g) are not as seasonally independent as those for Fe and Ni or as exaggerated as those displayed by Mn and Co. Up to around two thirds of total Pb is available as non-detrital metal. A significant discharge of stable, water-soluble organic lead species is known to enter the estuary *via* the Manchester Ship Canal (Riley and Towner, 1984; NRA, 1995). Riley and Towner (1984) performed a dissolved Pb speciation study and found that highest estuarine concentrations of alkyl lead compounds occurred primarily near the Weaver Sluices, with a secondary source emitted from the lock gates at Eastham. Tetra-alkyl lead compounds are rapidly lost by both evaporation and hydrolysis. From the results of this study, it would appear that these locations are still experiencing some of the highest lead concentrations in the estuary. Further studies by Riley and Towner indicated that di- and tri-alkyl components were considerably less particle reactive than inorganic lead ions and proposed that the former compounds could form the bulk of dissolved lead species occurring within the mid and lower estuary. The predominant form of particulate lead is therefore thought to be inorganic, as rapid removal of dissolved inorganic lead ions has previously been demonstrated throughout the estuarine mixing zone (Riley and Towner, 1984). Lead concentrations in PSPM and TSPM are more similar than for the other metals discussed so far and this indicates that bed sediments are sufficiently contaminated with Pb that equivalent concentrations are sustained in both SPM types. Concentrations of Pb in bulk SPM from the outer estuary tend to agree with the findings of Laslett (1995).

Seasonal axial profiles for Zn (Figure 4.2h) are fairly analogous to those of most of the other metals. There are however, several small additional inputs, which tend to appear more exaggerated in June and October 1998. Zinc concentrations, like those for Cd and Pb, are again elevated slightly in the lower estuary and Liverpool Bay (at a distance of ~ 40 –

55 km) in June 1998. These data could be suggesting an offshore 'hot spot' for these three metals, possibly in the form of sewage outfalls, dumped sewage deposits or, alternatively, contaminated spoil from constant dredging of the navigation channels which is also dumped in Liverpool Bay (Norton *et al.*, 1984). Campbell *et al.* (1988) concluded that zinc in the estuary primarily arose from sewage inputs. Since 1988, improved sewage treatment combined with the reduced use of Zn in the plating industry have led to a decrease in the load of anthropogenic zinc (NRA, 1995). Variations in the distribution of Zn are now thought to result from current effluents being advected upestuary by strong incoming tides or salinity-induced desorption from SPM. Historical metal burdens in deposited sediments may be released by desorption from resuspending sediments and possibly by the injection of metal-rich porewaters into the overlying water column. The resulting dissolved Zn is then either adsorbed onto SPM that is relatively depleted in Zn or remains freely in solution. Up to 65% of total Zn present in SPM is leached by 1M HCl. As for Pb, Zn concentrations in PSPM and TSPM appear to correspond more closely than for some of the other metals which again implies considerable enrichment of this element in bed sediments.

Metals data obtained from the analysis of settled SPM are quite ambiguous and difficult to interpret from the plots in Figure 4.2. Apart from Co (and possibly Mn), non-detrital metal concentrations do not reveal any obvious differences in geochemical reactivity between the two particle types. To investigate this further, the data have been statistically re-evaluated by means of a two-tailed t-test (assuming unequal variances), the results of which are given in Table 4.2. Statistical analyses, performed at the 95% confidence level, indicate that calculated values of t are greater than critical values of t for Cd, Co, Fe, Mn, Ni and Pb.

Table 4.2 Metal concentrations (mean ± 1σ) in PSPM and TSPM and t-test results where $p = 0.05$. Concentrations are in µg g^{-1} except for Fe (mg g^{-1}), v = degrees of freedom, t_{calc} = calculated values of t, t_{crit} = critical values of t.

Metal	v	PSPM	TSPM	t_{calc}	t_{crit}
Cd	36	1.32 ± 0.53	0.84 ± 0.42	3.13	2.03
Co	34	11.2 ± 3.6	3.4 ± 3.8	6.33	2.03
Cu	38	30.7 ± 14.9	24.2 ± 9.7	1.76	2.02
Fe	44	19.3 ± 3.1	14.1 ± 3.1	5.64	2.02
Mn	41	1915 ± 497	1460 ± 671	2.61	2.02
Ni	36	28.0 ± 11.8	15.8 ± 11.4	3.22	2.03
Pb	44	134 ± 53	93 ± 48	2.73	2.02
Zn	44	529 ± 196	419 ± 181	1.96	2.02

Therefore, concentrations of these metals in PSPM and TSPM are significantly different. This pattern reinforces the concept of permanently suspended particles having a greater adsorptive capacity for trace metals than those only temporarily in suspension (e.g. Williams and Millward, 1998; Liu, 1996; Liu *et al.*, 1998). The same trend does not hold for Cu and Zn, which show a lack of distinction between the two sub-populations of SPM. Where bed sediments are substantially enriched with metals, concentrations in resuspending particles approach those determined in seaward-fluxing particles. Further evidence for this may be provided in Figure 4.1f and Figure 4.1h, with higher concentrations in the > 63 μm fraction being recorded more consistently for Cu and Zn throughout the estuary than for the other metals under scrutiny here. The fact that distributions of particulate metals in the settled fractions reflect those of the bulk suspended population, indicates that independent measurement of trace metals in separated SPM fractions is both procedurally and analytically viable.

Settling experiments were used to simulate natural physical processes in the TMZ. The proportion of PSPM in each undifferentiated (bulk) SPM sample used for settling was calculated from the established concentrations of particles in the TSPM and PSPM fractions and these results are presented graphically in Figure 4.3. A clear and statistically significant ($n = 23$, $P \leq 0.0005$) inverse relationship exists between PSPM concentration and total suspended solids concentration. At low SPM loads PSPM predominates, accounting for around 80% of all suspended particles. As turbidity increases, TSPM becomes the major component due to the increasing occurrence of tidal disturbance of bed sediment and the amount of PSPM correspondingly falls to around 30% of the total suspended particle population. These results support the findings of Duinker (1983), Bale *et al.* (1990) and Williams and Millward (1998). It appears that PSPM could comprise the major constituent of SPM in the middle-lower reaches of the estuary where suspended solids concentrations are consistently around 200 mg l^{-1} (Figure 3.3b) and this is adequately demonstrated in Figure 4.4. Here, concentrations of PSPM and TSPM have been estimated for all stations sampled using the regression equation in Figure 4.3 and known concentrations of the total suspended solids load. Figure 4.4 shows that axial changes in the concentrations of the two SPM populations reflect the distribution of fine-grained bed sediments in the estuary (Figure 3.7) as well as relative changes in the magnitude of tidal and freshwater inflows (refer to Table 2.1 for river flows and tidal ranges for the respective surveys).

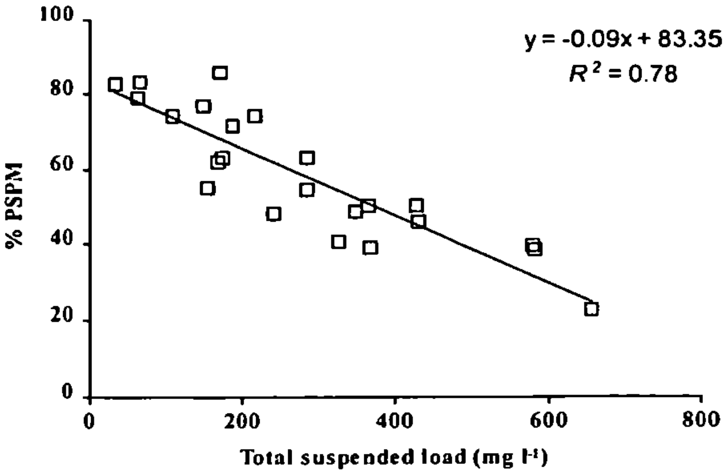
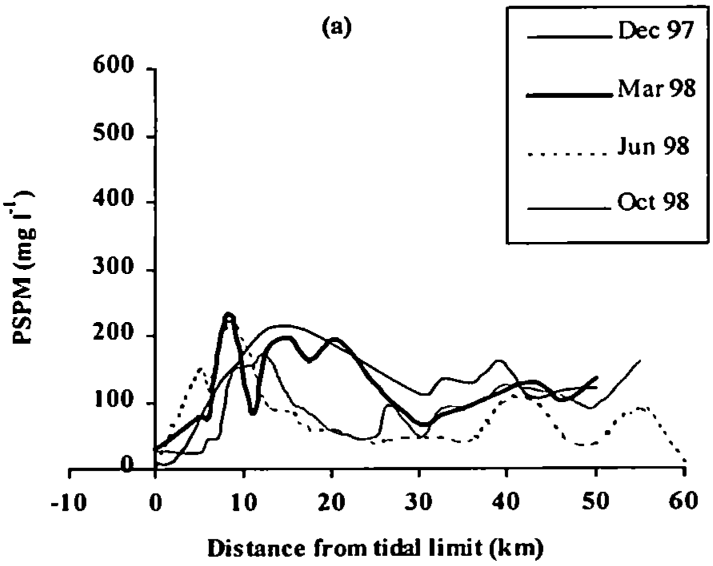


Figure 4.3 Variation in the proportion of PSPM with total suspended solids load.



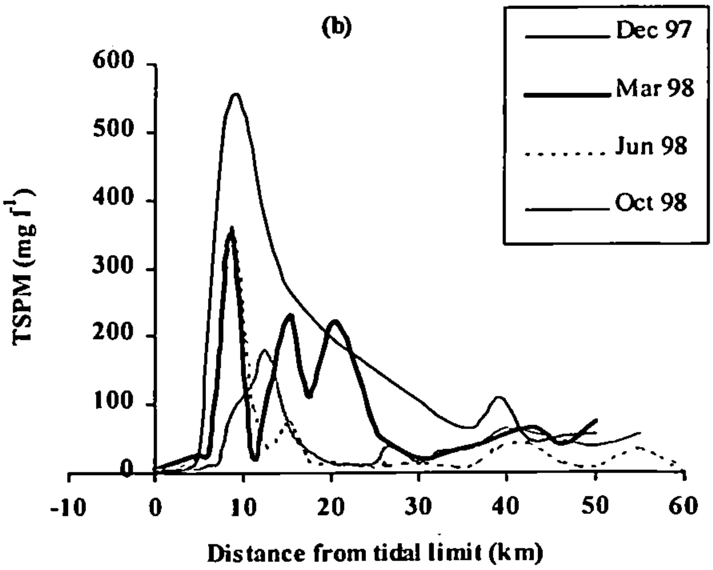


Figure 4.4 Variation in the concentration of (a) PSPM and (b) TSPM with distance along the estuary.

Assuming that the concentrations of particulate trace metals in the bulk SPM are only a consequence of the mixing of PSPM with TSPM, the data has been fitted using the particle mixing model in Equation 4.1:

$$[Me_E]=\left[\frac{[Me_{TSPM}]*\%TSPM+[Me_{PSPM}]*\%PSPM}{\%TSPM+\%PSPM}\right] \qquad \text{Equation 4.1}$$

where Me_E is the predicted concentration in whole SPM; Me_{TSPM} is the concentration of metal in TSPM; Me_{PSPM} is the concentration of metal in PSPM and % TSPM and % PSPM are the relative proportions of settled SPM components. Measured concentrations have been plotted against those predicted by the equation above in Figure 4.5. Regression statistics are provided in Table 4.3.

Table 4.3 Regression analyses of the data in Figure 4.5, where v = degrees of freedom.

Metal	v	Slope	Intercept	R^2	P
Fe	21	1.02 ± 0.14	-0.30 ± 2.41	0.71	≤ 0.0005
Ni	17	1.23 ± 0.44	1.22 ± 8.48	0.31	≤ 0.01
Mn	21	0.86 ± 0.14	338 ± 236	0.64	≤ 0.0005
Co	15	0.62 ± 0.18	2.80 ± 1.68	0.44	≤ 0.005
Cd	18	0.80 ± 0.14	0.21 ± 0.17	0.66	≤ 0.0005
Cu	21	0.85 ± 0.09	2.46 ± 2.88	0.81	≤ 0.0005
Pb	21	0.93 ± 0.13	5.06 ± 33.9	0.72	≤ 0.0005
Zn	21	1.23 ± 0.18	-53.0 ± 80.4	0.70	≤ 0.0005

Application of the mixing equation seems to have worked reasonably well in predicting the observed particulate metal concentrations in bulk SPM, producing statistically significant regression coefficients in the range 0.31 – 0.81. Theoretically, a perfect relationship between calculated and observed concentrations would pass though the origin and produce a gradient of 1. Errors on the gradients and intercepts indicate substantial variability in these parameters, the degree of which varies considerably between metals. However, overall, concentrations of metals in PSPM and TSPM can be used fairly successfully to predict metal contents in the total suspended particle population. Interestingly, this method works for Cu and Zn, despite the fact that mean concentrations of these two metals were not shown previously to differ significantly in PSPM and TSPM (Table 4.2). Predictions of particulate Co and Ni by this method were also significant, but significance was slightly reduced due to the fact that several TSPM samples had concentrations of Co and Ni below the limits of detection. Particle-water interactions are not accounted for in the particle mixing model. The extent of sorption processes (affected by axial and temporal changes in particulate or water chemistry) will affect the observed trace metal concentrations and this may account for some of the deviations shown between observed and predicted data.

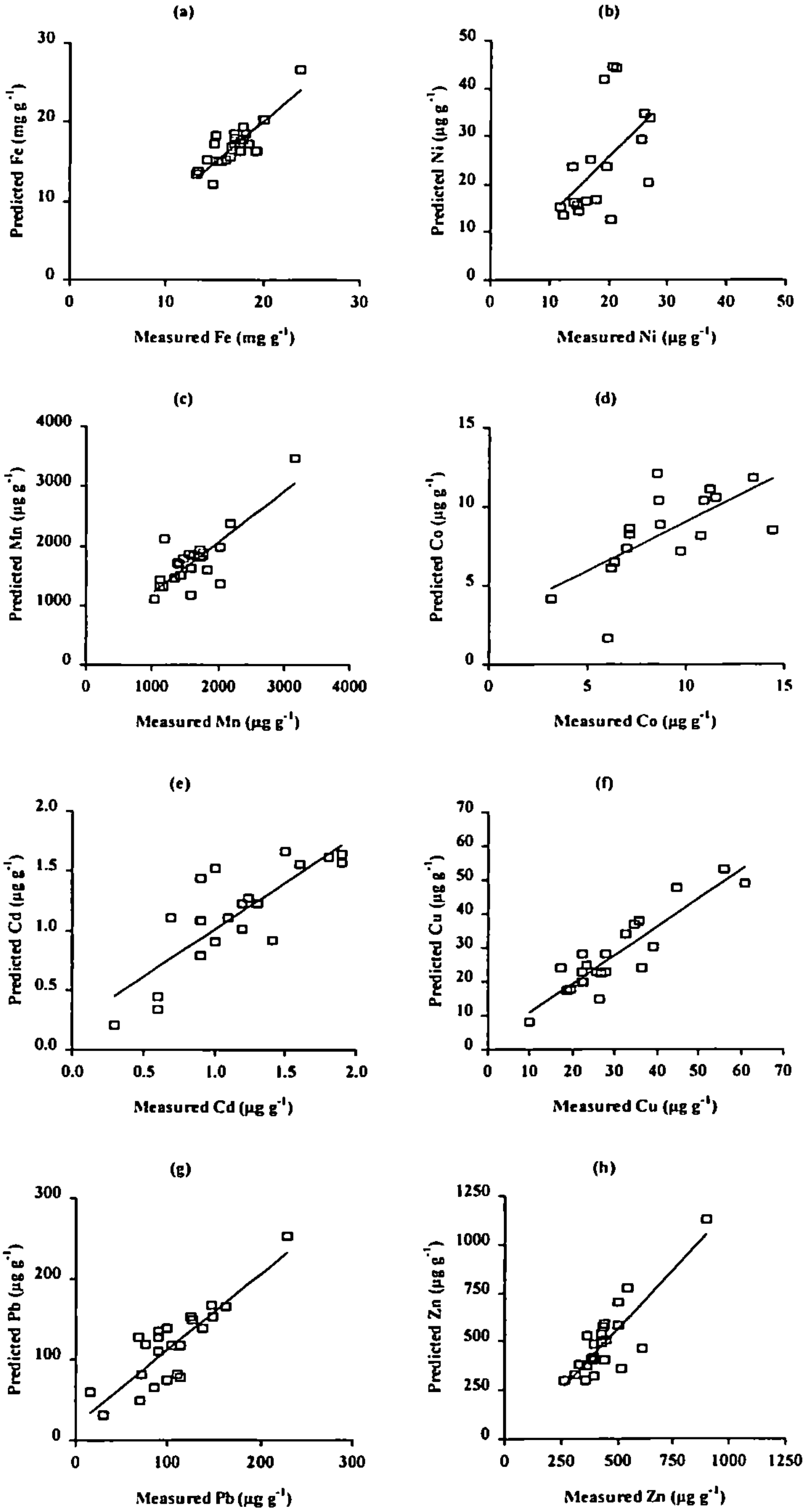


Figure 4.5 Observed *vs.* predicted non-detrital concentrations (available to 1M HCl) of (a) Fe, (b) Ni, (c) Mn, (d) Co, (e) Cd, (f) Cu, (g) Pb and (h) Zn in bulk SPM.

The relatively constant concentrations observed in the axial distributions of some of the trace metals studied indicate that the lower 45 km of the estuary are well-mixed, due to strong tidal transport, in turn leading to a complete re-dispersal of suspended particles and their associated metals throughout the estuary. Uniform suspended particulate trace metal concentrations have also been observed in the Gironde Estuary by Kraepiel *et al.* (1997) and were thought to result from a particle residence time in excess of 12 months. This was supported by the reduced organic carbon contents of the particles compared to those from the REM, indicating that estuarine particles were oxidised and therefore aged. Similarly, this work has already demonstrated (Table 3.3, Section 3.4.2) that the mean POC content of estuarine SPM is 1.35% (w/w), which is around half that associated with riverine SPM (1.79 - 3.54%, mean = 2.70%). In addition, POC in SPM varies only by around 2.5% throughout the mixing zone and between ~ 35 - 60% of riverine POC is mineralised in the estuary. This collective evidence suggests that, as with the Gironde, SPM in the Mersey Estuary is also aged.

The 1M HCl digest used in this study probably over-estimates the concentrations of exchangeable metals and therefore gives an upper limit to the amount of desorbable metal that could be contributed to the dissolved phase. However, it is presupposed that both chemically and biologically available fractions are present in the resulting analyte solutions (Luoma and Bryan, 1981; Turner and Millward, 2000). Concentrations of non-detrital trace metals in Mersey Estuary SPM are compared to those from two other estuaries in Table 4.4. As discussed previously, seasonality in trace metal distributions in Mersey SPM are linked to variations in fluvial flow and biogeochemical processes affected by seasonal fluctuations in pH, DO and carbon availability. For example, co-precipitation of Co and Mn on SPM becomes elevated in the presence of an oxygen sag (Zwolsman and van Eck, 1999) and additional metals may become available in the dissolved phase after being released from organic detritus by bacterial oxidation and sediment mobilisation. The data for Cu associated with Mersey SPM suggests that Cu may be strongly complexed with POC as estuarine Cu concentrations hardly vary during the year. Investigations into relationships between metals and POC have been made in this work and are reported later in Section 4.2.2. Concentrations of non-detrital Mn are higher in the Mersey than in the Humber and Thames, possibly indicating the effect of successful reoxygenation of the Mersey in recent years. This concurs with the findings of Zwolsman and van Eck (1999) where gradual reoxygenation of the Scheldt produced a doubling in the Mn content of fluvial SPM between the early 1970s and mid 1990s. Particulate Mn has also increased in the Thames in response to long-term improvements in water quality (Section 1.3.2). Non-

Table 4.4 Mean non-detrital trace metal concentrations (available to 1M HCl) in SPM from three UK estuaries. Concentrations are in μg g^{-1} (dry wt.) except for Fe (mg g^{-1}).

Site	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Humber Estuary, winter[a]	-	-	32	36.1	1020	-	102	177
Humber Estuary, spring[a]	-	-	34	33.0	1480	-	104	275
Humber Estuary, summer[a]	-	-	62	24.6	1280	-	81	270
Mersey Estuary, winter	1.2	7.0	26	18.8	1530	35	109	369
Mersey Estuary, spring	1.0	11.1	26	16.2	1530	15	40	381
Mersey Estuary, summer	0.98	12.0	29	16.4	1830	23	81	436
Thames Estuary, winter[a]	-	-	51	22.8	697	-	143	165

[a] Sampling performed near the mouth of the Humber Estuary (S>30) and in the lower Thames Estuary (S>20) (Turner and Millward, 2000).

detrital Zn in the Mersey is considerably higher than in the other two estuaries however, and this implies that bed sediments in the Mersey may be retaining this metal as inputs of Zn have dramatically reduced in the last 20 years. Equivalent concentrations of Pb are observed between Mersey and Humber SPM, whilst suspended particulate Fe in the Mersey is intermediate between that of the Thames and Humber.

4.2 Geochemical controls on trace metal reactivity

4.2.1 Metal-metal relationships in Mersey Estuary particles

The majority of trace metals tend to be adsorbed to or occluded within hydrogenous and biogenic coatings on natural particle surfaces (Turner *et al.*, 1991; Thomas and Bendell-Young, 1999; Dong *et al.*, 2003). Iron and manganese oxyhydroxides are often significant in this respect as they have high adsorptive capacities. Additionally, repeated cycles of oxide dissolution and precipitation reduce their crystallinity and thus aid the incorporation of metal ions (Chao, 1984). Turner (2000) surmised that intra-estuarine variations in Fe and Mn concentrations are a reflectance of local alterations in redox conditions and the hydraulic sorting of sediments. Inter-estuarine differences could be explained by the presence of different industrial activities, catchment geologies, pH and E_h conditions (the latter affecting Fe and Mn oxide precipitation rates). Following work performed by Turner (2000), regression analyses have been applied to Mersey sediment and bulk SPM data to allow exploration of the role of Fe and Mn in regulating contaminant metal concentrations. If the trace metal concentration, Me, is controlled by the concentration of either Fe or Mn, then the data follows one of the following equations:

$$[\mathrm{Me}] = a[\mathrm{Fe}] + c \qquad \text{Equation 4.2a}$$

$$[\mathrm{Me}] = a[\mathrm{Mn}] + c \qquad \text{Equation 4.2b}$$

where a and c are constants. Alternatively, if accumulation of trace metals is controlled by Fe and Mn acting synergistically, and effects of the two host phases are independent of their relative contributions by mass, then metal data can be defined thus:

$$[\mathrm{Me}] = a[\mathrm{Fe}] + b[\mathrm{Mn}] + c \qquad \text{Equation 4.3}$$

Models according to Equations 4.2 and 4.3 were tested against metals data for Mersey < 63 μm sediments and bulk SPM using single and multiple regression analyses respectively, and the results are reported in Table 4.5. Iron appears to be the significant oxidic phase for Cu in fine-grained sediments, whilst both Cu and Zn show a more marked dependence on Fe when it is present in combination with Mn. Close associations between Cu and Zn in fine-grained sediments from a variety of estuaries have previously been reported by Turner (2000). In the same work it was found that Fe was the dominant phase for both Cu and Zn in sediments of the Mersey. Results from the present study would tend to agree with this observation for Cu but not for Zn, which may possibly be explained by the fact that different digests have been used in the two investigations. Weaker correlations, especially for Pb and Zn, suggest that the impacts of diagenetic release or anthropogenic discharges are buffered by the dispersion of fine-grained sediments by energetic tidal stirring. For bulk SPM, significant relationships are produced for all metals with Fe whilst Mn is only implicated in the uptake of Ni onto suspended particles. The application of Equation 4.3 to SPM and sediment data improved the significance of the fits in almost all cases (seen as an increase in R^2) and a complex interplay between Fe and Mn in the regulation of contaminant metal concentrations is implied. However, it should be noted that although many of the relationships in Table 4.5 are statistically significant, they explain little of the variability, as indicated by the estimated errors on the gradients and intercepts of the individual regression lines.

Table 4.5 Results of regression analyses of trace metal concentration *versus* Fe or Mn (Equation 4.2) or Fe and Mn (Equation 4.3) for < 63 µm sediments and bulk SPM from the Mersey Estuary. *P* values are given where estimates are statistically significant.

Substrate / metal		**Equation 4.2a**				**Equation 4.2b**				**Equation 4.3**				
	n	*a*	*c*	R^2	*P*	*a*	*c*	R^2	*P*	*A*	*b*	*c*	R^2	*P*
< 63 µm sediments														
Cd	4	-0.0000504 ± 0.000175	2.59 ± 2.14	0.05		0.00362 ± 0.00383	-1.61 ± 3.76	0.31		0.00388 ± 0.00510	$-7.59 \times 10^{-5} \pm 1.98 \times 10^{-4}$	-0.959 ± 5.25	0.40	
Co	4	-0.00146 ± 0.00107	31.7 ± 13.2	0.48		-0.00859 ± 0.0378	22.6 ± 37.1	0.03		-0.00359 ± 0.0392	-0.00144 ± 0.00153	35.0 ± 40.4	0.48	
Cu	15	0.00402 ± 0.00199	-5.81 ± 28.0	0.24	**≤ 0.05**	-0.0145 ± 0.0169	66.2 ± 19.9	0.05		-0.0369 ± 0.0143	0.00629 ± 0.00188	4.53 ± 23.7	0.51	**≤ 0.005**
Ni	4	-0.000496 ± 0.000887	63.1 ± 10.9	0.14		-0.0271 ± 0.0153	83.7 ± 15.0	0.61		-0.0259 ± 0.0197	-0.000360 ± 0.000767	86.8 ± 20.3	0.68	
Pb	15	0.000939 ± 0.0277	292 ± 390	0.00		-0.171 ± 0.205	499 ± 242	0.05		-0.224 ± 0.240	0.0147 ± 0.0315	355 ± 398	0.07	
Zn	15	0.0117 ± 0.0105	258 ± 148	0.09		-0.0764 ± 0.0808	506 ± 95.0	0.06		-0.151 ± 0.0833	0.0210 ± 0.0110	300 ± 138	0.28	**≤ 0.025**
SPM														
Cd	69	0.153 ± 0.0157	-1.48 ± 0.289	0.59	**≤ 0.0005**	-0.000432 ± 0.000358	1.28 ± 0.589	0.01		-0.000356 ± 0.000229	0.157 ± 0.0156	-0.971 ± 0.436	0.60	**≤ 0.0005**
Co	52	0.718 ± 0.280	-2.51 ± 4.60	0.12	**≤ 0.01**	0.00273 ± 0.00175	4.85 ± 2.81	0.05		0.000822 ± 0.00195	0.651 ± 0.324	-2.72 ± 4.66	0.12	**≤ 0.01**
Cu	80	2.47 ± 0.236	-14.5 ± 4.53	0.58	**≤ 0.0005**	0.00537 ± 0.00635	21.2 ± 10.5	0.01		-0.000137 ± 0.00417	2.47 ± 0.239	-14.3 ± 7.68	0.58	**≤ 0.0005**
Ni	70	4.21 ± 0.202	-50.3 ± 3.96	0.87	**≤ 0.0005**	0.0228 ± 0.0119	-9.62 ± 19.2	0.05	**≤ 0.05**	0.00140 ± 0.00466	4.20 ± 0.209	-52.2 ± 7.61	0.87	**≤ 0.0005**
Pb	81	7.76 ± 0.796	-36.3 ± 15.8	0.55	**≤ 0.0005**	0.0141 ± 0.0228	83.2 ± 38.0	0.01		-0.0124 ± 0.0157	7.88 ± 0.810	-18.2 ± 27.8	0.55	**≤ 0.0005**
Zn	81	15.6 ± 1.74	167 ± 34.7	0.50	**≤ 0.0005**	0.0214 ± 0.0478	418 ± 79.7	0.00		-0.0322 ± 0.0343	15.9 ± 1.77	214 ± 61	0.51	**≤ 0.0005**

Several difficulties arise in the assessment of metal contamination of marine and estuarine sediments. These include the choice of extraction technique, adjustments for grain size effects, the presence of a natural background concentration and inconsistencies in analytical procedures (Grant and Middleton, 1990; Clifton *et al.*, 1999). Additionally, the choice of sites and methods for sample collection should be carefully considered in order to achieve the selection of samples that are truly representative of that area (Mudge *et al.*, 2001).

Grain size effects may be reduced by normalising concentrations to those of an element that is abundant in a range of minerals having different granular and textural forms and which should not be anthropogenically altered. Constituents commonly used for this purpose are Al, K and Fe (Loring, 1991), Cs (Ackermann, 1980) and Li (Loring, 1990) although other elements such as Co may be substituted if more appropriate to the study site (Matthai and Birch, 2001). Another example of this is provided by Grant and Middleton (1990, 1993) using Rb as a grain size proxy in place of Al, Fe and Ti which are all contaminants in the Humber Estuary.

The effects of sediment granulometry can alternatively be accounted for by sieving the sample prior to metal analysis. Subsequent calculation of metal contents is then possible by normalising values with respect to an averaged grain size distribution. For the Mersey, a mean estuarine value of 40% silt content (w/w) has been ascribed by previous researchers (Taylor, 1986; Harland and Riddle, 1997; Harland *et al.*, 2000). This value has been subsequently confirmed by both this study and laser particle size determinations performed by the Environment Agency for surface sediments collected in July 2000 which produced a mean value of 41.2% silt (EA, unpublished data). The following discussion of sediment trace metal concentrations therefore refers to data normalised to 40% silt. Relationships between metals have been explored for the two bed sediment surveys in this study and the findings are pooled and presented in Table 4.6.

Higher regression coefficients are reported for Fe with Cu, Pb and Zn and for Mn with Cu and Zn in Table 4.6 than those given in Table 4.5. This implies that > 63 μm particles supply an important contribution of these metals in bed sediments. Other evidence of this has previously been given in Figure 4.1, where concentrations of Cu, Pb and Zn in coarse-grained sediments exceeded those in the fine-grained material. Analysis of the data in Table 4.6 suggests that Fe could be the main carrier for Pb and Cu. Zinc appears to be equally associated with both oxide phases. Common anthropogenic sources may be indicated for Pb with both Cd and Cu whilst the negative R^2 value produced between Zn and Ni negates a common input for these two metals.

Table 4.6 Correlation matrix indicating only significant R^2 values ($P \leq 0.025$, n = 16 for Cd, Cu, Fe, Mn, Pb and Zn, n = 4 for Co and Ni) for 1M HCl digestion of Mersey Estuary surface sediments. Sediments have been normalised to 40% silt content. The figure in bold denotes an inverse relationship.

	Cd	**Co**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Cd	*							
Co		*						
Cu			*					
Fe			0.77	*				
Mn			0.28	0.37	*			
Ni						*		
Pb	0.56		0.38	0.32			*	
Zn				0.35	0.36	**0.96**		*

Statistically significant contaminant metal relationships in bulk SPM are similarly reported in Table 4.7. Data for Fe and Mn are omitted as these have already been displayed in Table 4.5. A larger number of significant associations are observed in SPM than in bed sediments which will be due in part to the larger sample size for SPM samples. However, some of these relationships may also be due to geochemical modification of estuarine particles.

Table 4.7 Correlation matrix indicating only significant R^2 values ($P \leq 0.0005$, n = 71 for values involving Co and Ni, n = 82 for all other metal combinations) for 1M HCl digestion of Mersey Estuary bulk SPM.

	Cd	**Co**	**Cu**	**Ni**	**Pb**	**Zn**
Cd	*					
Co		*				
Cu	0.47		*			
Ni	0.58		0.44	*		
Pb			0.35	0.37	*	
Zn	0.21	0.16	0.58	0.33	0.38	*

This is strongly suggested for Ni and Zn for example, which have an inverse association in bed sediments but a positive one in SPM. For this and other metal combinations, trace metal binding to POC may be more significant in sediments whilst reduced POC and proportionately more Fe and Mn in suspended particles means that trace metals would tend to bind instead with oxidic phases in SPM.

4.2.2 Metal-POC relationships in Mersey Estuary particles

As with Fe and Mn in the previous section, if the amount of POC present in the particulate phase is involved in the regulation of trace metal concentrations, the following equation can be used:

$$[\mathrm{Me}] = a[\mathrm{POC}] + c \qquad \text{Equation 4.4}$$

Corresponding data describing relationships between metals and particulate organic carbon are provided in Table 4.8. Data are shown for regressions of POC% (w/w) against metal concentrations determined by extraction with 1M HCl for a limited number of sediments collected in July 1999 and bulk SPM sampled in March, June and October 1998. Rather than pooling the data for SPM, separate analyses have been performed for each survey. This has been done in order to try and establish whether or not seasonal differences in sources of POC to the estuary (Section 3.4.2) have any impact on the amount of non-detrital metal adsorbed to suspended particles.

As reported earlier for the analyses of Fe, Mn and Fe+Mn against the other metals (Table 4.5), there is a considerable amount of scatter in the data in Table 4.8 as indicated by the errors estimated for a (the gradient) and c (the intercept) for each regression line. Despite this, and also the fact that only four sediments were co-analysed for metals and POC in July 1999, positive and statistically significant relationships are produced between POC and Cu, POC and Fe and also POC with Pb. The statistical data produced for SPM display even greater variability than that for bed sediments and no clear patterns can be discerned. The relationship between POC and Co in March 1998 is significant but the negative gradient indicates that this is an inverse one, with Co concentrations declining in SPM as POC content increases. The same trend occurs for Co and POC in June 1998 but is more marked than in the earlier survey. Copper on the other hand, is shown to co-vary positively with POC at this time and has the same degree of significance as POC-Co. Particulate organic carbon and Cu were also shown to be positively correlated in Weser SPM by Turner *et al.* (1991). Significant co-associations are also produced in October 1998 between Co, Fe, Ni, Pb and Zn with POC, but with the exception of POC-Co, the relationships are all negative.

Table 4.8 Results of regression analyses of non-detrital (available to 1M HCl) trace metal concentration *versus* particulate organic carbon (Equation 4.4) for < 63 µm sediments and bulk SPM from the Mersey Estuary. *P* values are given where estimates are statistically significant.

		Equation 4.4			
Substrate/ metal	**n**	***a***	***c***	***R²***	***P***
< 63 µm sediments July 1999					
Cd	4	-0.07 ± 0.47	2.12 ± 1.33	0.01	
Co	4	-4.24 ± 2.51	25.6 ± 7.15	0.59	
Cu	4	23.3 ± 2.88	-14.0 ± 8.20	0.97	**≤ 0.01**
Fe	4	2.62 ± 0.22	5.01 ± 0.62	0.99	**≤ 0.005**
Mn	4	18.7 ± 71.2	927 ± 202	0.03	
Ni	4	-1.64 ± 2.23	61.5 ± 6.34	0.21	
Pb	4	219 ± 22.9	69.8 ± 65.2	0.98	**≤ 0.005**
Zn	4	5.62 ± 23.0	312 ± 65.5	0.03	
SPM March 1998					
Cd	17	0.15 ± 0.24	0.73 ± 0.36	0.03	
Co	17	-2.55 ± 1.22	14.8 ± 1.88	0.22	**≤ 0.05**
Cu	17	-1.60 ± 5.25	28.5 ± 8.07	0.01	
Fe	17	-1.14 ± 1.07	17.9 ± 1.65	0.07	
Mn	17	-32.4 ± 155	1579 ± 239	0.00	
Ni	17	-2.08 ± 2.06	18.4 ± 3.17	0.06	
Pb	17	-19.7 ± 13.2	69.0 ± 20.3	0.13	
Zn	17	-34.0 ± 35.0	431 ± 53.8	0.06	
SPM June 1998					
Cd	17	-0.09 ± 0.35	1.19 ± 0.38	0.00	
Co	13	-3.70 ± 1.00	16.4 ± 1.28	0.55	**≤ 0.005**
Cu	19	8.75 ± 2.69	16.5 ± 3.01	0.38	**≤ 0.005**
Fe	19	1.50 ± 0.94	15.2 ± 1.06	0.13	
Mn	19	-84.7 ± 152	1843 ± 171	0.02	
Ni	19	-3.91 ± 4.38	27.1 ± 4.90	0.04	
Pb	19	-17.1 ± 13.0	75.7 ± 14.5	0.09	
Zn	19	-22.3 ± 43.9	472 ± 49.2	0.01	
SPM October 1998					
Cd	16	-0.30 ± 0.38	1.13 ± 0.39	0.04	
Co	13	2.85 ± 1.56	2.32 ± 1.79	0.23	**≤ 0.05**
Cu	19	-6.36 ± 7.49	27.3 ± 7.47	0.04	
Fe	19	-3.95 ± 1.38	20.4 ± 1.38	0.32	**≤ 0.01**
Mn	19	46.2 ± 192	1331 ± 191	0.00	
Ni	18	-5.92 ± 2.45	23.4 ± 2.50	0.27	**≤ 0.025**
Pb	19	-26.9 ± 14.1	172 ± 14.0	0.18	**≤ 0.05**
Zn	19	-233 ± 85.2	692 ± 84.9	0.31	**≤ 0.01**

Earlier in the thesis, it was demonstrated through the use of C:N and POC:Chl *a* ratios, that the type of POC present in the estuary varies in both space and time. The presence of algal blooms, particularly in May and July 2000 were readily identified and ratios also suggested the increased presence of terrestrially-derived organic matter in the estuary in October 1998 when freshwater runoff was high (see Section 3.4.2 and Figures 3.12 and 3.13). At other times, and at different points along the estuary axis, the type of POC present was more mixed and also suggested the presence of other organic materials such as sewage, bacteria and labile organic compounds.

Paulson *et al.* (1994) proposed that Cu partitioning in estuarine and coastal waters is likely to be controlled by chemical competition between dissolved and particulate organic matter. More specifically, they showed that Cu complexed with dissolved organic matter from an industrialised estuary had a reduced affinity for adsorption onto estuarine particles than inorganic species. The only positive regression between POC and Cu occurred in June 1998 when 'terrestrial' POC and phytoplankton POC contributions tended to dominate over that from sewage. It may be that during March and October 1998, a greater proportion of POC consisted of anthropogenic compounds arising from industrial and municipal sources. The resulting complexes formed between anthropogenic ligands and Cu may in fact be partially resistant to the HCl digest, particularly if Cu binds with any residual organic carbon present in the particles (see Figure 3.9). Such resistance to acid extraction has previously been demonstrated by Turner (2000) using a weaker digest (hydroxylammonium chloride-acetic acid) to release reducible Cu (and other metals) from Mersey sediments. Additionally, Comber *et al.* (1995) demonstrated that Cu was concentrated in the residual and organic phases of Mersey SPM. These factors may help to explain the two poor correlations observed between POC and Cu in March and October 1998. The inverse relationships and low R^2 values observed between POC and other metals may be due to the same mechanism and/or preferential binding or co-precipitation with hydrous oxides of Fe and Mn.

4.2.3 Control of particle reactivity by Fe, Mn and POC

It has previously been demonstrated (Section 4.2.1) that oxidic phases of Fe, Mn or a combination of both these elements are important for the carrying capacity of contaminant metals by bed and suspended particles in the Mersey. The derivation of Fe/Mn ratios can be used to assess spatial and temporal intra-estuarine variations in the relative dominance of these two major sorbent phases. Ratios have been calculated for Mersey SPM and the results are displayed graphically in Figure 4.6. Also shown are the mean and standard deviations of Fe/Mn ratios in < 63 μm sediments. Ratios in riverine and upper estuary SPM change with fluctuations in freshwater discharge, tidal range and the extent of water oxygenation. Riverine signals become rapidly dispersed in the estuary, particularly in spring and summer. The upestuary advection of particles by tidal pumping is combined with a fresh supply of riverine material, which may be more or less enriched with iron or manganese than that already present in the estuary.

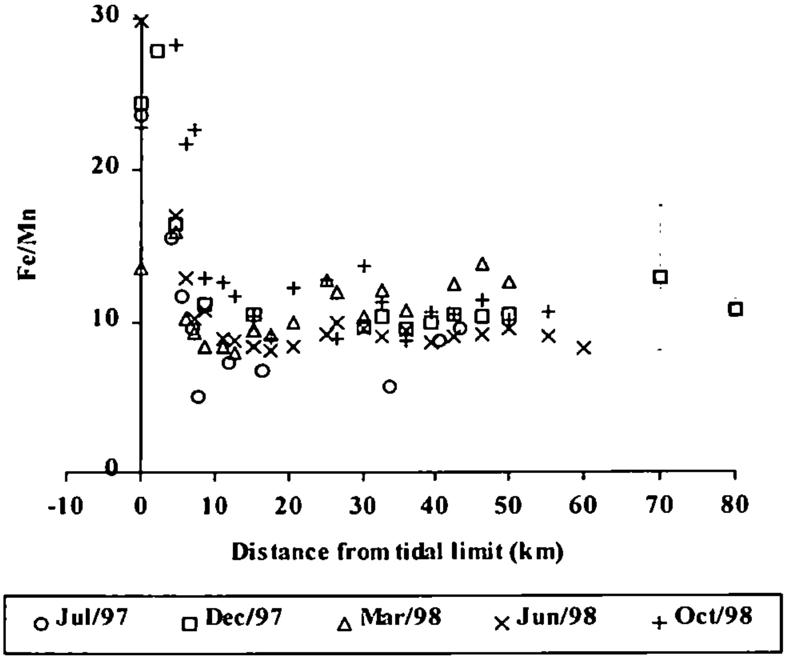


Figure 4.6 Fe/Mn ratios (available to 1M HCl) in Mersey Estuary bulk SPM as a function of distance along the estuary. Also shown at 70 and 80 km are mean ± 1 standard deviation of Fe/Mn ratios in < 63 μm sediment from July 1997 and July 1999, respectively.

Mixing of the two particulate pools leads to some elevated Fe/Mn ratios close to the tidal limit. Ratios are lowered around the TMZ in July 1997, March 1998 and June 1998 where lowest DO levels promote the release of both Fe and Mn into the dissolved phase (Duinker *et al.*, 1979). With increasing distance from the main freshwater influence, Fe/Mn ratios begin to stabilise due to increased oxygenation of the water column. A relatively homogeneous distribution of Fe/Mn is observed throughout the remainder of the estuary, although fluctuations do arise from localised alterations in hydrochemistry. These appear to alter the amount of Mn present (see Figure 4.2c(ii)) but do not produce similar changes in Fe, the axial distribution of which is more consistent (Figure 4.2a(ii)). Ratios in SPM from the majority of the estuarine mixing zone tend to agree with the range of Fe/Mn ratios measured in fine-grained sediments.

Millward *et al.* (1990) investigated the particle microstructure and chemical composition of suspended solids from four large estuaries – the Elbe, Humber, Mersey and Tamar. They found that the mean SSA of SPM from the Mersey was reduced in comparison to that originating from the other estuaries and proposed that this was due to the relative proportions of carbon (total) to iron and manganese in the samples. For instance, the high SSA in the Humber (24.0 m^2 g^{-1}) was associated with a C/Fe + Mn ratio of 4, whereas that for the Mersey, (mean SSA = 9.6 m^2 g^{-1}) was found to be around 11. The lack of an apparent turbidity maximum during the Mersey survey in 1987 resulted in uniform SSAs throughout the salinity gradient and the authors implied that the removal of dissolved constituents at low salinity would not be favoured in this estuary. When the findings of Millward *et al.* (1990) are compared with relevant data from this study, a number of interesting features arise (Table 4.9). As stated in the preceding chapter, SSAs of suspended particles appear to have increased as a consequence of reductions in the amount of SPM carbon present. This effect may have been exacerbated by the additional increase in Fe/Mn ratios observed between 1987 and 1999. Different digests have been used in the two studies to extract Fe and Mn and it is not clear what effect this may have on the relative contributions of both metals in relation to each other. The consequence of higher Fe/Mn ratios and lower carbon therefore provides a substantial reduction in the carbon:ferromanganese contents of Mersey SPM. The adsorptive capacity of suspended particles could thus be enhanced compared to that existing in 1987, with a greater chance of irreversible adsorption taking place, *i.e.* the migration of metal ions into the particle matrix. It also appears that fine-grained (< 63 μm) sediments could be a reservoir for carbon as well as metals. Mersey Estuary bed sediments and SPM now exhibit characteristics approaching those of Tamar Estuary bed sediments determined in 1985-6 (Millward *et al.*, 1990).

The mean combined concentrations of Fe and Mn are plotted against mean SSA for Mersey Estuary fine-grained sediments from July 1999 and compared to corresponding data for SPM from a variety of European estuaries (Turner *et al.*, 1991) as demonstrated in Figure 4.7. Inclusion of the Mersey data point reduces the significance of the linear fit of the data from an R^2 of 0.91 (n = 8, $P \leq 0.005$) to an R^2 of 0.44 (n = 9, $P \leq 0.05$). The SSA of Mersey particles is limited even though Fe+Mn are analogous to that in Humber SPM. In the preceding chapter (Table 3.3) it was shown that less particulate carbon is present in most of the Mersey mixing zone compared to corresponding data for the Humber (Uncles *et al.*, 2000). This may suggest that the form of amorphous Fe and Mn oxides on particle surfaces differs between the two estuaries and/or that Mersey particles are more degraded and aged than those from the Humber, as the latter would reduce the amount of effective surface available for trace metal sorption.

Table 4.9 Characteristics of Mersey Estuary particulate material, where n = number of stations sampled and R = range of values.

Survey dates & matrix	Statistical parameters	Turbidity (mg l^{-1})	SSA (m^2 g^{-1})	Fe (mg g^{-1})	Mn (mg g^{-1})	Total carbon (%)	Fe/Mn	C/Fe + Mn	Reference
Nov/87	Mean ± σ	86 ± 36	9.6 ± 2.4	4.8 ± 0.9	1.2 ± 0.3	6.4 ± 1.6	4.0	10.7	Millward *et al.*
SPM	N	10	10	9	10	10			(1990)
	R	50 - 155	6.0 – 14.9	3.5 – 6.5	0.7 – 1.6	4.7 – 9.4			
Jul/97	Mean ± σ	180 ± 158	-	15.7 ± 1.6	2.0 ± 0.6	-	8.0	-	This study
SPM	N	10	-	10	9	-			
	R	19 - 461	-	13.7 – 18.6	1.2 – 3.2	-			
Dec/97	Mean ± σ	243 ± 191	-	18.8 ± 8.9	1.5 ± 0.2	-	12.3	-	This study
SPM	N	11	-	11	11	-			
	R	15 - 702	-	14.8 – 45.6	0.9 – 1.8	-			
Mar/98	Mean ± σ	228 ± 141	-	16.2 ± 2.0	1.5 ± 0.3	1.8 ± 0.6	10.6	1.05	This study
SPM	N	17	-	17	17	17			
	R	88 - 579	-	13.1 – 20.1	0.9 – 2.0	0.9 – 3.3			
Jun/98	Mean ± σ	139 ± 136	-	16.7 ± 2.0	1.8 ± 0.3	1.2 ± 0.6	9.5	0.67	This study
SPM	n	20	-	20	20	19			
	R	10 - 581	-	10.3 – 20.0	1.2 – 2.3	0.2 – 2.6			
Oct/98	Mean ± σ	144 ± 84	-	16.8 ± 2.9	1.4 ± 0.3	1.1 ± 0.5	12.2	0.66	This study
SPM	n	19	-	19	19	19			
	R	31 - 347	-	11.9 – 25.4	0.9 – 2.0	0.4 – 2.7			
Jul/99	Mean ± σ	-	9.3 ± 3.0	10.6 ± 0.9	1.0 ± 0.1	3.0 ± 0.3	10.6	2.58	This study
< 63 µm	n	-	9	3	3	3			
sediment	R	-	6.6 – 15.0	9.6 - 11.4	0.8 – 1.1	2.6 – 3.2			
May/00	Mean ± σ	212 ± 115	11.0 ± 1.6	-	-	2.0 ± 0.5	-	-	This study
SPM	n	7	7	-	-	16			
	R	39 - 371	7.8 – 12.5	-	-	1.1 – 2.9			
Jul/00	Mean ± σ	175 ± 108	15.1 ± 1.3	-	-	1.8 ± 0.5	-	-	This study
SPM	n	8	8	-	-	8			
	R	60 - 345	13.4 – 16.8	-	-	1.3 – 2.5			

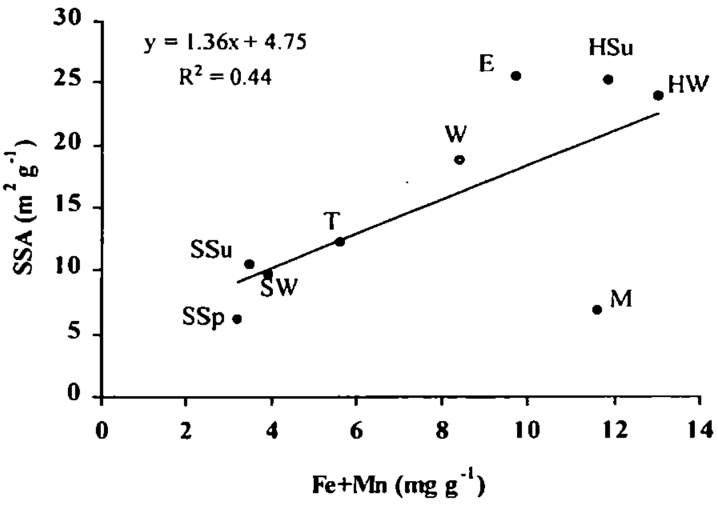


Figure 4.7 Relationship between mean specific surface area and mean combined concentrations of Fe and Mn in estuarine particles. Estuary key: HW = Humber, winter; HSu = Humber, summer; T = Thames; SW = Scheldt, winter; SSp =Scheldt, spring; SSu = Scheldt, summer; W = Weser; E = Elbe; M = Mersey < 63 μm sediment from July 1999.

Turner (1996) also investigated the effect of chemical composition of riverine particles on the key partitioning variables $K_D{}^0$ (describing metal partitioning in freshwater) and *b* (the rate of change in K_D with changes in salinity) for Cd and Zn for a number of estuaries. The results are plotted with corresponding data for the Mersey in Figure 4.8. Data from Turner (1996) refers to the partitioning of radioisotopes instead of stable metal isotopes. Correspondingly, values for $^{109}CdK_D{}^0$ and $^{65}ZnK_D{}^0$ for June and October 1998 (for the same survey dates as in this study) have been taken from Le Roux (2000). However, different leaches have been used to obtain Fe and Mn in Turner (1996) and this work.

However, it can still be seen that the proportion of Fe+Mn:C in Mersey SPM always exceeds that for the other rivers. Additionally, wide temporal variations are evident for Mersey REM particle composition and the freshwater partitioning of Zn (although not for Cd). Inclusion of the Mersey data reduces the correlations for both Cd and Zn with Fe+Mn/C from those provided in the other study (R^2 = 0.81 for Cd, R^2 = 0.50 for Zn (excluding the data point for the Dee)). Turner (1996) was able to demonstrate that the freshwater partitioning of Cd and, to a lesser extent of Zn, were the result of competing and additive effects of multiple sorbent phases such as ferromanganese hydroxides, carbonates and organic carbon. Results for the Mersey indicate that whereas in previous years, the abundance of POC (including that arising from direct anthropogenic sources) probably led to it being a more significant phase for trace metal sequestration, hydrous oxides of Fe and

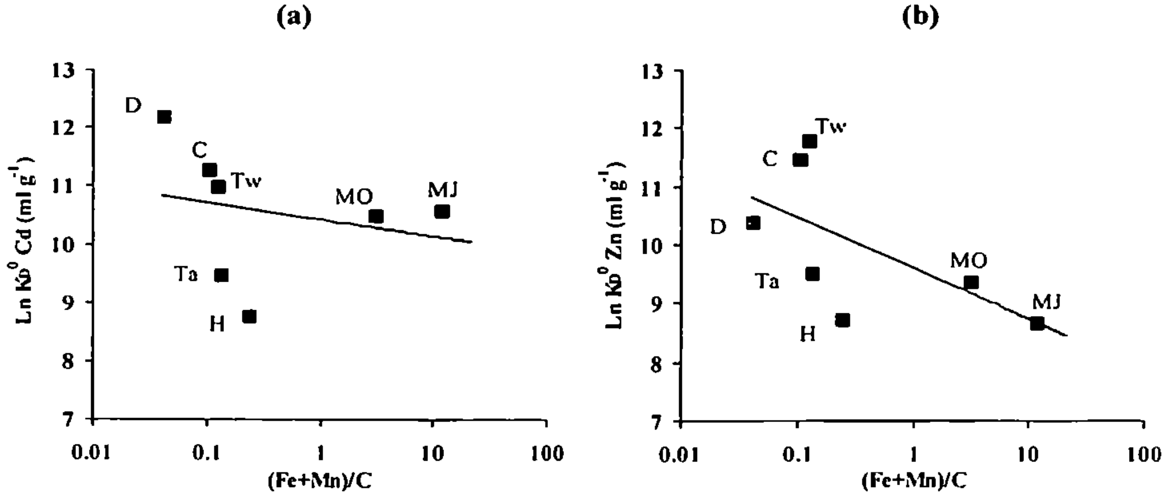


Figure 4.8 Relationships between (a) ^{109}Cd and (b) ^{65}Zn freshwater partition coefficients and the chemical characteristics of riverine particles from a number of UK rivers. Key: C = Clyde; D = Dee; H = Humber; Ta = Tamar; Tw = Tweed; M = Mersey in June (MJ) and October (MO) 1998. Equations of the two lines are (a) $y = -0.12\text{Ln}(x) + 10.42$ ($R^2 = 0.05$) and (b) $y = -0.38\text{Ln}(x) + 9.60$ ($R^2 = 0.38$).

Mn are currently assuming a greater importance in the adsorption of metals to SPM. This change in sorptive control fluctuates however in response to cyclic changes in instantaneous freshwater flow recharging estuarine waters with terrigenous organic carbon, the presence of phytoplankton blooms and the tidally-mediated injection of organic-rich interstitial waters from a sedimentary reservoir of organic carbon in the estuary as well as localised alterations in pH, DO, salinity and suspended load.

4.2.4 The partition coefficient, K_D

The measurement of particulate metals conducted in this study was supported by complementary analyses of total dissolved trace metals, the results of which are described in full in another text (Martino, 2000). It is important to note that measurement of dissolved metals was performed on the same water samples used to obtain the suspended particulate metal data discussed in Section 4.1.2 and all filtration was completed within 24 hours of sample collection. As estuarine systems are naturally complex and heterogeneous, the approach taken in this work therefore allows the most accurate insight into natural *in situ* metal partitioning.

Conditional distribution coefficients for stable metal isotopes (field K_Ds) have been calculated from the ratio between dissolved and non-detrital (available to 1M HCl) particulate trace metal data according to Equation 1.2. To test the variation of K_D with salinity, $\log_{10}K_D$ values are plotted against $\log_{10}(S+1)$ according to Bale (1987) in Figure 4.9. Linear regressions have been applied to seasonal data for Cd, Co, Cu, Ni, Pb and Zn and $\log_{10}$ values of K_D^0, the freshwater partition coefficient and the constant *b*, the rate of change in K_D with respect to salinity are also provided. Regressions have been forced through the y-axis when riverine data is available. The seasonal variability of trace metal partitioning is also shown graphically in Figure 4.10, which has the percentage of non-detrital particulate metals *vs.* the total suspended solids concentration, calculated using the following algorithm:

$$\%\,\text{Particulate Metal} = 100 - \left[\frac{100}{1 + K_D * [\text{SPM}] * 10^{-6}}\right] \qquad \text{Equation 4.5}$$

Increased dilution is apparent for Cd (Figures 4.9a and 4.10a) under the high flow conditions of the October 1998 survey. At this time, K_Ds are reduced throughout the estuary, K_D^0 is more than an order of magnitude lower than that determined during December 1997 and a maximum of only 40% of Cd is in particulate form. Values of *b* indicate that the extent of desorption of Cd in December under low flow conditions is more significant than at other times. For other surveys, up to 90% of Cd can be held on particles, particularly in December, when the highest turbidity was recorded. Desorption of Cd along the salinity gradient is always indicated but is somewhat reduced in both March and, more especially, in June. Kuwabara *et al.* (1989) and Turner *et al.* (1991) have previously shown correlations of particulate Cd (and Zn) with organic carbon released from phytoplankton blooms whilst Valenta *et al.* (1986) reported increases in K_DCd during blooms. Alternatively, intensification of pH minima in the spring and summer months may destabilise soluble metal-carbonate complexes including those for Cd, leading to metal precipitation (Sarin and Church, 1994) and consequently, less desorption. This may hold true in the Mersey in March 1998 when pH values tend to be lower than for other seasons, but do not clearly explain the results for June.

In contrast to Cd, values for *b* are always positive for Co, indicating progressive uptake onto SPM as salinity increases (Figure 4.9b). However, it should be noted that for three of the surveys, Co concentrations in riverine SPM were below the limits of detection. Correspondingly, freshwater K_Ds have been estimated on these occasions by extrapolating the regression line. The lack of particulate data in the REM also accounts for the apparent loss of some of the data at low turbidities in Figure 4.10b. It has already been established in previous sections in this chapter, that reduced water oxygenation promotes the release of

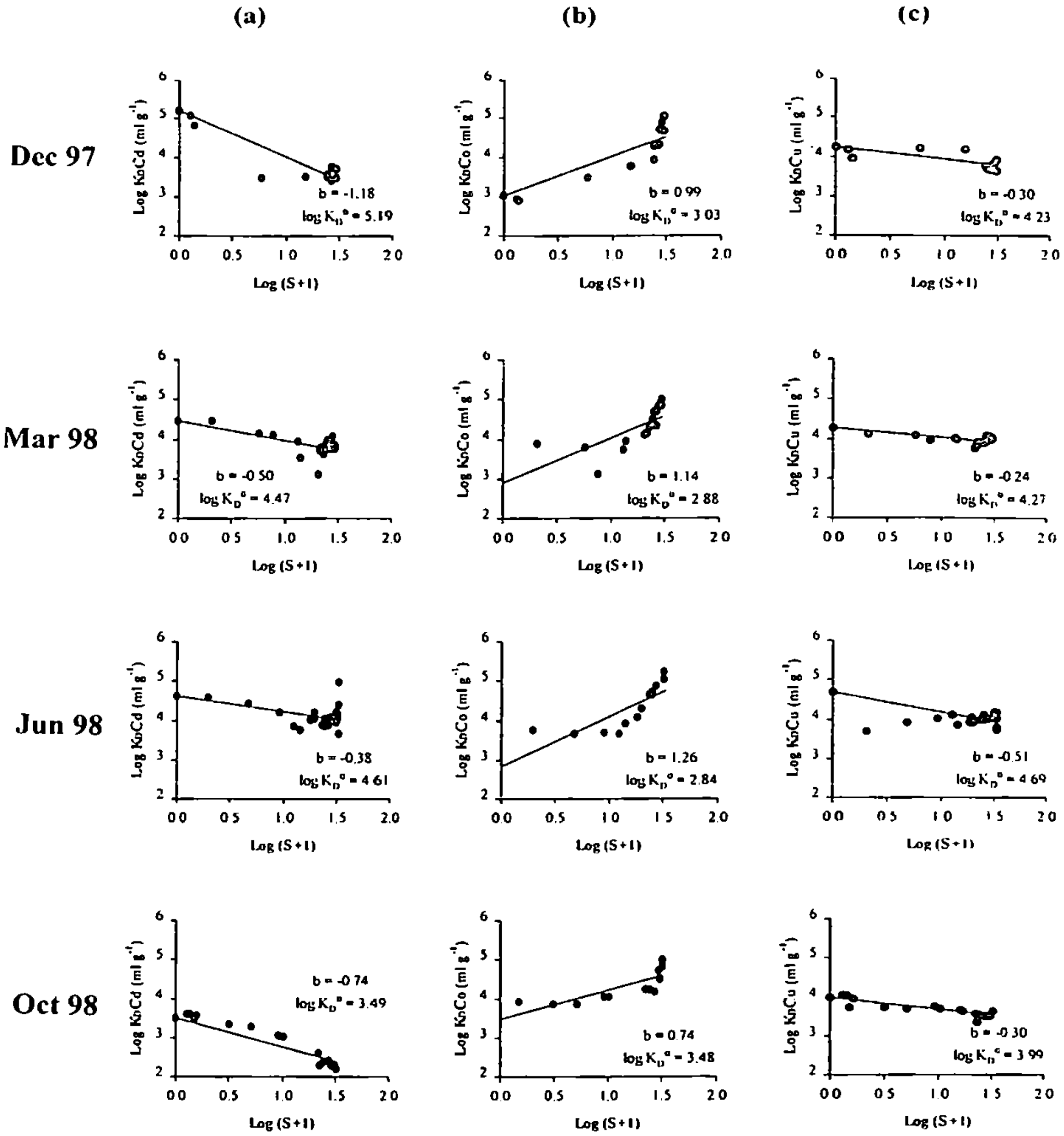


Figure 4.9 The variation of field K_Ds for (a) Cd, (b) Co and (c) Cu with salinity in the Mersey Estuary.

dissolved Co from sediment porewaters and/or the desorption of Co from resuspending sediments followed by subsequent adsorption of Co to SPM in waters where DO is replenished. The extent of Co uptake by SPM is thus greatest when temperatures are low (e.g. b = 0.99 in December) and reduced when DO levels and pH are progressively depressed as in March and June (b = 1.14 and 1.26, respectively). At all times of year K_DCo rapidly increases in the mid-outer estuary ($S \geq 17.4$) as pH rises and DO is replenished. At least 60% of Co is present in the particulate phase in October 1998 and December 1997 but this can fall to 30-40% in the upper-mid estuary in March and June 1998 (Figure 4.10b) when temperatures are higher and DO saturation is lowered.

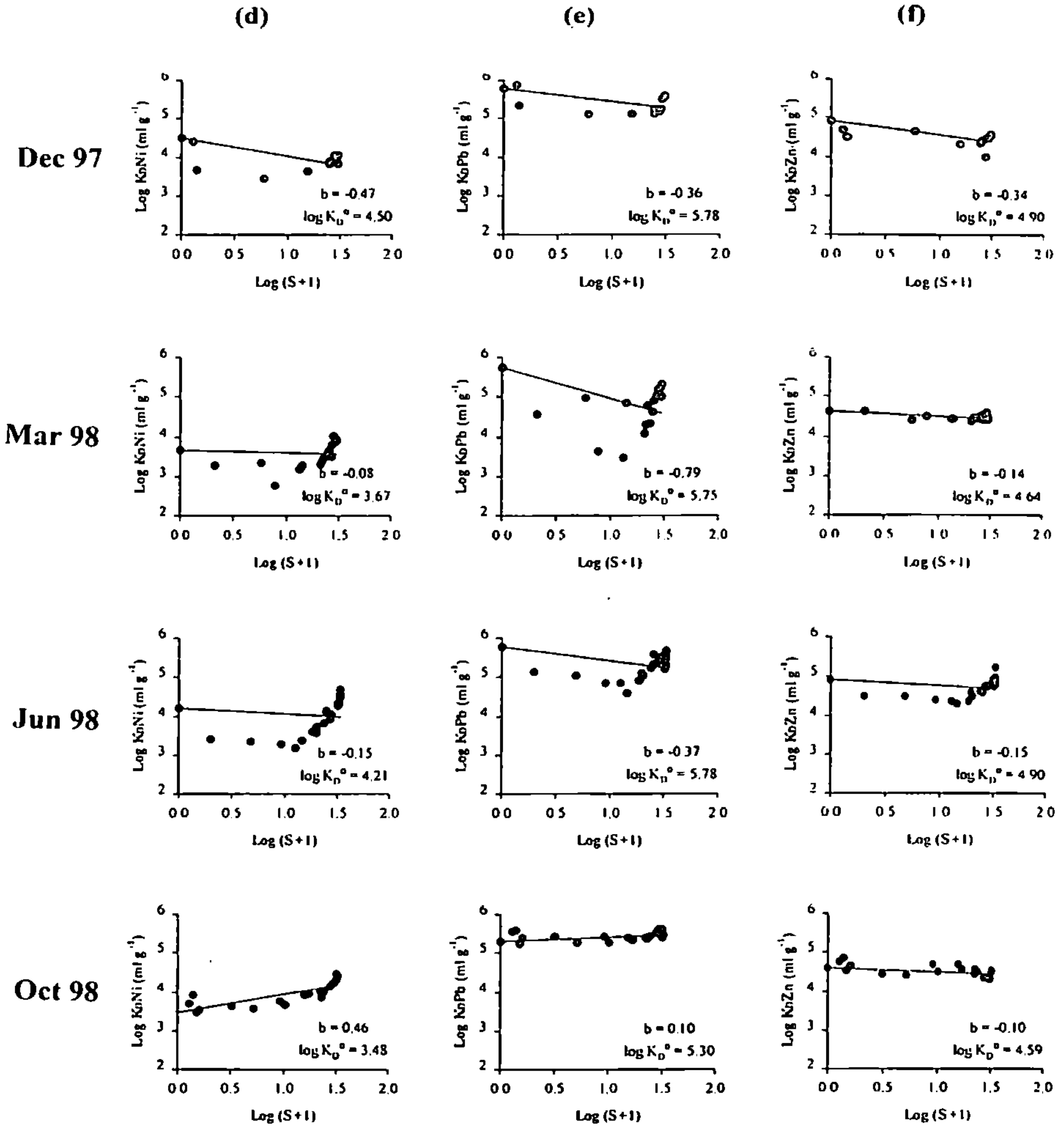


Figure 4.9 Continued – The variation of field K_Ds for (d) Ni, (e) Pb and (f) Zn with salinity in the Mersey Estuary.

Copper (Figure 4.9c) exhibits only limited seasonal changes in its phase distribution. Overall trends of salinity-induced desorption, whilst always indicated, are generally less pronounced than for Cd. A moderate inverse relationship between K_DCu and pH in June ($R^2 = 0.20$) may indicate the uptake of Cu onto SPM after release of the metal from tidally-resuspended organic-rich detritus in the TMZ. The value of $K_D{}^0$ for Cu is highest in June and a noticeable decline in K_D occurs at a low salinity at this time. The highest amount of Cu in the particulate phase is consistently observed in the TMZ for all surveys except October 1998 when the turbidity maximum is forced downestuary and overall turbidities are slightly reduced (Figure 4.10c).

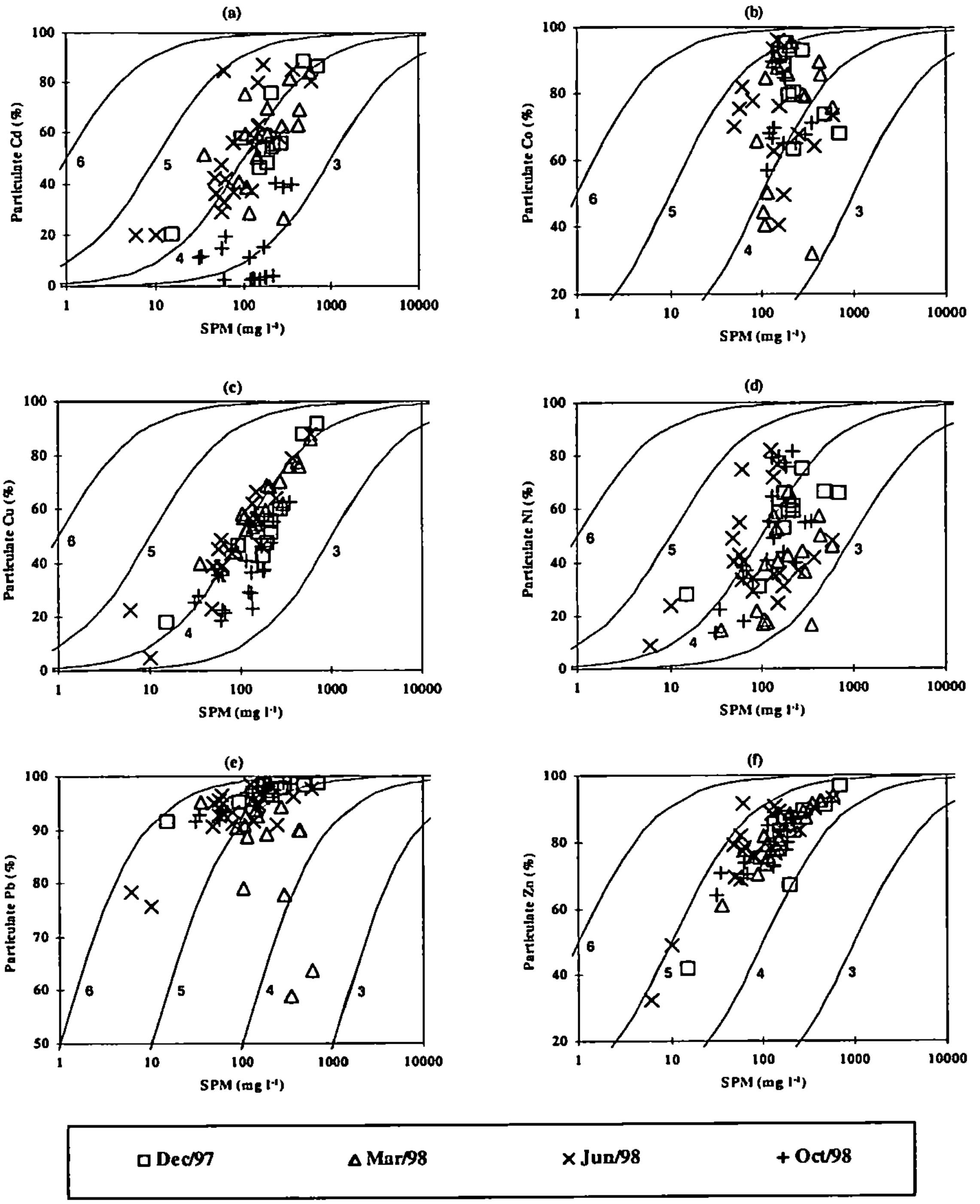


Figure 4.10 The variation in percentage non-detrital particulate (a) Cd, (b) Co, (c) Cu, (d) Ni, (e) Pb and (f) Zn with SPM concentration in the Mersey Estuary. The isopleths represent lines of constant K_D for which the $\log_{10}K_D$ values are indicated.

The solid-solution partitioning of Ni is quite variable (Figure 4.9d). In December, March and June K_DNi is reduced at low-moderate salinities. The salinity range over which Ni desorption ensues varies between surveys: <1 – 14.4 in December; 1.1 – 19.7 in March; 1.0 – 22.7 in June. Desorption of Ni is most significant during low flow in December (seen by the highest negative value for *b*) whilst slow but progressive adsorption predominates along the salinity gradient during October when runoff is considerable. Moderate to strong inverse relationships occur between K_DNi and DOC in March, June and October (R^2 = 0.41 - 0.72) and indicate that Ni readily combines with labile dissolved organic matter. This serves to reduce K_D^0 and estuarine K_Ds in March and June compared to December by helping to keep Ni in solution. However, a high negative correlation exists between K_DNi and chlorophyll-*a* in March (R^2 = 0.67), suggesting that Ni may be assimilated by phytoplankton, for which there is some evidence in the estuary in both March and June 1998 (e.g. see Figure 3.12). A maximum of 80% of the metal is associated with the particulate phase in waters of moderate turbidity in June and October 1998 (Figure 4.10d).

In common with Ni, Pb is desorbed from SPM at low-moderate salinities in December, March and June with the trend being most exaggerated in March (Figure 4.9e). Freshwater K_Ds are highly consistent and is only slightly reduced under the high flow conditions in October. Partition coefficients for Pb correlate positively with DO in March and June (R^2 = 0.58 and 0.21, respectively). More than 50% of Pb is held in the particulate phase at all times of year (Figure 4.10e) but particulate lead is lowest when suspended solids and chlorophll-*a* concentrations are high and DO concentrations are low. Under these conditions the presence of Pb in the dissolved phase increases in the upper-mid estuary including the TMZ region reflecting the position of the DO sag, after which K_DPb increases rapidly with higher salinity and higher DO concentrations. Away from the low salinity zone and the TMZ, at least 85% of Pb is associated with SPM. During October and December, the presence of more stable geochemical conditions such as greater DO saturation mean that only relatively minor variations are seen in Pb partitioning. This is particularly evident in the data for October when high runoff produces a homogeneous K_D-salinity distribution for Pb.

Overall trends of desorption are indicated for Zn for all surveys, being most obvious in June but limited in March and more particularly in October (Figure 4.9f). Freshwater K_DZn responds to changes in freshwater flow. The same K_D^0 is observed in December and June when flows are minimal and declines as runoff increases in March (moderate Q_f) and October (high Q_f). Uptake of dissolved Zn has been attributed to incorporation of the element in the opaline exoskelta of diatoms (Hunter and Tyler, 1987). The partition coefficient of Zn would be expected to increase under such conditions but there is no obvious demonstration of this process in the data for the Mersey. In June, only around 30% of the metal is present in the particulate phase in the REM (Figure 4.10f). At least 90% of Zn is held by SPM in the TMZ for all surveys. The relationship between K_DZn and DOC in June (R^2 = 0.24) is in fact negative and suggests that as for Co and Ni at this time, Zn adsorption is reduced and this may be due to a high concentration of natural organic ligands in the water column. Conversely, in October, the partition coefficient of Zn changes positively with DOC concentration ($R^2 = 0.36$), possibly implying that interaction between DOC and SPM promotes the migration of Zn deeper inside the particle matrix in some samples. However, overall, as for Cu, localised physicochemical conditions in the water column (including salinity) appear to be less important to the phase distribution of Zn than for those of Cd, Co, Ni and Pb. Turner (1996) demonstrated that reductions in the magnitude of *b* for Weser Estuary SPM followed the same order as the reduction in stability constants of the respective metal chlorocomplexes of Cd, Cu and Zn (*i.e.* Cd > Zn > Cu, Turner *et al.* (1981)). A review of the data given in Figure 4.9 indicates that in the Mersey, different patterns emerge for different surveys and that the behaviour of all three metals is somewhat modified in the Mersey compared to the Weser.

Figure 4.10 also indicates K_Ds as isopleths, with partition coefficients given as $\log_{10}$ values. The data for Cu and Zn tend to follow a uniform value of K_D. Millward and Glegg (1997) found that Cu and Zn partitioning were similarly seasonally independent in the Humber and proposed that this was connected to the invariant physico-chemical composition of suspended particles in the estuary. Considering previous discussions regarding the relative uniformity of Mersey SPM, it is somewhat surprising that seasonal differences in geochemical behaviour occur for other metals. Primary productivity affects oxygen saturation, water pH and the amount and type of organic carbon available for metal complexation and could be associated with some seasonal changes in the phase association of metals other than Cu and Zn. High POC concentrations may be associated with phytoplankton blooms leading to seasonal variations in overall SPM composition (Balls, 1990; Zwolsman and van Eck, 1999) and this can also influence metal uptake by lithogenic particles. The preferential incorporation of some elements by phytoplankton has also shown to result in seasonally variable removal of metals from the dissolved phase (Balls, 1990). The derivation of POC:Chl-a ratios in Section 3.4.2 is restricted for surveys other than May 2000 and July 2000 due to a lack of chlorophyll-*a* data, but does provide some evidence for phytoplankton blooms in March and more especially in June 1998 (see Figure 3.12). As K_Ds for Cd, Co, Ni and Pb increase at mid-high salinities during June, uptake of these metals in the dissolved phase by primary producers could be the mechanism responsible for this. Thus, it appears that the reactivity of Cd, Co, Ni and Pb are more readily influenced by periodical changes in the amount and possibly more significantly, the chemical nature and specificity of DOC and POC present at the time of sampling, particularly if this coincides with cycles of primary production. However, the elevated degradation of organic matter in bed sediments in the warmer months and the subsequent release of this material to the water column by tidal stirring could also be an important mechanism affecting metal phase partitioning in the Mersey.

The magnitude of K_D gives an indication of particle affinity for metals. The following sequence of decreasing particle reactivity has been generated by calculating the average estuarine partition coefficient for each metal:

$$\mathrm{Pb} > \mathrm{Zn} > \mathrm{Co} > \mathrm{Cu},\ \mathrm{Ni} > \mathrm{Cd}$$

Trends closely follow those observed in two other historically-contaminated turbid estuaries, the Scheldt and the Seine, where ranges in field K_Ds for each metal are generally similar to those in the Mersey even though different mineral acids have been used to obtain the data (Table 4.10). This may indicate that some geochemical equivalence may exist in the three systems. The Rio Tinto is substantially affected by acid-mine drainage. The low K_D values there result from waters of very low pH (2.5 - 6.6) promoting strong competition between protons and metals for binding sites on SPM and Achterberg *et al.* (2003) have estimated that consequently ≥ 99% of Cd, Cu and Zn are transported in the dissolved phase. Partition coefficients for the nearby Conwy Estuary in North Wales are generally

Table 4.10 Comparisons of ranges of field K_Ds ($\log_{10}$ values) for trace metals in estuaries and coastal waters.

Study site	**Cd**	**Co**	**Cu**	**Ni**	**Pb**	**Zn**
British coastal waters[a]	3.5-5.0	-	4.0-5.0	4.0-4.5	5.0-7.0	4.0-5.0
Conwy Estuary[b]	-	-	4.5-6.5	4.3-6.0	-	4.2-5.2
Forth Estuary[c]	3.8-5.9	-	4.4-4.9	4.4-5.0	5.2-6.2	4.5-5.3
Lena Estuary[d]	-	-	4.6-5.0	4.6-4.9	-	5.7-5.8
Mersey Estuary[e]	-	-	-	3.8-4.7	-	4.5-4.9
Mersey Estuary[f]	2.2-5.1	2.9-5.2	3.4-4.2	2.8-4.7	3.5-5.9	4.0-5.2
Rhone Estuary[g]	-	-	4.5-4.6	4.4-4.5	-	-
Rio Tinto[h]	1.0-2.3	-	1.4-3.7	-	-	0.9-2.7
Scheldt Estuary[i]	4.5-5.0	-	4.8-5.0	-	6.2-6.5	-
Scheldt Estuary[j]	3.9-6.3	-	4.2-5.7	3.5-4.2	-	4.3-5.2
Seine Estuary[k]	3.9-4.0	5.0	4.5-4.7	4.2-4.4	6.1-6.3	4.4-4.7

[a] Balls (1989); [b] Zhou *et al.* (2003); [c] Balls *et al.* (1994); [d] Martin *et al.* (1993); [e] Campbell *et al.* (1988); [f] This study; [g] Regnier *et al.* (1990); [h] Achterberg *et al.* (2003); [i] Valenta *et al.* (1986); [j] Paucot and Wollast (1997); [k] Chiffoleau *et al.* (1994).

higher than for the Mersey, and this could be indicative of differences in particle character or the amounts of organic carbon present in the two estuaries. Comparison of historical and present-day data for the Mersey suggests that the decrease in lowest values of K_DNi and K_DZn result from recovering conditions in the estuary over a period of 25 years, including the loss of suspended particulate carbon effected by reductions in organic effluents.

4.3 Evidence of recent trends in recovery

So far in this thesis, variations in particle compositional properties and the distributions of estuarine master variables, nutrients, carbon and trace metals have been assessed over short-term (seasonal) timescales. Relevant data for these parameters have been compared to other major estuaries experiencing varying pollutant burdens and degrees of anthropogenic pressure in order to assess the relative contaminant status of the Mersey. At this juncture it is also necessary to evaluate the advances made to date of metal decontamination in the Mersey, the details of which comprise the next three subsections of this chapter.

4.3.1 Comparisons with metals data from the literature

Numerous studies have undertaken determinations of particulate and dissolved trace metal concentrations in the Mersey Estuary in the last 25 years. A compilation of published data from these investigations is presented in Table 4.11, which also incorporates data from the current programme of work (including dissolved metal concentrations from Martino (2000)).

Several major difficulties arise when comparing temporal changes in trace metal concentrations in estuarine sediments and these are captured in Table 4.11. Firstly, only Harland *et al.* (2000) and this study report concentrations that have been normalised to the mean estuarine silt content of 40%. The effect of grain size normalisation is demonstrated clearly when comparing data for 1974 from Taylor (1986) with that of Harland *et al.* (2000). These values refer to mean concentrations in exactly the same sediment samples taken from the same transects. However, those from Taylor (1986) are not adjusted for silt content (which varied from 0.04 - 99.0% in 1974), whereas those for Harland *et al* (2000) were corrected. Reported values are additionally complicated by the use of different acid digests, which leach varying quantities of metals from particulate matter and consequently directly influence the value recorded. Thirdly, the number and locations of sampling

Table 4.11 Particulate and dissolved trace metal concentrations measured in the Mersey Estuary, 1974-1999. Mean values and concentration ranges are provided where available.

Phase	Year	Trace metal concentration								Reference
		Cd	Co	Cu	Hg	Mn	Ni	Pb	Zn	
Sediments (mg kg^{-1})	1974	0.7	8.6	49.7	1.7	332	16.1	82.2	319	Taylor (1986)[a]
		(0.1-4.0)	(2.0-22.3)	(0.9-219)	(0.05-9.2)	(0.8-2054)	(1.0-115)	(10.8-316)	(8.8-944)	
	1983	0.8	5.3	33.1	1.0	-	-	60.8	221	Taylor (1986)[a]
		(0.2-5.8)	(1.0-19.0)	(4.0-150)	(0.02-4.2)			(1.0-209)	(7.0-684)	
	1980-1984	1.3	-	94	3.01	1251	31.5	138	422	Langston (1986)[b]
		(0.2-3.9)		(31-144)	(0.4-6.2)	(633-2183)	(17.7-44.0)	(67.6-205)	(217-627)	
	1974	2.44	11.1	71.5	2.04	-	20.5	113	410	Harland *et al.* (2000)[c]
	1998	0.65	5.99	21.8	0.60	-	11.2	51	181	Harland *et al.* (2000)[c]
	1997	-	-	24	-	787	-	110	532	Turner (2000)[d]
				(13-31)		(301-1160)		(70-331)	(122-997)	
	1997	*	-	35.8	-	783	-	160	441	This study[e]
				(11.6-68.5)		(454-1104)		(64-422)	(234-639)	
	1999	1.5	14.3	38.0	-	837	55.9	476	284	This study[f]
		(1.1-1.8)	(8.6-18.0)	(18.9-51.3)		(655-941)	(53.9-59.9)	(355-542)	(260-298)	
SPM (mg kg^{-1})	1980	-	-	-	-	-	50-130	-	300-1000	Campbell *et al.* (1988)[g]
	1991	0.49-1.2	-	24-56	-	280-970	19-55	33-140	310-450	Laslett (1995)[h]
	1997-1998	1.0	9.2	26.0	-	1604	21.6	93	425	This study[i]
		(0.10-5.4)	(2.3-16.0)	(7.9-61.1)		(880-2572)	(4.6-175)	(3.0-240)	(250-810)	
	1997-1998	1.4	15.9	55.8	-	1803	48.3	170	505	This study[j]
		(0.1-7.0)	(5.2-26.5)	(31.1-95.2)		(1151-3150)	(17.0-195)	(51.0-319)	(267-929)	
Dissolved (µg l^{-1})	1980-1984	-	-	-	-	-	0.8-17.4	-	4.2-56.0	Campbell *et al.* (1988)
	1982-1984	0.06-1.7	-	0.20-13.3	0.0005-0.17	-	1.0-13.3	0.13-53.1	8.6-50.0	Cole and Whitelaw (2001)
	1991	0.009-0.052	-	1.4-3.3	-	0.1-11.0	0.80-9.4	0.032-0.460	1.5-16.0	Laslett (1995)
	1991-1992	0.015-0.070	-	0.9-2.4	-	-	2.3-10.4	0.65-2.5	7.5-17.0	Comber *et al.* (1995)
	1997-1998	0.03-0.48	0.04-2.39	1.5-5.5	-	-	0.46-11.9	0.06-1.24	2.8-32.0	Martino (2000)

* Not shown as only one sample was above LOD; Digests used: [a] aqua regia, whole sediment (not normalised to average silt content); [b] conc. HNO_3, < 100 µm; [c] Aqua regia, normalised to 40% silt; [d] 0.05M $NH_2OH.HCl$ in 25% CH_3COOH, < 63 µm; [e] 1M HCl, normalised to 40% silt, samples taken from axial transect of most of the estuary; [f] 1M HCl, normalised to 40% silt, samples taken from extreme upper estuary only; [g] digest not stated; [h] conc. HNO_3; [i] 1M HCl; [j] HF digest.

stations may vary considerably, depending on the means of access (whether from shore, boat or hovercraft) and the selection of specific regions of interest. Therefore, for all the reasons outlined, care must be exercised in interpreting the data in Table 4.11.

The most comparable studies of sediment metal concentrations (in terms of grain size normalisation and acid digests used) are those of Harland *et al.* (2000) and this work and the results from these are highlighted in Table 4.11. The former study is the most comprehensive and consistent data set on intertidal sediment metal concentrations in the Mersey in existence and demonstrates that sediment metal concentrations have generally declined by a factor of 2-3 for the elements studied (and almost a factor of 4 for Cd) between 1974 and 1998. This is to be expected given the reductions in metal loads to the catchment from changes in industrial practice, the tightening of discharge contents and improvements in sewage treatment (Jones, 2000).

Comparison of metal concentrations in SPM is made slightly easier as all data refer to samples collected during axial transects. However the selection of acid digest again varies between studies. Between 1980 and 1991, maximum concentrations of suspended particulate Ni and Pb have halved in response to the initial clean-up and volume reduction of direct discharges into the estuary. Assuming that the amount of metal liberated by concentrated HNO_3 as used by Laslett (1995) is intermediate between that of the 1M HCl and HF digests used in this study, it can be deduced that for most metals, concentrations have stabilised or even slightly increased since 1991. The amount of Mn in SPM has at least doubled due to overall improvements in DO, a feature also noted in the Thames and Scheldt estuaries in response to the clean-up of oxygen-consuming organic effluents (Section 1.3.2). Concentration ranges for other metals have widened and maximum values have risen between 1991 and the late 1990s. Thus, earlier reductions in SPM-associated metals do not appear to have been sustained.

Data for dissolved metals in Table 4.11 show that the same trends are apparent for some dissolved metals as for metals in SPM. Reduced concentrations of dissolved Cd, Cu, Ni, Pb and Zn are observed in 1991 compared to 1980-1984. Concentrations then appear to reach a plateau between 1991-1992. Later, in the period 1997-1998, the trend appears to be reversed for dissolved Cd, Cu, and Zn which all begin to increase slightly, whilst Ni concentrations remain approximately the same and those for Pb continue to fall. Despite recent trends, the latest measurements made by Martino (2000) give dissolved metal concentrations that are well within current EQS values (see Table 1.2).

From studying the data in Table 4.11, it seems that decreases in both the number and concentrations of metal inputs into the Mersey which began in the 1970s, resulted in steady declines in metal concentrations in the estuary up until the early 1990s. Subsequent declines have slowed or even possibly begun to reverse in the last few years and this implies that processes occurring within the estuary itself are assisting in attenuating metal concentrations at present day levels.

Additional evidence for an apparent slow-down in metal reduction trends has been provided in sediment core studies. For example, differences of up to x3 for Cu, x22 for Pb and x5 for Zn exist between apparent 'pre-industrial' concentrations in saltmarsh cores (Fox *et al.*, 1999) and contemporary concentrations in surface sediments from the extreme upper estuary (this study). Examination of core maxima indicates that for these three metals, contamination has returned to intermediate, rather than baseline, levels. Additionally, these intermediate values appear to have been consistently retained since 1992 when the core was taken. This suggests that contaminant concentrations of Cu, Pb and Zn in deposited sediments have reached a plateau in the last decade after previously rapid declines had taken place over the preceding 40 years. This continuance could result either from metals issuing from point discharges or from dispersed sources. The latter could include the introduction of fresh contaminated sediment from fluvial inputs, the redistribution of reworked contaminated sediment from elsewhere in the estuary or the return of relatively metal-rich particles from the immediate Irish Sea area (*i.e.* Liverpool Bay). It is important however, to first assess the significance of any variations in external metal loads before observed temporal patterns are primarily attributed to the recycling of trace metals from internal sources.

4.3.2 Metal loads

Abatement of trace metal loads from industrial sources to the Mersey has occurred over many years, with generally the most significant improvements to effluent quality taking place in the 1970s and 1980s (NRA, 1995). For example, Cd inputs have lowered through improved operational practices and the use of alternative specifications and disposal methods since new EU legislation concerning its control were implemented in 1985. In 1985, 10 industrial sites (mainly electroplaters) discharged 0.282 tonnes of Cd to untreated sewers but by 1991, this had fallen to 0.052 tonnes (NRA, 1995). This was achieved by a combination of the factors above, along with improved wastewater treatment. The most notable reduction has been for Hg, the loads of which have fallen by more than two orders of magnitude since peak inputs in the mid 1970s, constituting a reduction of 90% (Harland *et al.*, 2000; Jones, 2000). One of the major inputs of Ni into the upper estuary, located at approximately 1.6 km from the tidal limit and responsible for the manufacture of Ni catalysts, ceased production in 1996 and other Ni-containing industrial effluents are now treated (P. Jones, Environment Agency, pers. comm.). Currently, there are few remaining major point sources of Cu, Ni and Zn and inputs into the estuary are now dominated by contributions from tributaries and the non-tidal River Mersey (NRA, 1995).

The loads of five metals entering the estuary from 1990-1999 have been obtained from the Environment Agency website (EA, 2002b). The data are presented graphically alongside corresponding mean sediment metal concentrations (averaged over a depth of 2 cm) determined by Harland *et al.* (2000) for the same period in Figure 4.11. Load data refer to high load collective inputs from industrial, riverine and sewage sources. Discharges of some metals (Hg, Pb and Zn) show marked fluctuations compared to other metals (Cd, Cu) in Figure 4.11a. The most obvious increase was more than a trebling for Hg between 1990 and 1992. A very significant decline in Zn loads (and to a lesser extent for Pb) in 1991 were followed over the next 1-2 years by increased inputs. After this date, metal loads either slowly reduced or remained relatively stable until 1998. Discharges then rose by varying degrees for all five metals (by only 25% for Pb but 50-70% for other metals) compared to those for the previous year. With the exception of Pb, all metals had smaller loads in 1999 than in 1990.

Monitoring was not performed for metals other than Hg in 1992 and 1993 by Harland and his co-workers, and the sharp inclines for Pb and Zn loads were not captured in the their measurements. A response to increased Hg inputs to the estuary in 1991 and 1992 is observed in the sediments in Figure 4.11b. Quoting less accurate load data at the time of publication, Harland *et al.* (2000) ascribed the rise in sediment Hg in three successive surveys between 1989 and 1992 to the remobilization of Hg-contaminated sediments derived from the erosion of previously consolidated saltmarsh. This theory can now effectively be ruled out for the 1992 rise in sediment Hg, which is almost certainly due to elevated loads instead. However, higher bed sediment concentrations of Cd, Pb and Zn in 1995 and of Hg in 1996 are not consistent with the corresponding trends in load data at those times. The possible reintroduction of contaminated saltmarsh sediments throughout the monitoring area during 1995 and 1996 could therefore explain the observed rise in sediment-bound Cd, Hg, Pb and Zn. The rise in all metal loads in 1998 do not produce any appreciable increases in sediment metal concentrations, most notably not even for Zn. Thus, any signal from enhanced inputs is effectively quenched in 1998. This is

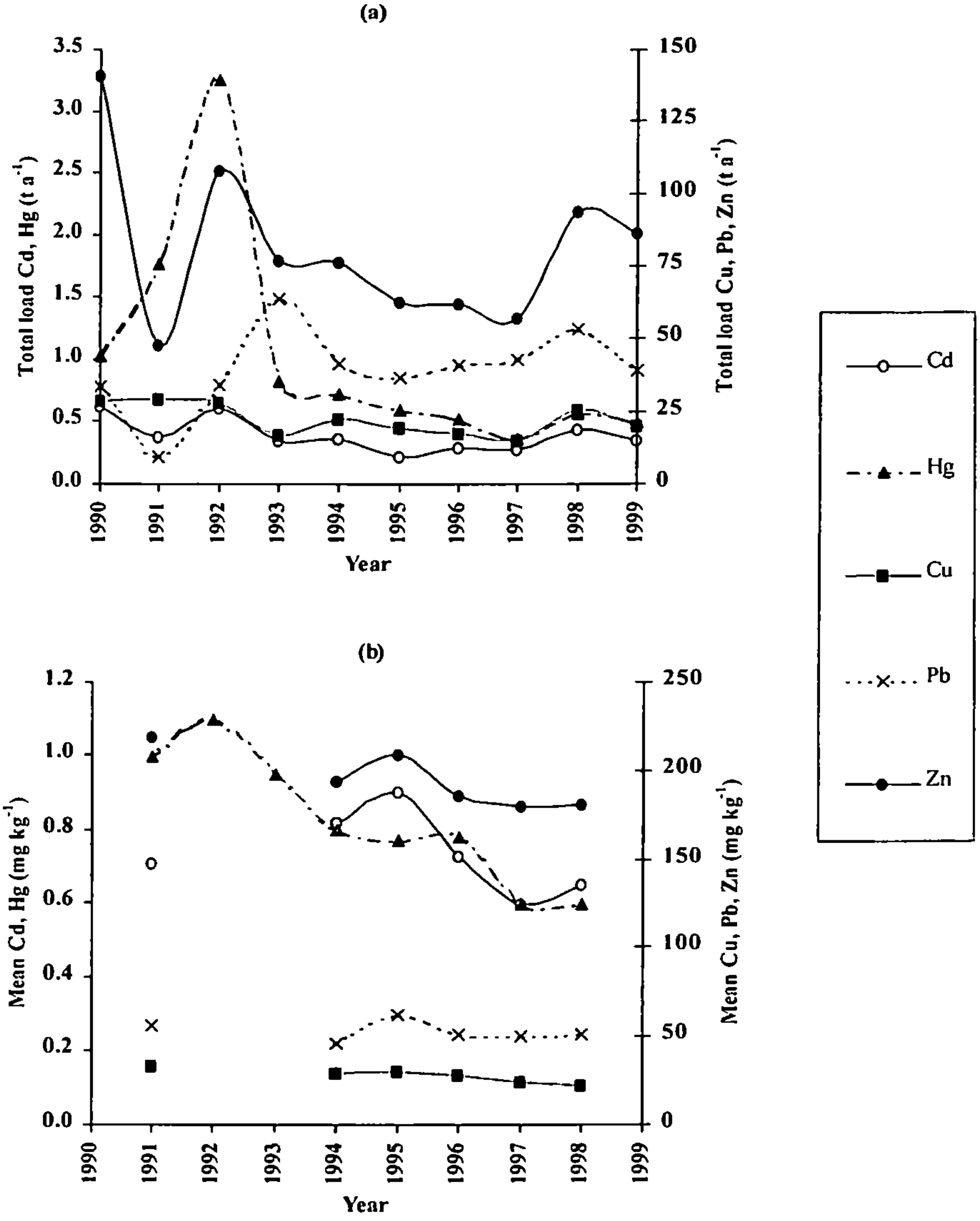


Figure 4.11 (a) OSPAR reported discharges to sea, 1990-1999 (Environment Agency, 2002b) and (b) mean concentrations in bed sediments in the Mersey Estuary (normalised to 40% silt) of Cd, Cu, Hg, Pb and Zn, 1991-1998 (Harland *et al.*, 2000).

possibly aided by the introduction of minimally metal-enriched particles from offshore or an increase in the amount of larger particles such as sands present in estuarine sediments. In conclusion, the overall correspondence between metal inputs and sediment metal concentrations are neither clear nor predictable. In fact, the only statistically significant correlation produced between annual input and sediment concentration data between 1991 and 1998 is for Hg ($R^2 = 0.69, P \leq 0.01, n = 8$).

Examination of the above data indicates that whilst a direct relationship could be discerned between elevated sediment Hg concentrations and Hg loads in 1992, at other times and for other metals, sediment metal concentrations do not simply reflect changes in the amount of metal released from various sources within the catchment.

Disparity between trends in sediment metal concentrations and metal loads are likely to result from strong hydrodynamic and sedimentary as well as geochemical control. The sheer dynamicity of the Mersey actively promotes the dispersion of erodable sedimentary material from elsewhere in the estuary and this sediment may be more (e.g. in 1995/1996) or less (e.g. in 1998) contaminated than the ambient sediment contained within the fixed monitoring area continually used by Harland *et al.* (2000). Saltmarsh erosion continues in the estuary, contrary to the belief of Harland *et al.* (2000) that erosion has significantly lessened since the mid-1990s. Surveys performed in 2000 by the British Geological Survey for example, have shown that the position of the mean high water mark on the South bank of the Mersey has changed since 1992 as a result of significant retreat of parts of the Ince Banks saltmarsh development (Ridgway and Shimmield, 2002). In common with many other macrotidal estuaries, the continuous re-working and flux of particulate matter within the Mersey allows the redistribution of mobile sediments and any associated contaminants which are then made available for extended periods of internal recycling. Importantly, the physical removal of topmost layers of consolidated marsh deposits will establish a new redox gradient and thus promote the vertical diffusion of diagenetically modified metals towards the sediment-water interface. The mobilisation of previously unavailable metals buried within the sediments would result in a new reservoir of metals able to take part in geochemical interactions either at the sediment surface or in overlying waters and this could also assist in explaining some of the patterns observed in the published data.

4.3.3 Recovery of Mersey sediments from metal contamination

Long-term monitoring performed by Harland *et al.* (2000) has demonstrated continual declines in the concentration of most metals in sediments of the Mersey Estuary over a 25-year period. This has proceeded despite perturbations in reduction trends induced by fluctuating metal inputs, the occasional introduction of sedimentary material possessing higher trace metal burdens from other regions of the estuary and any additional contributions emanating from diagenetic processes.

The provision of a relatively comprehensive and temporally extended data set can be used to derive approximations of sediment metal residence times. The time-dependent declines for metals in sediments (normalised to 40% silt content, the validity of which is explained in Section 4.2.1) from Harland *et al.* (2000) are shown in Figure 4.12. Data for Ni has not been included, as consecutive annual measurements have only been made since 1995.

Exponential trendlines have been fitted to the data for Cd, Cu, Pb and Zn and the equations describing them are also provided. This was not possible for Co, where an apparently large injection of the metal occurred in 1994 and consequently a declining trend is not observed. For metals where a curve is generated, values for R^2 are excellent ($P \leq 0.005$ or better) and the metals exhibit strong exponential declines over time. The exponents in the equations for Cd, Cu, Pb and Zn are the time constants for the evolution of sediment metal content and have units of years^{-1}. The reciprocals of these values offer an approximate residence time for each metal, which are given in Table 4.12. The corresponding value for Hg has also been included due to the fact that its historical elevated presence in the estuary has always been of significant interest and also because this work has investigated the sorptive behaviour of Hg in the Mersey (Chapter 5).

Table 4.12 Sediment metal residence times in the Mersey Estuary as estimated from data in Harland *et al.* (2000).

	Cd	**Cu**	**Hg**	**Pb**	**Zn**
Residence time (y)	23	23	23	27	37

The figures above indicate that removal of metals from the monitoring area could be achieved within the next 20-40 years, providing that extraneous sources are minimised. Hence, and based on the data from Harland *et al.* (2000) alone, it could be said that in 2003, sediment recovery from metal contamination is anticipated to have reached an approximate halfway stage.

However, it should be noted that Figure 4.12 provides additional data on mean sediment metal concentrations obtained in this study during 1997 and 1999 which are higher than published values for around the same periods. The strength of digests used in both studies can effectively be considered comparable and both data sets have been normalised to an estuarine mean silt content of 40%. Disagreement between this research and the end-point

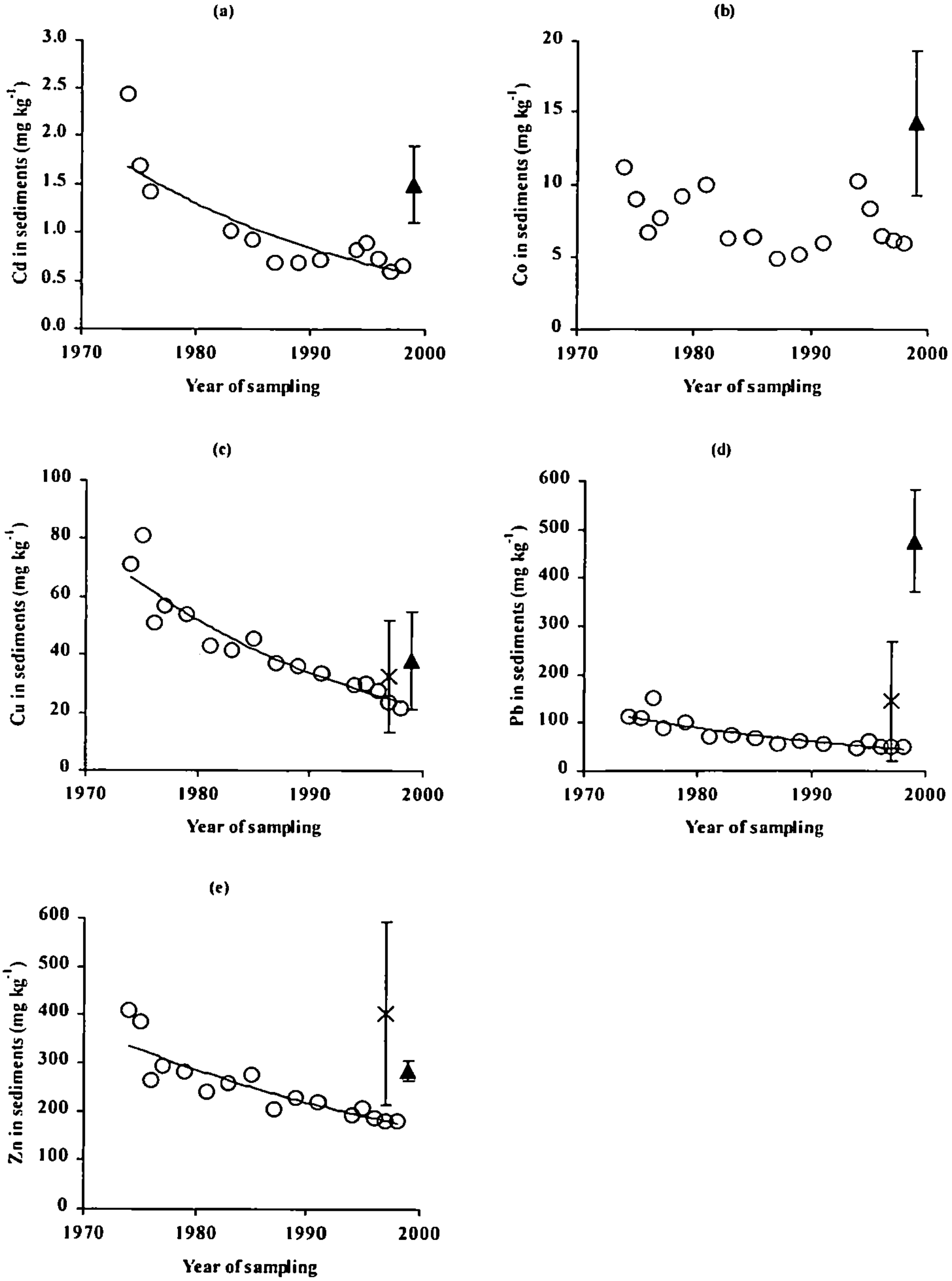


Figure 4.12 Reduction of sediment metal concentrations, 1974-1998 (from Harland *et al.*, 2000). Data are for (a) Cd, (b) Co, (c) Cu, (d) Pb and (e) Zn available to *aqua regia*. Equations describing the lines are: (a) Cd = $1.7e^{-0.043x}$ (R^2 = 0.77); (c) Cu = $67e^{-0.043x}$ (R^2 = 0.93); (d) Pb = $112e^{-0.037x}$ (R^2 = 0.82); (e) Zn = $336e^{-0.027x}$ (R^2 = 0.83). Also shown are the mean ± 1σ of sediment metal concentrations available to 1M HCl determined in this study from sampling throughout the estuary in 1997 (X) and samples taken from the first 5 km of the upper estuary in 1999 (▲).

of the monitoring series performed by Harland *et al.* (2000) therefore comes primarily from the choice of sampling location. Sampling for the purposes of this study focussed on areas accreting larger quantities of fine, mobile, contaminated sediments. Harland *et al.* (2000) used a fixed monitoring grid throughout their campaign, taking relatively few samples from the upper estuary and excluding the top 14 km downstream of the tidal limit. Interestingly, this work has shown that concentrations of most metals studied herein are in fact elevated in the upper reaches compared to sites downestuary (Figure 4.12). As such, the results from Harland *et al.* (2000) may under-represent the true extent of metal contamination in Mersey sediments and more time may be required for significant metal loss to occur. The implications of enhanced metal levels in upper estuary bed sediments and predictions of their future recovery from metal contamination will be addressed later in Chapter 6.

4.4 Summary

This chapter has established that a combination of hydrodynamic, sedimentary and geochemical processes are responsible for maintaining trace metal concentrations at present-day levels in the Mersey Estuary. Bed sediments, particularly those in the upper reaches, remain substantially enriched for most metals studied. Evidence suggests that historical metal loadings were high, as coarse-grained sediments are as equally contaminated with Cu, Ni, Pb and Zn as the < 63 µm grain size fraction at some locations. Further indication of this is provided by the equivalent contamination of PSPM and TSPM by Cu and Zn. The incidence of peak concentrations of trace metals in bed sediments is not thought to be closely linked to the position of inputs but to result instead from the hydraulic sorting and energetic dispersal of particles in a highly dynamic tidally dominated system. The metal content of bed sediments therefore mainly reflects sediment granulometry but is also affected by differences in sedimentary POC.

Distributions of PSPM and TSPM are related to that of bed sediments and respond to changes in tidal range and river flow in line with conventional theory. Apart from Cu and Zn, metals in PSPM tend to exceed those in TSPM, especially for Co and Fe and concentrations of most metals in bulk SPM have shown to arise simply from the mixing of naturally differing amounts of PSPM and TSPM at any one locale. Apart from Cu and Zn, the phase partitioning of most metals studied herein is quite variable and is primarily exerted by estuarine gradients of salinity and particle composition and concentration. Partial restoration of water quality in the estuary means that Fe and Mn are now probably more important for trace metal sequestration than organic carbon. However, spatial and temporal changes in DO and the delivery of organic carbon (from external and/or internal sources) influence concentrations of Fe, Mn and C in SPM. Sorptive control may shift slightly between these phases such that the extent of uptake and subsequent retention of metals varies depending on the time of year, in addition to longitudinal changes in salinity and suspended load. Nevertheless, the overall effect is to maintain high concentrations of metals in the particulate phase.

Metals are retained very effectively in Mersey particles as a consequence of increasing adsorptive capacities and the fluctuating but continued (although now somewhat reduced) presence of particulate organic carbon (see Chapter 3). Particulate metal concentrations in the Mersey are similar to those in other moderately contaminated systems such as the Severn, Tamar, Tyne, Humber and Thames. However, regulation of metal uptake by the physical (SSA) and chemical properties (Fe, Mn and C content) of SPM and the relative uniformity of metal concentrations throughout the mixing zone for many of the metals studied mark Mersey SPM as being significantly different to that of other estuaries. It is postulated that efficient sediment trapping generates a well-mixed pool of aged and modified suspended particles in the Mersey. As a consequence, it is anticipated that only small contributions of particulate metals are permanently flushed out of the estuary into the surrounding coastal zone.

Comparisons of metals data from this study with those from the literature have shown that continuous and relatively rapid declines in particulate and dissolved metal concentrations occurred over a period of almost 20 years. Since 1991 however, the momentum has slowed and metal concentrations in both phases have effectively stabilised. Examinations of metal load data and corresponding bed sediment metal concentrations from Harland *et al.* (2000) during the period 1990-1998 reveals a lack of coherence between the two data sets. The attenuation of sediment metal concentrations has instead been attributed to the internal cycling of metals in the estuary, including the redistribution of formerly consolidated and contaminated saltmarsh sediments. Sediment metal residence times have been calculated using long-term monitoring data in Harland *et al.* (2000). Assuming that metal inputs and underlying physico-chemical conditions in the estuary remain unchanged, then decontamination of Cd, Cu, Hg, Pb and Zn in bed sediments from the inner and outer Mersey Estuary is predicted to take a further 20-40 years (from 1998). However, this work has shown that higher Cd, Co, Cu and Pb concentrations occur in bed sediments in the upper estuary, a region that is not wholly accounted for in the Harland *et al.* (2000) study.

Although direct intercomparisons between studies are not straightforward due to differences in sampling and/or analytical methodologies, it is envisaged that the amount of time required for significant sediment metal loss may vary for different stretches of the estuary as well as for different metals.

Chapter 5

Implications of Metal Sorption

5 Implications of metal sorption

The first half of this chapter gives an account of the solid-solution interaction of Hg with different SPM fractions in controlled laboratory radiotracer uptake experiments. Environment Agency data for stable dissolved and particulate Hg from the same axial transects are included for comparative purposes. The effects of salinity, turbidity and seasonal changes in water column and particulate matter chemistry on Hg partitioning are discussed. Subsequent sections describe mechanisms by which a number of metals, experiencing different degrees of interaction with particulate matter, may be mobilised and transported within the Mersey Estuary. Complementary data for dissolved trace metals are included to facilitate the interpretation of metal phase partitioning and the derivation of sorption models that may be used to describe observed dissolved metal profiles in the estuary.

5.1 Radiochemical experiments

5.1.1 The use of radioisotopes to study metal uptake by natural particles

Partition coefficients derived from field measurements of dissolved and particulate constituents rely on total or partial extraction by mineral acids (Millward and Turner, 1995). However, these techniques are often not adequately selective toward the immediately reactive components (*i.e.* the truly exchangeable metal fraction), with the analytical particulate fraction resulting from a combination of physico-chemical reactions occurring over different timescales (Turner, 1996). Instantaneous particle-water interactions may be replicated instead by using radioisotopes in controlled laboratory experiments, allowing a more direct insight into trace metal estuarine reactivity (Li *et al.*, 1984a,b; Turner *et al.*, 1993; Millward *et al.*, 1994). Resulting analysis of only the adsorbed metal fraction is relatively simple and reproducible and contamination problems are largely avoided. The use of radioisotopes to simulate the behaviour of their stable analogues possesses additional advantages. These include the possibility of working at ultra-trace (pico- to nano-molar) concentrations offered by the low detection limits of gamma spectrometry, accurate mass balance determinations and the direct analysis of particulate and dissolved samples (Amdurer *et al.*, 1983; Anderson *et al.*, 1987; Turner *et al.*, 1992a,b). Short-term incubation studies have however failed to identify how reaction kinetics may affect the ultimate location of metal on particles, although recent efforts have attempted to discriminate between non-specific sorption reactions such as ionic exchange, with more specific interactions between surface ligands and trace metals by modelling coupled kinetic and salinity effects (Ciffroy *et al.*, 2003).

5.1.2 The phase partitioning of mercury in the Mersey Estuary

The general physico-chemical characteristics of water samples and SPM used in radiochemical partitioning experiments are provided in Table 5.1. Distribution coefficients derived from the incubation of ^{203}Hg with natural water samples containing bulk SPM, PSPM and TSPM from the March 1998, June 1998 and October 1998 surveys are plotted against salinity in Figure 5.1. Also shown are stable K_Ds derived from measurements of dissolved (R = 0.010-0.031 μg l^{-1}) and particulate (R = 0.35 – 19.9 μg g^{-1}) Hg made by the Environment Agency from a limited and variable number of sites. Upon first inspection, a number of features may be discerned.

Table 5.1 Characteristics of estuarine water samples employed in radiotracer experiments.

Survey	**Salinity**	**SPM (mg l^{-1})**	**pH**	**DO (%)**	**POC (%)**	**DOC (mg l^{-1})**	**Chl-*a* (μg l^{-1})**
March 1998	0.3–29.0	36-579	7.3-7.7	65-94	0.76–2.75	2.7–10.6	11.2 – 20.9
June 1998	1.0–27.0	62-581	7.5-7.7	50-61	0.76–2.08	2.8–8.6	19.5 – 44.6
October 1998	0.3–31.2	34-347	7.2-7.9	77-92	0.56–2.15	1.9–9.3	8.6 – 15.2

Strong coherence between radiotracer and stable K_Ds are generally achieved, with any discrepancies between the two data sets arising from the different analytical methods employed. Secondly, overall, the results for ^{203}Hg concur with the trends for stable Hg. For example, a general trend of enhanced K_D with with increasing salinity is observed for both in March 1998. Thirdly, individual radiotracer K_Ds derived from triplicate analyses of dissolved and particulate fractions, show limited variability, indicating the high reproducibility of the technique. Additionally, as for other contaminant metals in Chapter 4, differences in the sorptive capacities of PSPM and TSPM are seen, with more exchangeable ^{203}Hg tending to become associated with PSPM rather than TSPM. This is especially evident at salinities < 10 in the upper estuary during June. Further along the salinity gradient, the two particle types appear to become less distinct from each other in their ability to adsorb the radiotracer. The preferential association of Hg with PSPM may

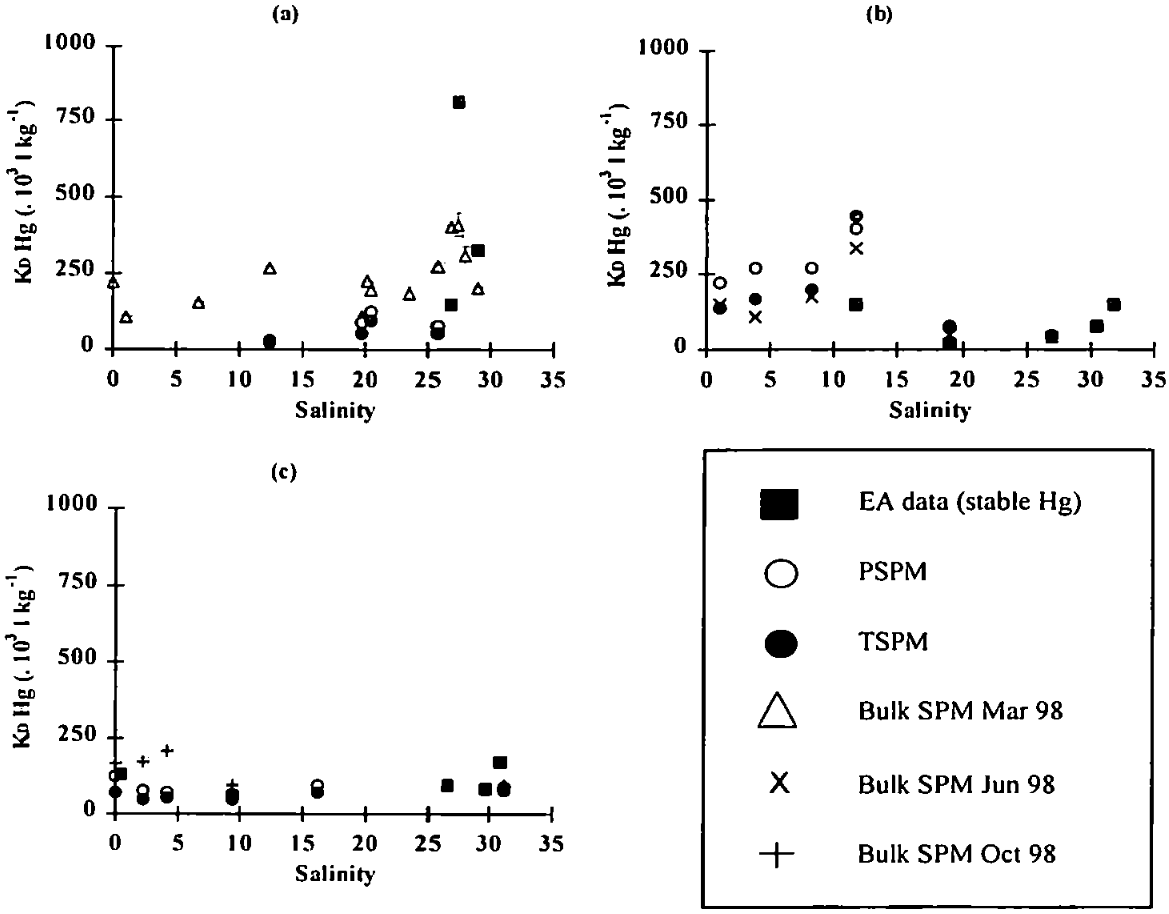


Figure 5.1 Variation in the solid-solution partitioning of ^{203}Hg and stable Hg with salinity in (a) March 1998, (b) June 1998 and (c) October 1998.

be partly explained by the fact that estuarine PSPM is richer in carbon (estuarine mean = 3.1 ± 0.7%) than estuarine TSPM (1.0 ± 0.9%), much of which is present in organic form. Turner and Millward (1994) reported a magnitude of difference in 5-day K_Ds between PSPM and TSPM from the nearby Dee Estuary with increased metal (Cd, Cr, Cs, Fe, Mn, and Zn) K_Ds measured for the permanently suspended fraction. This has significant implications in the Dee, for passage of PSPM past the estuarine freshwater-saltwater interface would allow considerable down-estuary transport of metals bound to and subsequently released from these particles. Unlike the Dee, the ^{203}Hg data for this study do not show as dramatic a difference in the ability of PSPM over TSPM in the Mersey to sequester even as highly particle reactive a metal as Hg. Despite the close proximity of the two estuaries, and the fact that both receive the same material from Liverpool Bay, evidence suggests that SPM pools in the two estuaries may be physically and/or geochemically quite dissimilar.

To further explore the relationship between K_D and salinity, $\log_{10}K_D$ values are plotted against $\log_{10}(S+1)$ according to Bale (1987) in Figure 5.2. Linear regressions have been applied to the ^{203}Hg data for bulk SPM and equations describing the lines of best fit which include the freshwater partition coefficient, $K_D{}^0$, and the constant, *b*, are included in the figure caption. It has long been recognised that Hg has a strong affinity for organic matter (e.g. Nyffeler *et al.*, 1984; Gagnon and Fisher, 1997; Turner *et al.*, 2001b). For this reason, POC data are also shown in Figure 5.2.

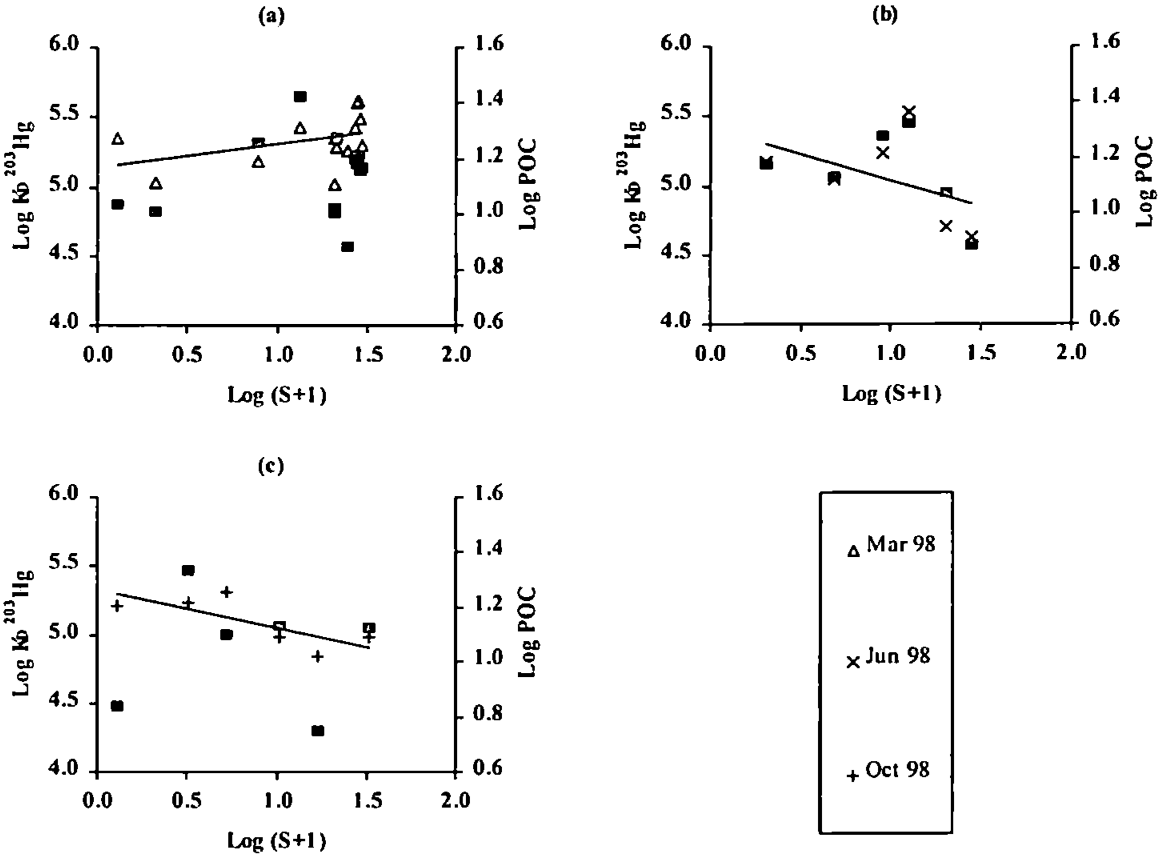


Figure 5.2 Linear regressions of $\log_{10}K_D$ ^{203}Hg versus $\log_{10}(S+1)$ and POC data (■) for bulk SPM in (a) March 1998, (b) June 1998 and (c) October 1998. Equations for the regression lines are: (a) $\log K_D{}^{203}Hg = 0.17\ (\pm\ 0.11)\ \log(S+1) + 5.13\ (\pm\ 0.14)$, ($R^2 = 0.18$); (b) $\log K_D{}^{203}Hg = -0.38\ (\pm\ 0.36)\ \log(S+1) + 5.41\ (\pm\ 0.37)$, ($R^2 = 0.22$); (c) $\log K_D{}^{203}Hg = -0.28\ (\pm\ 0.12)\ \log(S+1) + 5.33\ (\pm\ 0.12)$, ($R^2 = 0.58$).

The relationship between the partitioning of ^{203}Hg and salinity, both spatially and temporally, is somewhat erratic. Results from the March survey (Figures 5.1a and 5.2a) indicate that distribution coefficients for bulk SPM lie between 1.05×10^5 - 4.09×10^5 l kg^{-1} and that Hg increasingly favours the particulate phase as salinity rises. However, the error on the gradient of the regression line is quite large and indicates rapid changes in either aqueous or particulate chemistry along the estuary axis. Similar trends of increases in K_D for Hg with salinity have been noticed for Hg(II) by other authors (Li *et al.*, 1984a; Stordal *et al.*, 1996) and further comment upon this is provided later. Estimated values for K_D^0 of 1.35×10^5, 2.57×10^5 and 2.14×10^5 l kg^{-1} are produced for the March, June and October surveys, respectively. The relatively low K_D^0 for March coincides with the highest freshwater DOC concentration for the three surveys (10.6 mg l^{-1}), suggesting that Hg is retained more effectively in the dissolved phase in the REM by complexing with dissolved organic ligands. Sorption enhancement in the presence of dissolved organic matter has been observed in natural systems due to the greater affinity of organic complexes of Hg(II) (compared to inorganic species) for mineral surfaces (Xu and Allard, 1995). In contrast, for the Mersey in March, K_Ds increase as salinity rises and DOC concentrations simultaneously decline, which is reflected in a statistically significant negative correlation between estuarine DOC concentrations and K_Ds ($R^2 = 0.45$, $P \leq 0.01$). Thus, it may be implicated that the binding of Hg^{2+} to specific dissolved organic ligands is sufficiently strong at low to mid salinities to inhibit adsorption of ^{203}Hg to particle surfaces. However, the observed pattern in K_D correlates positively with dissolved oxygen concentrations during March ($R^2 = 0.38$, $P \leq 0.025$) suggesting that K_Ds are repressed due to high BOD exerted by bacteria in the upper estuary. The same general trends are exhibited for K_D and POC (Figure 5.2a), as general sorptive properties of particle surfaces are ameliorated by the presence of adsorbed organic matter (Zhou *et al.*, 1994), although the relationship between the two parameters is not statistically significant in this instance.

In June, when river flow is reduced to 29 m^3 s^{-1}, the influence exerted by salinity on Hg partitioning appears to be stronger although as in March, the strength of this relationship varies considerably throughout the mixing zone. Bulk SPM K_Ds range between 0.42×10^5 - 3.4×10^5 l kg^{-1} (Figure 5.1b). Estuarine K_Ds show a generally declining trend with salinity, although increased adsorption of Hg occurs between salinities of 8.2 - 11.7. These samples are taken from the TMZ where chlorophyll and suspended solids concentrations are at a maximum, DO is reduced and POC concentrations are enhanced. Significant positive correlations exist between K_D and turbidity ($R^2 = 0.90$, $P \leq 0.005$) and K_D and POC ($R^2 = 0.82$, $P \leq 0.01$). Although data are limited, it could suggest that the inverse of the 'particle concentration effect' described by Turner (1996) is occurring. Downestuary of the TMZ, K_Ds decline again due to reductions in POC and increasing interaction between Hg and seawater ions.

In October 1998, the distribution of ^{203}Hg is more uniform, with K_Ds for bulk SPM only varying between 0.69×10^5 l kg^{-1} and 2.05×10^5 l kg^{-1} (Figure 5.1c). A continuous trend of declining K_D with increasing salinity is observed. The relationship between K_D and POC (Figure 5.2c) is not as clear as for the other surveys ($R^2 = 0.34$). This could be due to either enhanced dilution of estuarine waters by a high river flow of 82 $m^3\ s^{-1}$ or increased uniformity in the amount or form of organic carbon present compared to the other two surveys. The high fluvial input promotes more effective mixing of fresh and saline waters and encourages the downestuary transport of SPM from which Hg is progressively lost to the dissolved phase.

Overall trends of declining K_D with increasing salinity as shown in Figures 5.1b,c and 5.2b,c imply that Hg uptake by SPM becomes progressively hindered as ionic strength of estuarine waters rise. This is due either to an increasing tendency for Hg(II) to form highly stable, soluble chloro-complexes with Cl^-, competition between Hg and other seawater ions or changes in the concentration and/or composition of estuarine particles. Jones (1978) suggested that intra-estuarine variations in K_DHg were predominantly due to dilution of the estuarine SPM pool by differing amounts of uncontaminated (marine) particles. It was also implied that estuaries that are inadequately mixed or which receive numerous and complex input sources will contain water masses having the same salinity but very different mixing histories and that this would also affect Hg partitioning along the salinity gradient.

The non-detrital fraction of ^{203}Hg held by Mersey SPM was determined by digesting bulk SPM, PSPM and TSPM from the uptake experiments performed in June and October 1998 with 1M HCl. The resulting data from these experiments are plotted against salinity in Figure 5.3. Results show that up to around 60% of the radiotracer is held in a leachable form (available to 1M HCl) on Mersey Estuary particles. The proportion of Hg released by the digest varies throughout the salinity gradient. The same pattern is produced for both June and October, despite the existence of underlying differences in particulate and water chemistry between the two surveys. On the whole, changes in salinity of ≤ 1 - ≥ 27 units causes an approximate 30 - 40% increase in the amount of non-detrital Hg leached from all SPM types. Chlorocomplexes are increasingly formed between mercury and chloride ions, leading to more efficient removal of Hg by the acid under increasingly saline conditions. Loss of the metal appears to be impeded at low salinities, the range of which varies seasonally (3.8 - 8.2 in June and 2.2 in October) and are related to the position of the TMZ in response to the magnitude of freshwater discharge. Given the analytical uncertainty, it can be seen that no real differences in leachable metal content exist between the two settled fractions of SPM, although there is a suggestion that at salinities exceeding 2 - 4, the radiotracer is held more effectively by TSPM than PSPM. This may indicate that Hg is bound to more inaccessible higher energy sites in TSPM, but is predominantly associated with surface (including organic) phases in PSPM. A maximum of 40% of ^{203}Hg is present in a leachable form and the majority of the metal is presumed to remain irreversibly bound to highly active sites located deep within particle matrices (and possibly in association with residual POC). This factor, combined with a long flushing time, the cyclic tidal pumping of particles into the upper estuary labyrinth and the dominance of TSPM in the TMZ contribute significantly to the long-term retention of Hg within the Mersey sediment reservoir as indicated in Section 4.3 of the previous chapter.

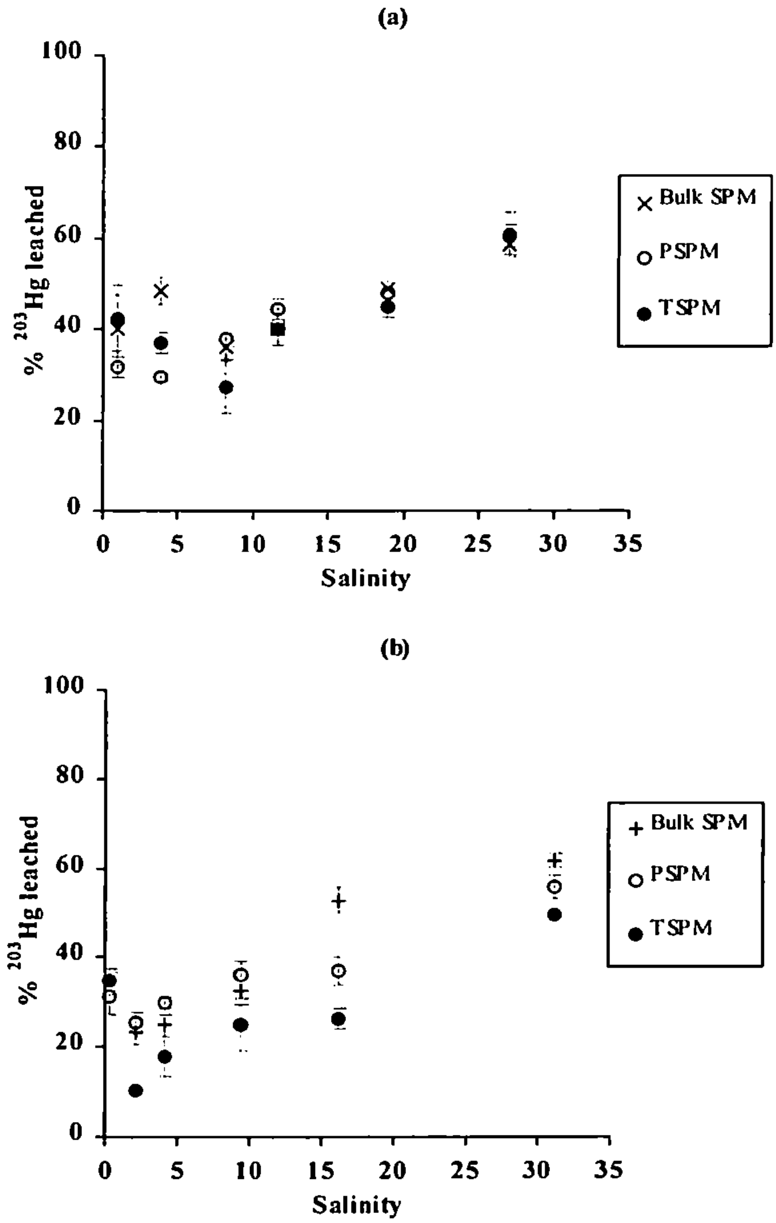


Figure 5.3 Percentage of ^{203}Hg released from bulk SPM, PSPM and TSPM by 1M HCl as a function of salinity in (a) June 1998 and (b) October 1998.

Other workers have interpreted the rise in ^{203}Hg K_Ds with increasing salinity (as observed in March 1998), in different ways. Li *et al.* (1984a,b) for example, ascribed this behaviour to the formation of hydroxide colloids through hydrolysis, possibly in combination with adsorption onto pre-existing colloids after which resulting radiocolloids coagulate into or onto suspended particles. Later, Turner *et al.* (2001b) attributed the same pattern observed in mixing experiments using samples from the Beaulieu, Mersey and Plym estuaries, to the process of salting out (a reduction in the solubility of Hg^{2+} or Hg(II)-organic complexes) *via* electrostriction or destabilisation-coagulation. They concluded that the biogeochemical behaviour of Hg resembled that of a neutral organic chemical rather than an inorganic ion and that the organically complexed species of Hg(II) salted out was dependent on the nature and concentration of DOC and POC available. For the Mersey, data indicated that Hg(II) complexes salted out were more hydrophobic than those from the Plym and Beaulieu. Large, alkylated molecules containing 16-26 C atoms and Hg-binding functional groups such as thiols (Loux, 1998), were presented as candidates. More specifically, industrially produced anthropogenic compounds are anticipated to exert a key role within the organic pool in the Mersey. These compounds would have greater aromaticity and contain more sulphur than naturally occurring ligands prevalent in the other two estuaries. An empirical sorption model was used by Turner *et al.* (2001b) to successfully describe the salinity-dependent salting out of Hg(II) in the presence of organic matter and the same approach was attempted in this work for the March survey data. However, this method proved inadequate in describing the observed variance in ^{203}Hg partitioning, which could be due to experimental differences between the two studies (Turner *et al.* (2001b) employed batch mixing experiments where salinity and turbidity were controlled and only riverine particles were used, whilst the current study used *in vivo* water samples of naturally varying water and particle composition).

The salting out theory has more recently been applied to interpret the phase distributions of other metals in the Mersey Estuary (Turner *et al.*, 2002). In this paper, salting constants were estimated for a number of classes of organic compound, including selected aromatic and aliphatic hydrocarbons, natural ligands such as humic acids, anthropogenic ligands, sedimentary organic matter and transition metal complexes. However, it was not possible to identify any specific organic ligands that may be responsible for the salting out effect in the Mersey. The seasonal changes observed in C:N ratios and metal partitioning data from this work (Figure 3.13) would tend to suggest that the metal behaviour ascribed to salting out is likely to be controlled, at least partly, by the periodicity of different pools of organic ligands in the estuary throughout the year.

As seen previously in Figure 5.2, the extent of ^{203}Hg uptake is linked to the amount of organic carbon on particles. Figure 5.4 further illustrates the effect of POC concentration on the sorption of inorganic Hg(II) to natural particles in seawater (S > 30), including results from this study. It is clearly demonstrated that sorption of Hg(II) to mineral surfaces is enhanced in the presence of organic matter. For example, Gagnon and Fisher (1997) demonstrated a 30-fold enhancement of Hg(II) sorption to montmorillonite in seawater when the clay had a coating of fulvic acid. Similarly, removal of POC from River Mersey bed sediment by 30% H_2O_2 (shown as the open and filled triangles in Figure 5.4) reduced Hg(II) sorption by 1-2 orders of magnitude (Le Roux, 2000).

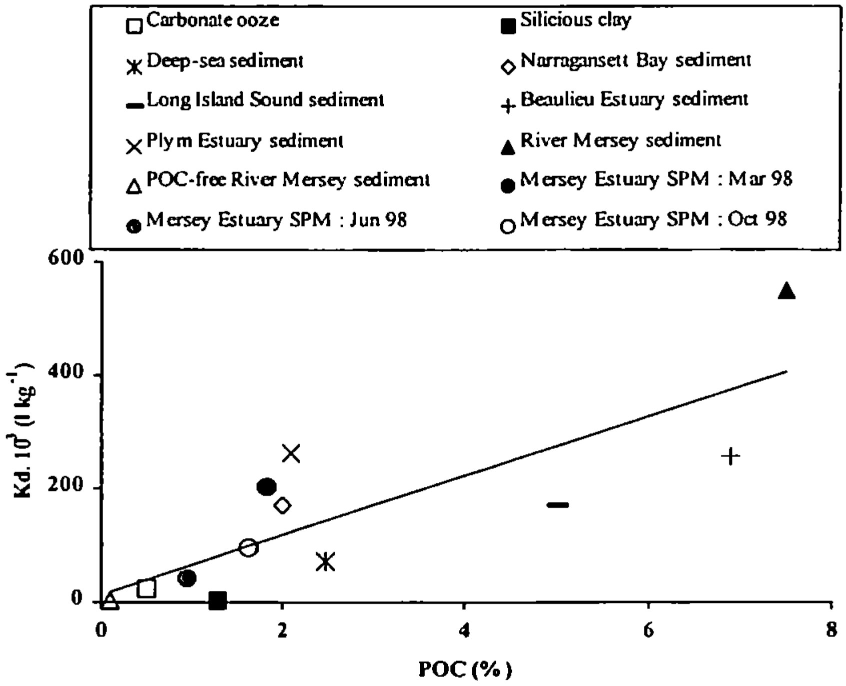


Figure 5.4 K_Ds defining the sorption of inorganic Hg(II) to natural particles in seawater versus POC concentration (after Turner *et al.*, 2001b). Data are from the following references: carbonate ooze, silicious clay and deep-sea sediment (Buchholtz *et al.*, 1986); Narragansett Bay (Nyffeler *et al.*, 1984); Long Island Sound (Gagnon and Fisher, 1997); Beaulieu, Plym and River Mersey sediments (Le Roux, 2000); Mersey Estuary SPM (this study, where S = 29.0 in March, 27.0 in June and 31.2 in October). The equation defining the trendline is $y = 52.23x + 13.42$ ($R^2 = 0.67$).

The association of Hg(II) with sedimentary organic matter is signified by the strong relationship between seawater K_D and POC content. Inclusion of data for Mersey SPM reduces the value for R^2 by as little as 2% and the correlation retains the same level of significance ($P \leq 0.005$) as in the original graph in Turner *et al.* (2001b). The degree of scatter implies that the chemical nature of POC (age, polarity, and aromaticity) is highly variable between aquatic systems. Data for Mersey SPM indicate that seasonal alterations in the amount of POC available are fairly minimal, but that the type of POC present (whether allochthonous, autochthonous or anthropogenic in origin) may be critical to the partitioning process.

The partitioning of ^{203}Hg (expressed as logK_D) in bulk SPM, PSPM and TSPM, as a function of total suspended solids concentration is presented in Figure 5.5. Each data point represents the percentage of added Hg present in the particulate phase (calculated from the measured activities of ^{203}Hg in filtrates and on filters) found by using Equation 4.5 (Chapter 4, Section 4.2.4). Also shown are the Environment Agency data for stable Hg.

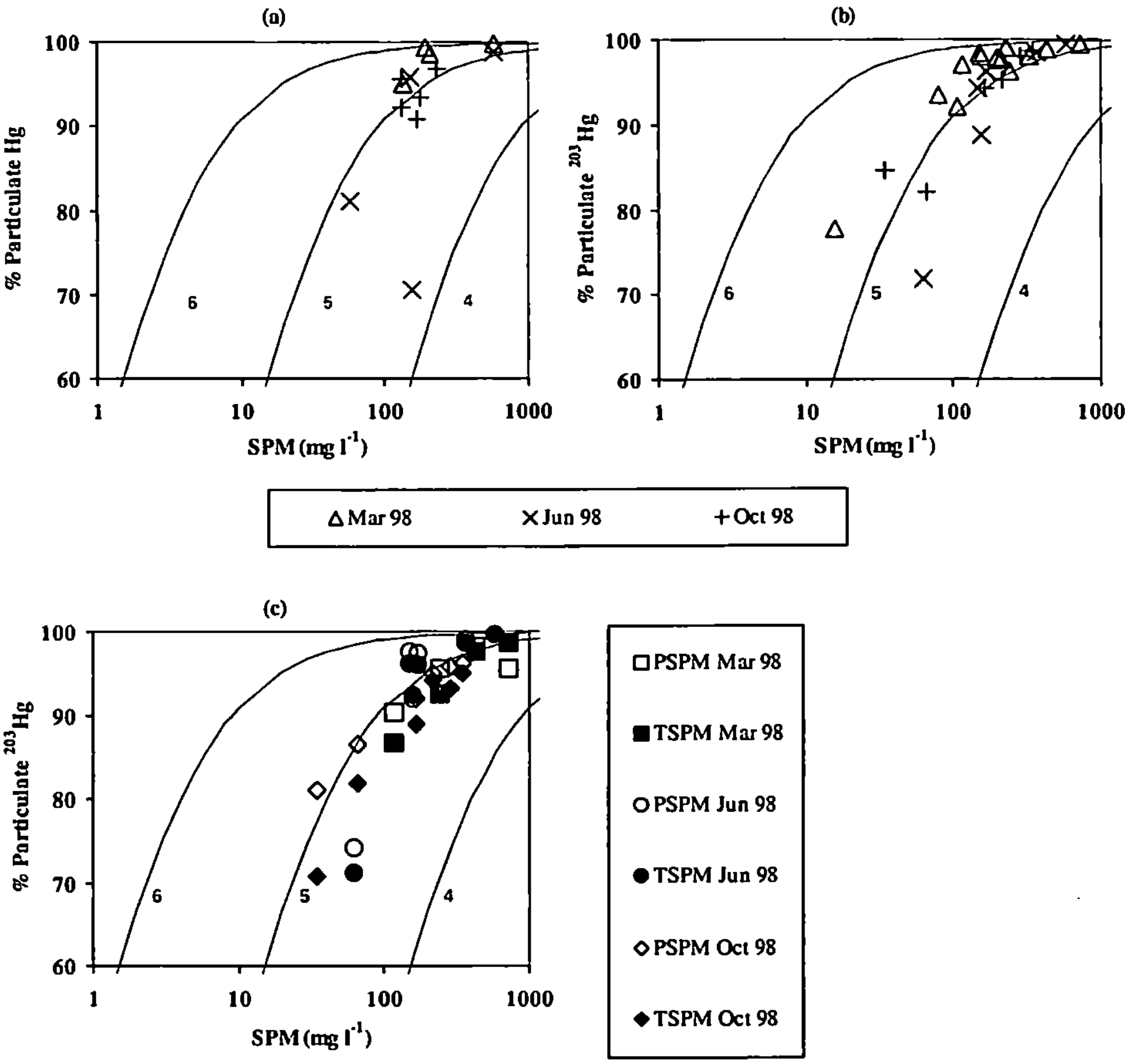


Figure 5.5 Variations in percentage particulate Hg with SPM concentration for (a) EA measurements of stable Hg, (b) ^{203}Hg in bulk SPM and (c) ^{203}Hg in PSPM and TSPM. The isopleths represent lines of constant K_D for which the $\log_{10}K_D$ values are indicated.

The solid-phase partitioning of stable Hg (Figure 5.5a) is generally in accord with that for ^{203}Hg (Figure 5.5b,c) and any differences can be explained by the different methodologies used. The trends exhibited are notably uniform, with the data consistently fitting a K_D of approximately 10^5, which rises to 10^6 when suspended loads approach those in the TMZ. This constancy is particularly striking, as the data have been obtained over three seasonally distinct survey periods when environmental conditions have varied significantly. A consistently high particle affinity of Hg similar to that of Pb (Figure 4.10e) is demonstrated. Regardless of the time of sampling, at least 70% (increasing to 99.9% in highly turbid waters) of Hg present is in the particulate phase and this, together with other indications in Chapters 3 and 4, may be reaffirming the presence of aged and relatively homogeneous SPM. Adsorption of Hg generally rises as turbidity increases and higher (but variable) adsorptive capacities are repeatedly expressed by PSPM over TSPM. It should be noted that incubation studies used a total of 25 separate water samples for bulk SPM whilst 16 were used in settling experiments and this explains apparent 'missing' data when comparing Figures 5.5b and 5.5c. Deviations from the line describing a K_D of 10^5 occur when SPM concentrations are relatively low and/or particulate carbon is reduced. For example, the two points in June that lie to the right of the 10^5 isopleth in Figures 5.5a,b correspond to samples containing the least POC (0.76% and 1.17%). The relationship between POC and the fraction of particulate Hg in Mersey SPM is further illustrated in Figure 5.6. The dependence of particulate Hg on particulate organic carbon is highly

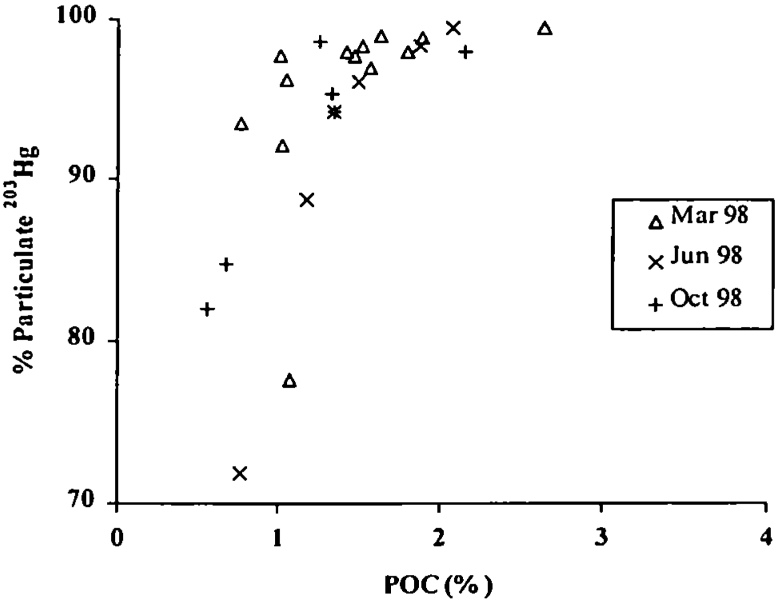


Figure 5.6 Seasonal variations in percentage particulate ^{203}Hg in bulk SPM as a function of particulate organic carbon content.

significant in June (low flow, R^2 = 0.92) and October (high flow, R^2 = 0.86), but far weaker in March (intermediate flow, R^2 = 0.24). Phytoplankton contributions to total POC are fairly high in June 1998 (Figure 3.12b). Detrital POC, largely exhibited by higher C:N ratios indicative of terrestrial organic matter such as decaying higher plant material, humic and fulvic compounds have also been identified in both June and more especially, in October 1998 (Figures 3.12a and 3.13). As discussed previously, salting out of Hg is suggested in March. This mechanism may be responsible in some way for producing the lack of correlation between particulate Hg and particulate organic carbon. Specifically, the nature and elevated concentrations of dissolved ligands (Table 5.1) may be more crucial at this time. Carbon:nitrogen ratios in SPM from the March 1998 survey show a dominance of sewage-related POC (Figure 3.13) and this may be contributing to the salting out process. Thus, the prevalence of any one type of POC in the estuary at the time of sampling or even at a given location appears to play a major part in the phase partitioning of Hg in the Mersey.

The radiotracer experiments described in this work have shown that salinity, particle concentration and the nature and concentration of POC and DOC all have a role in influencing the transport and sorptive behaviour of inorganic Hg(II) in the Mersey Estuary. Results indicate that both salting out and reduced uptake of Hg can occur with increasing salinity, depending on the specific environmental conditions encountered at the time. Experiments have shown that due to its high particle reactivity, the loss of Hg from SPM traversing the salinity gradient would, in theory, be minor compared to, for example, Cd. In addition, any dissolved Hg released into solution could be highly susceptible to salting out *via.* electrostriction or coagulation and particularly if raw or partially treated sewage is present, to subsequently become (re-)adsorbed to sedimentary organic matter and therefore be largely retained within the system. Comprehensive monitoring of Hg has been performed in the Mersey since significant reductions in Hg loads to the estuary began in 1974 (Harland *et al.*, 2000). However, the authors describe inconsistent declines in bed sediment Hg concentrations, which have partly been attributed to the mobilisation of Hg from subsurface layers of previously consolidated saltmarsh sediments. The additional Hg recycling mechanism outlined above, combined with the near-field deposition of resuspendable TSPM and upestuary accumulation of fines by vigorous tides may provide additional explanations as to why the loss of particulate Hg from estuarine sediments is not proceeding as rapidly as expected (see Section 4.3).

5.2 Mechanisms of metal remobilization in the Mersey Estuary

So far in this thesis, work has largely concentrated on identifying the underlying physical and geochemical conditions in the Mersey and how seasonal and axial changes in a range of estuarine parameters influence the distribution and reactivity of particulate trace metals. Waters and particles have been characterised and the data have provided insights into the means by which the attenuation of trace metal concentrations at current levels has been allowed to occur. More specifically, it has been suggested that the loss of particles and associated contaminants from the estuary is likely to be relatively insignificant. As the continuing removal of historical metal burdens in the estuary is more likely to occur from loss *via* the dissolved phase, the discussion in this section focuses on three routes by which this may be achieved and assesses the relative importance of each in terms of further progress in restoration.

Analyses of total dissolved metals (Cd, Co, Cu, Ni, Pb and Zn) collected during some of the same axial transects as this study, demonstrated that with the exception of Cu, metals displayed positive deviation from conservative behaviour (Martino, 2000). Furthermore, the positions and magnitudes of peaks varied between metals, due largely to differences in their reactivity and the rate of fluvial input on the day of sampling. Using data from Martino (2000) and this work, it has since been suggested that internal metal sources could supply additional dissolved metals to the water column (Martino *et al.*, 2002). This is thought to arise because fine-grained (< 63 μm) bed sediments show up to a 6-fold enrichment of Cd, Co, Cu, Ni, Pb (and C) compared to SPM, which is exemplified in the summary diagram provided in Figure 5.7. Higher trace metal concentrations would normally be expected to occur in SPM since suspended particles are significantly enriched with Fe and Mn (by a further 60%) compared to those at the bed. Thus metal on SPM is at equilibrium with dissolved metal in the water column, whilst the bed sediment supports a surplus of metal, which is upheld by physico-chemical conditions occurring near or within the bed.

5.2.1 Porewater processes

One possible source of dissolved metals is the interstitial waters of heavily contaminated sediments in the upper 5 km of the estuary. Depending on the prevailing wind, the saline intrusion penetrates as far as Howley Weir in Warrington when high water elevations at Liverpool are predicted to be at least 9.2 m whereas the tidal excursion on neap tides barely

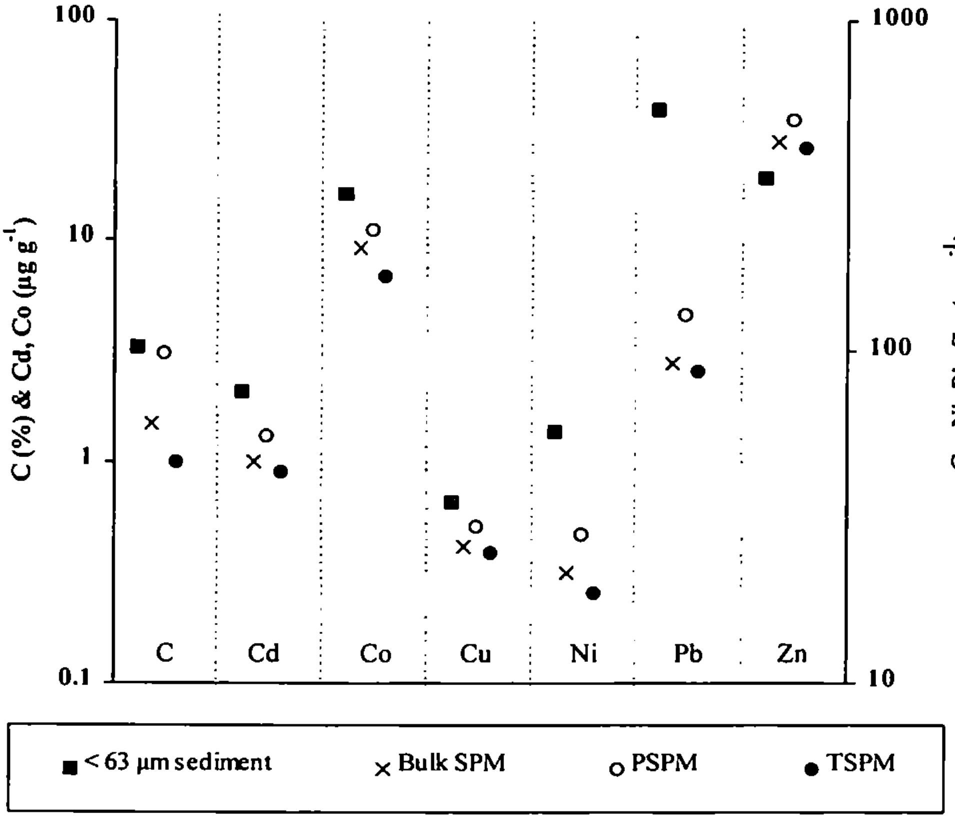


Figure 5.7 Field diagram summarising the mean non-detrital trace metal content (available to 1M HCl) of Mersey Estuary particles. Carbon data refer to total particulate carbon and are expressed as the percentage contribution to dry mass.

approaches the tidal limit (P. Jones, EA, pers. comm.). It is feasible that early sediment diagenesis may occur during the considerably smaller and less energetic neap tides, particularly during the summer months when DO saturation is more effectively repressed in the upper estuary. Subsequent sampling and analysis of water samples collected during springs may, in part, contain elevated concentrations of dissolved metals that have been mobilised through early diagenesis and then released from sediment porewaters by vigorous tidal stirring. For this mechanism to support the observed dissolved metal maxima reported by Martino (2000), porewater concentrations must exceed ambient concentrations in the overlying water column, as illustrated below.

The upper 5 km of the estuary has an average depth of 5 m and width of 100 m, giving rise to 5 m^3 of water per unit area of water surface. The same area of sediment has a porewater volume of 0.04 m^3, assuming that the tidal incursion mixes sediments to a depth of 20 cm and the sediments have a porosity of 80%. This results in a tidally induced water column: porewater mixing ratio of the order of 125. Porewater concentrations of dissolved metals must therefore exceed concentrations in the water column by at least two orders of magnitude for porewater inputs to account for the observed dissolved metal maxima. Table 5.2 shows the derivation of porewater concentrations of dissolved metals based on known maximum observed deviations of dissolved metal concentrations from the TDL. Here it is assumed that porewater infusion alone, accounts for dissolved metal addition. Porewater concentrations are simply estimated by multiplying the maximum concentration above the TDL by 125 (e.g. for Cd: 0.45 μg l^{-1} x 125 = 56.3 μg l^{-1}).

Table 5.2 The estimation of sediment porewater concentrations in the extreme upper region of the Mersey Estuary.

			Metal			
Parameter	**Cd**	**Co**	**Cu**	**Ni**	**Pb**	**Zn**
Maximum concentration above TDL (μg l^{-1})	0.45	1.47	1.27	2.94	0.84	9.81
Porewater: water column ratio	←			125		→
Estimated porewater concentration (μg l^{-1})	56.3	184	159	368	105	1226

The resulting porewater concentrations probably describe the maximum concentration of each metal in interstitial waters as they have been based on the greatest positive deviations from conservative mixing of total dissolved metals from the four campaigns conducted between December 1997 and October 1998. It is unlikely that these concentrations would be maintained when they are being diluted down to a depth of 20 cm on successive tidal cycles. Nevertheless, it is believed that the abundance of metals contained within mobile and predominantly fine-grained sediments in this section of the estuary, combined with earlier evidence for processes that could support the onset or maintenance of diagenesis, could supply the necessary conditions for producing the observed dissolved metal maxima. Additionally, as explained earlier, this mechanism is only anticipated at the onset of large spring tides (and especially during the warmer months), rather than being a frequent occurrence, thus providing a longer time scale for the re-equilibration of metal concentrations in sediment porewaters.

Estimated porewater concentrations for the upper Mersey are compared with those measured in other areas in Table 5.3. The data suggest that porewater metal concentrations

Table 5.3 Trace metal porewater concentrations in bed sediments from a variety of aquatic environments.

Site	Mean porewater concentration ($\mu g\ l^{-1}$) Cd	Co	Cu	Ni	Pb	Zn	Reference
Ansedonia Bay, Tyrrhenian Sea	0.21	2.89	1.72	5.87	1.10	23.5	Ciceri *et al.* (1992)
Conway Estuary	-	490	210	490	300	260	Elderfield *et al.* (1971)
Gullmarsfjorden, Sweden	0.0044	0.071	0.13	0.76	0.17	0.58	Sundby *et al.* (1986)
Upper Mersey Estuary **(estimated)**	56.3	184	159	368	105	1226	This study
Quartermaster Harbour, Puget Sound	3.03	-	5.66	3.05	-	-	Emerson *et al.* (1984)
Sabin Point, Narragansett Bay	-	-	4.45	2.35	-	-	Elderfield *et al.* (1981)
Tees Estuary	-	46.0	365	-	-	62.1	Elderfield *et al.* (1971)

in Mersey sediments could be more comparable to those of the Tees and Conway estuaries than the other systems. The tidal Tees was described in the 1970s as 'grossly polluted' by the Northumbrian River Authority (Elderfield and Hepworth, 1975), whilst the Conway is relatively free of anthropogenic inputs but does receive trace metals from mine spoil tips and Pb-Zn mineralisation in the catchment (Elderfield *et al.*, 1971). A notable feature of Table 5.3 is the exceptionally high estimated Zn porewater concentration in Mersey sediments, which is a factor of 5 greater than that in the Conway and 20 times that of sediments in the Tees Estuary. For the Mersey, this could signify an important route for the reduction of Zn in sediments as energetic disturbance of surface sediments and the replacement of large tidal volumes during spring tides could lead to substantial declines in Zn concentrations over a relatively short time. Porewater concentrations of Co, Cu, Ni and Pb in the Mersey are consistently lower than in the Conway, but the difference between the two estuaries is highly variable. Concentrations of Co in Mersey porewaters are intermediate between those of the Tees and Conway whilst Mersey Cu porewater concentrations are low compared to the other two estuaries. For Mersey sediments, the magnitude of porewater concentrations follows the sequence Cd < Pb < Cu < Co < Ni < Zn. Elderfield and Hepworth (1975) showed that the relative stabilities of metal complexes in sediment porewaters from the Conway and Tees matched the Irving-Williams series of metal-ligand stabilities, implying that trace metal mobility in estuarine sediments is controlled by organic matter. Data for the Mersey do not follow the same order and this may be reinforcing the concept that organic ligands in the Mersey are chemically different to those in other estuaries. It is nevertheless suggested that in the Mersey, the importance of metal release from porewaters differs between metals. For example, for those metals in the second half of the series above, porewater infusion may assume increasing importance, whilst those to the left supply metals to the water column *via* another mechanism, such as desorption from resuspending sediments, as described in the following section.

5.2.2 Desorption from resuspending particles

Desorption (and dissolution) of metals from SPM could also give rise to the dissolved metal maxima observed in the Mersey by Martino (2000). Desorption from pre-suspended, advected or resuspended particles can occur in a variety of ways (Garnham *et al.*, 1991; Paalman *et al.*, 1994; Schlekat *et al.*, 1998; Turner *et al.*, 2002). Particles traversing the salinity gradient may release metals as dissolved seawater ions compete for sorption sites or complex with sorbed metals. Resupending particles that are enriched with metals compared to ambient particles in the water column (as shown for Cd, Co, Ni and Pb in Figure 5.7), may also release metals and this may be assisted by local changes in redox conditions and pH or by bacterial or chemical breakdown of particulate organic matter.

Martino *et al.* (2002) tested the likelihood and extent of metal desorption from contaminated resuspending particles by applying an empirical sorption model, that was originally used by Morris (1986) to predict the extent of trace metal removal onto resuspended bed particles in the vicinity of the Tamar Estuary TMZ:

$$\frac{C}{C_R} = \frac{[1 + K_D * SPM_r]}{[1 + K_D * SPM_r + K_D * SPM_a(1-\alpha)]} \qquad \text{Equation 5.1}$$

In the model, the ratio of dissolved metal concentration in a zone of high turbidity to that in river water, C/C_R, is determined by the concentration of additional (resuspending) particles, SPM_a, above the background turbidity of river water, SPM_r, the particle-water distribution coefficient, K_D, and the term α, which defines the extent of metal depletion on resuspending particles compared to those at equilibrium in the overlying water column. Resuspending particles may hold an over-abundance of metals relative to equilibrium in the water column if: (a) less readily exchangeable metals are held on binding sites of slightly higher energy; (b) metals are adsorbed on multiple layers; and (c) the particles have temporarily equilibrated in a dissolved metal-rich environment such as the interstitial waters of contaminated bed sediment (as discussed in the previous section). This study and those of Harland *et al.* (2000) and Turner (2000), have demonstrated that the accumulation and retention of trace metals in bed sediments and the hydraulic dispersal of bed particles within the Mersey are highly consequential and could favour application of the model to explain dissolved metal distributions in the low salinity zone.

Dissolved Co and Pb showed greatest addition in the estuary and these two metals were modelled using Equation 5.1 by Martino *et al.* (2002). The model has been developed further in the present work by the inclusion of a 'mixing factor' to account for changes in C/C_R caused by mixing and dilution by seawater along the salinity gradient. This is equivalent to the fractional freshwater concentration used by Dyer (1997):

$$\text{Mixing}\frac{C}{C_R} = \frac{C}{C_R} * \frac{S_{max} - S_a}{S_{max}} \qquad \text{Equation 5.2}$$

where S_{max} corresponds to the maximum surface salinity measured by the EA during quarterly tracking surveys in Liverpool Bay (from the EA NACOMS data archive) and S_a corresponds to the ambient salinity in any given segment of the estuary. Equations 5.1 and 5.2 have been used together to calculate estuarine-riverine dissolved metal concentration ratios for Cd, Co, Ni, Pb and Zn for the four axial transects from which dissolved metal concentrations were measured. Ratios for Cd, Co, Pb and Zn were determined using radiochemically-generated equilibrium K_Ds from the literature whilst those for Ni employed equivalent K_Ds from Martino (2000). Values for SPM_r were taken as mean particle concentrations above the tidal limit for each sampling occasion and SPM_a values as the difference between estuarine particle concentrations and SPM_r. Values for α were used that gave the closest fits to measured concentration ratios and, as such, therefore do not describe any changes in equilibrium sediment-water partitioning induced by alterations in salinity. The results for Cd, Co, Ni, Pb and Zn are presented collectively in Figure 5.8.

Generally, observed and predicted peak concentrations of dissolved metals are shown to occur in freshwater or the low salinity region, where salinity-induced desorption is anticipated to play a minor role. Agreement between measured and modelled C/C_R ratios tend to decline with progression down the estuary due to changes in equilibrium sediment-water partitioning and maximum values of measured and modelled C/C_R are not always coincident. This is presumed to arise partly because desorption occurs more slowly than the rates of particle resuspension and settling. Furthermore, axial gradients in pH, DO and

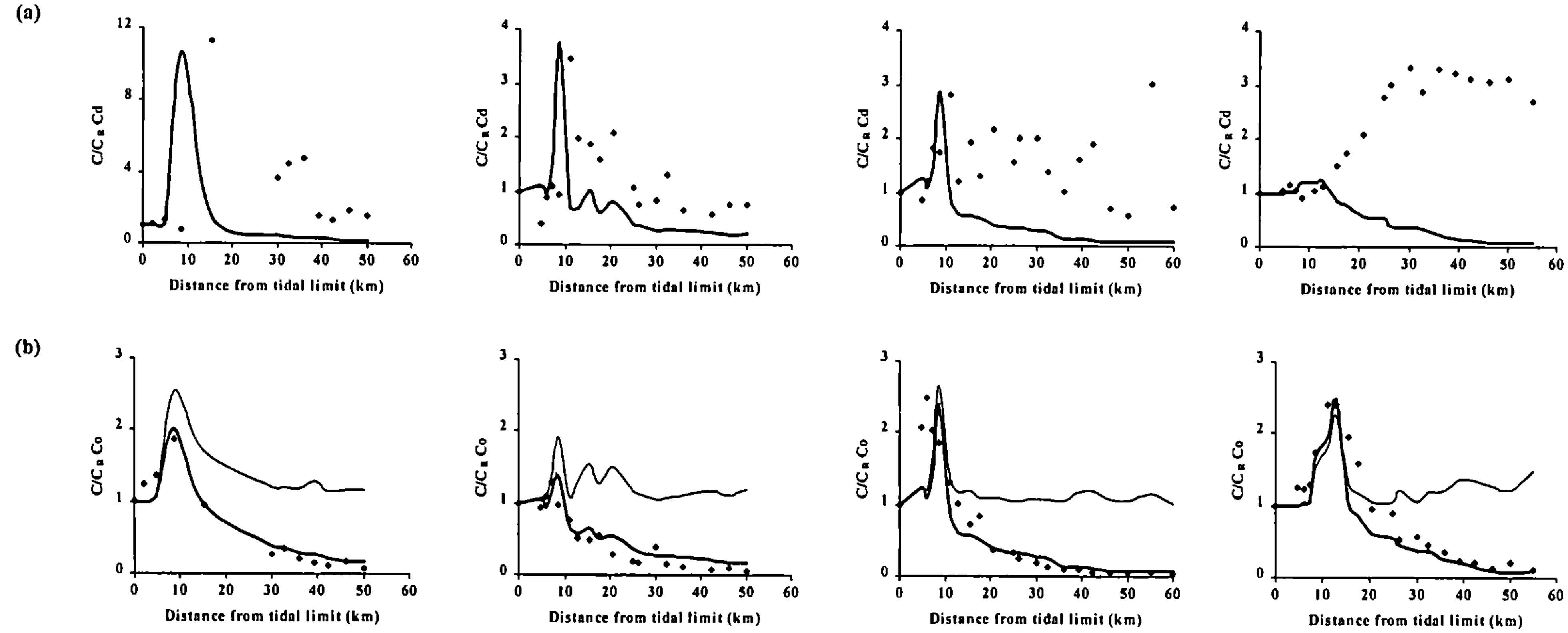


Figure 5.8 The extents of desorption of (a) Cd and (b) Co, as dissolved estuarine to riverine concentration ratio, C/C_R, as a function of distance from the tidal limit. Measured (◆) and modelled (thick line) C/C_R ratios are given. Modelled C/C_R ratios for Co from Martino *et al.* (2002) are indicated by the thin line.

The full line for Cd is predicted using $K_D = 1.7 \times 10^4$ l kg^{-1} (Li *et al.*, 1984) and (in sequence) $\alpha = 1.016$ (December 1997); $\alpha = 1.055$ (March 1998); $\alpha = 1.008$ (June 1998); $\alpha = 1.030$ (October 1998).

The full line for Co is predicted using $K_D = 3.1 \times 10^5$ l kg^{-1} (Li *et al.*, 1984) and (in sequence) $\alpha = 1.010$ (December 1997); $\alpha = 1.025$ (March 1998); $\alpha = 1.007$ (June 1998); $\alpha = 1.070$ (October 1998).

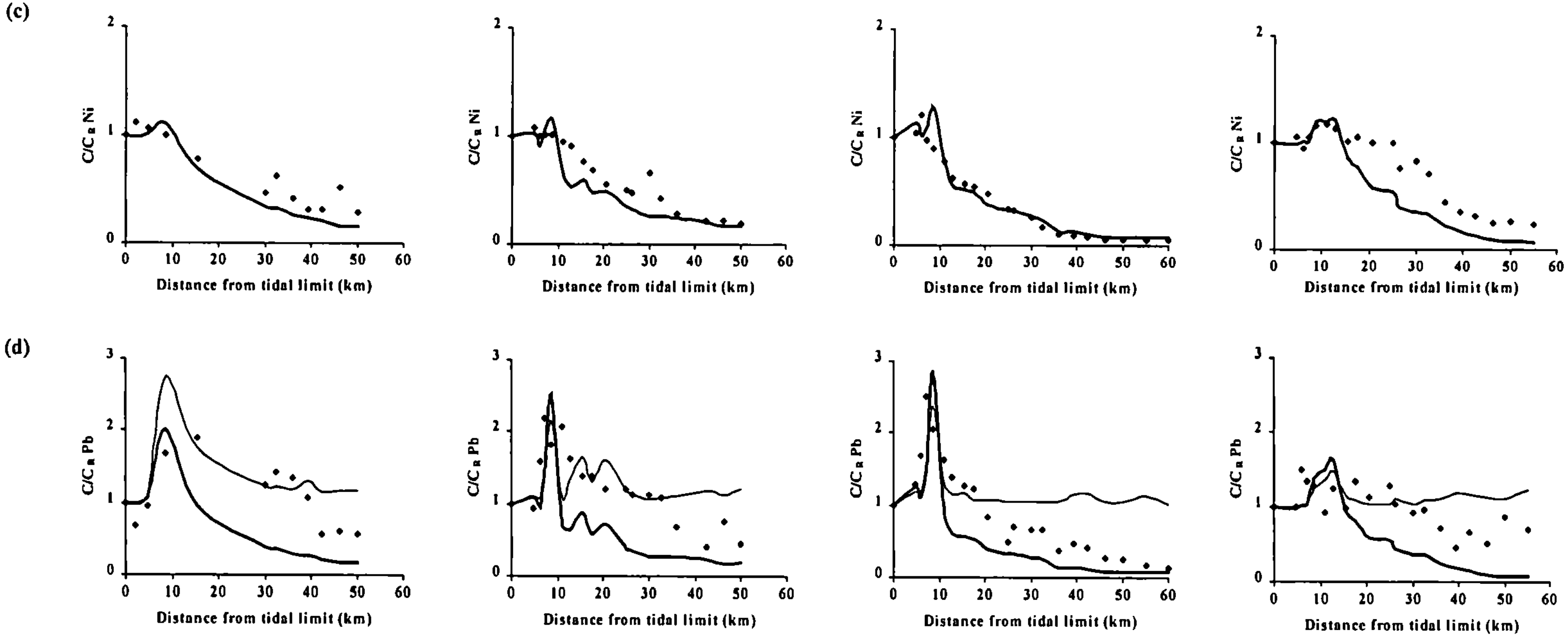


Figure 5.8 The extents of desorption of (c) Ni and (d) Pb, as dissolved estuarine to riverine concentration ratio, C/C_R, as a function of distance from the tidal limit. Measured (◆) and modelled (thick line) C/C_R ratios are given. Modelled C/C_R ratios for Pb from Martino *et al.* (2002) are indicated by the thin line.

The full line for Ni is predicted using $K_D = 2.93 \times 10^3$ l kg^{-1} (Martino, 2000) and (in sequence) $\alpha = 1.004$ (December 1997); $\alpha = 1.030$ (March 1998); $\alpha = 1.005$ (June 1998); $\alpha = 1.030$ (October 1998).

The full line for Pb is predicted using $K_D = 1.0 \times 10^5$ l kg^{-1} (Baskaran *et al.*, 1997) and (in sequence) $\alpha = 1.010$ (December 1997); $\alpha = 1.035$ (March 1998); $\alpha = 1.008$ (June 1998); $\alpha = 1.050$ (October 1998).

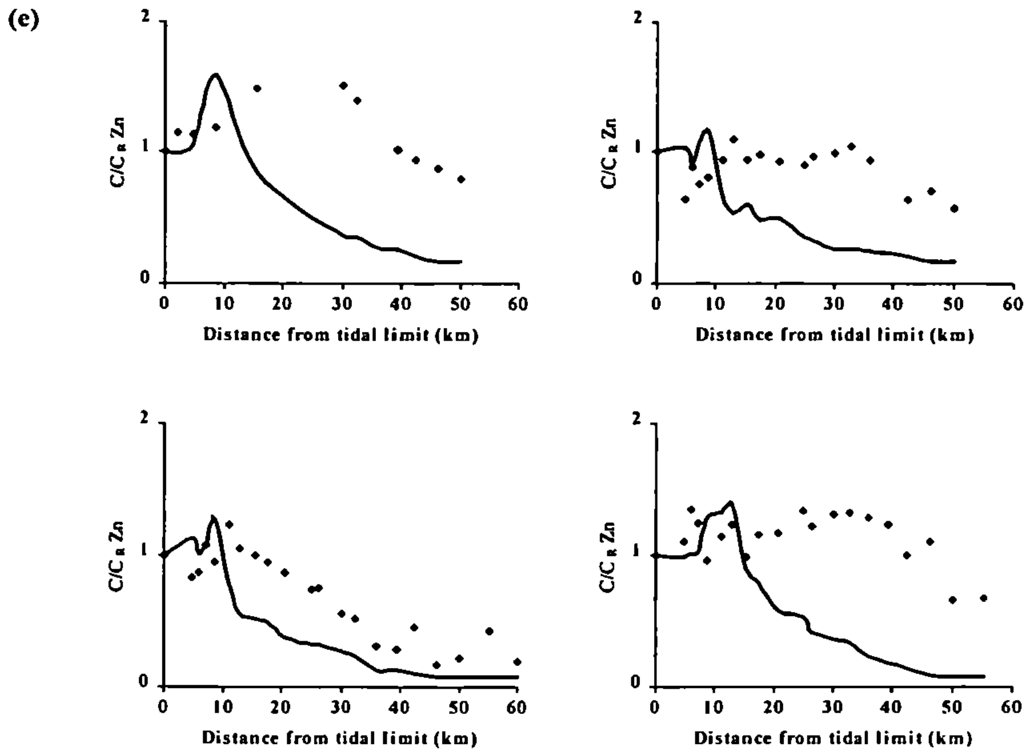


Figure 5.8 The extent of desorption of (e) Zn as dissolved estuarine to riverine concentration ratio, C/C_R, as a function of distance from the tidal limit. Measured (◆) and modelled (thick line) C/C_R ratios are given.

The full line for Zn is predicted using $K_D = 1.2 \times 10^4$ l kg^{-1} (Li *et al.*, 1984) and (in sequence) $\alpha = 1.008$ (December 1997); $\alpha = 1.030$ (March 1998); $\alpha = 1.005$ (June 1998); $\alpha = 1.040$ (October 1998).

carbon can produce changes in water or particulate chemistry resulting in shifts in metal solid-solution partitioning as previously discussed in Sections 4.2 and 5.1. The extent of metal enrichment required to produce dissolved metal maxima appears to be directly related to river flow for some metals. Regression analyses of α values against river flow rates for the day of sampling gave rise to R^2 values of 0.99 for both Zn and Ni, and 0.95 for Co (where $P \leq 0.05$, n = 4). This implies that due to natural dilution effects resulting from elevated freshwater volume flows, higher concentrations of available Co, Ni and Zn need to be present on bed particles in order to favour desorption and give rise to the observed dissolved metal peak concentrations.

Minimal metal enrichment of bed sediment relative to SPM ($\leq$ 7%) is necessary to reproduce the magnitude of observed dissolved metal peaks in the upper reaches of the estuary. Thus, desorption from resuspended fine-grained mobile sediment in the Mersey could supply a sizable and persistent source of metal to the water column and it is likely that decontamination of bed sediments in this way could take many years (refer to Table 4.12 for example), despite reductions in the number of direct metal sources into the estuary mixing zone. This mechanism is predicted to occur in moderately to highly contaminated estuaries that are physiographically and hydrographically similar to the Mersey and where dissolved metal addition is reported. Conversely, for macrotidal estuaries where metal contamination is relict, partly mineralised or insignificant and bed sediment is depleted in trace metals relative to SPM, adsorption of dissolved metals in the TMZ would be observed, as demonstrated by Ackroyd *et al.* (1986) for the Tamar.

5.2.3 Desorption from seaward-fluxing particles

Application of the desorption model outlined above appears to have worked reasonably well (especially for Co and Pb) in predicting the locations and magnitudes of dissolved metal concentrations but, as mentioned previously, cannot account for salinity-induced desorption from seaward-fluxing SPM. Axial variations in suspended particulate metal concentrations are relatively minor in the Mersey for most of the metals studied (see Figure 4.2). Consequently, loss of labile metal from any particles traversing the salinity gradient may be negligible. Nevertheless, a secondary diffuse (and desorptive) source of dissolved metals may be responsible for the deviations in conservative behaviour observed in the mid-outer estuary (Figure 5.8) and requires investigation. By way of example, Williams and Millward (1998) showed that it was theoretically possible for the desorption of Zn from PSPM to contribute significantly to mid-estuarine dissolved Zn maxima in the Humber Estuary.

Salinity-induced desorption of metals is dependent on the condition that a proportion of the adsorbed metal is held reversibly or exchangeably (Li *et al.*, 1984a; Turner *et al.*, 1993). The extent of desorption can be quantified from mass balance of labile metals on SPM encountering the salinity gradient (Li *et al.*, 1984a), as given by Equation 5.3. The salinity dependence of K_D is given by Equation 5.4 (Turner and Tyler, 1997).

$$\frac{C}{C_R} = \frac{SPM * K_D{}^0 + 1}{SPM * K_D{}^S + 1} \qquad \text{Equation 5.3}$$

and

$$K_D{}^S = K_D{}^0 * (S + 1)^{-b} \qquad \text{Equation 5.4}$$

The ratio C/C_R again corresponds to the increase in concentration of metal in solution relative to that in river water, SPM is the concentration of suspended particulate matter, K_D^0 is the partition coefficient in river water, K_D^S is the partition coefficient in estuarine water of salinity S and *b* is the slope factor. Values of K_D^0 and *b* obtained from radiochemical experiments involving the adsorption of ^{109}Cd and ^{65}Zn (Le Roux, 2000) and ^{63}Ni (Martino, 2000) onto Mersey SPM as a function of salinity are reported for June and October 1998 in Table 5.4.

Table 5.4 Values of the parameters K_D^0 and *b* obtained from radiochemical experiments.

Survey	Radiotracer	K_D^0 (l kg^{-1})	*b*
June 1998	^{109}Cd	41 700	-0.46
	^{63}Ni	2 930	-0.018
	^{65}Zn	6 000	0.23
October 1998	^{109}Cd	37 440	-0.55
	^{63}Ni	-	-
	^{65}Zn	12 100	0.028

Using Equations 5.2, 5.3 and 5.4 in combination, the extent of desorption from seaward-fluxing PSPM can be estimated. Dissolved metal concentration ratios have been calculated using data from Table 5.4, the known salinity distribution, the maximum surface salinity in Liverpool Bay and PSPM concentrations at each sampling site for the June 1998 and October 1998 surveys and these are displayed alongside measured ratios as a function of distance along the estuary in Figure 5.9. Salinity-induced desorption is only suggested for Zn in June 1998 (Figure 5.9c(i)). In October 1998, the freshwater K_D for Zn is doubled, which signifies an alteration in particulate chemistry. Concentrations of Fe and Mn in riverine SPM are reduced in October 1998 due to the high river flow (Figure 4.2a,c). Increased sorptive capacity results instead from a > 20% decrease in REM particulate organic carbon in October 1998, compared to that of June 1998 (Figure 3.11a). Concomitantly, the slope factor describing the change in partitioning with increasing salinity is reduced by almost an order of magnitude from June to October 1998.

Due to the nature of the calculations used, changes in K_D^0 do not affect the final C/C_R ratio but C/C_R will be affected by a change in *b*, and it is this which produces the lack of agreement between measured and modelled C/C_R for Zn in October 1998 as *b* approaches zero. The calculations assume that estuarine K_Ds are a function of salinity alone and are independent of any other factors that may be influencing either particle character or water chemistry, which as this study has already shown, is unrealistic. As values of *b* for Cd and Ni are negative, C/C_R values < 1 are generated by the model.

A comparison of modelled C/C_R ratios describing desorption of Zn from both resuspending and seaward-fluxing particles in June 1998 is provided in Figure 5.10. The magnitude of maximum modelled C/C_R is the same for both models (1.28) but occur at slightly different locations. As axial changes in salinity are only accounted for in the second model,

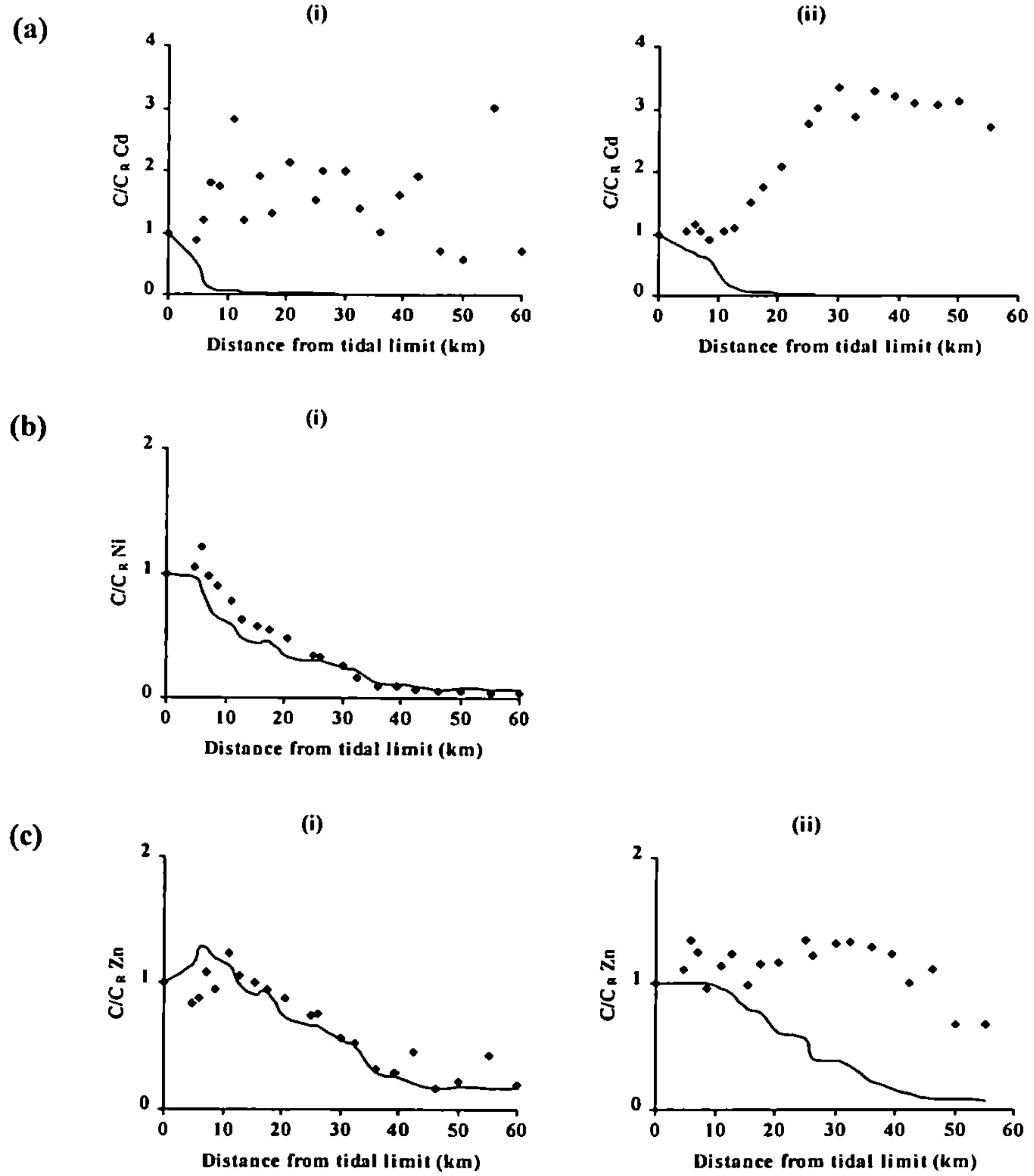


Figure 5.9 The extent of desorption, expressed as the dissolved estuarine to riverine concentration ratio, C/C_R, of (a) Cd, (b) Ni and (c) Zn from seaward-fluxing SPM in (i) June 1998 and (ii) October 1998 as a function of distance from the tidal limit. Measured (◆) and modelled (—) C/C_R ratios are given.

agreement between measured and modelled ratios using a variable population of seaward-fluxing PSPM is better with distance along the estuary than for the first model, although the latter does partly account for the removal of dissolved Zn in the upper estuary. Maximum C/C_R due to desorption from PSPM is predicted to occur at a salinity of 3.8 and 2.5 km upstream of the TMZ, where in June 1998, salinity reached 11.7. It is feasible therefore that either or both desorption mechanisms may be responsible for producing the observed dissolved Zn profile measured for the June 1998 survey. Whilst it is acknowledged that desorption from resuspending particles in the TMZ and low salinity zone is likely to produce the most prominent dissolved metal peaks in the upper estuary, it is proposed that a smaller secondary input may be provided through salinity-induced desorption if geochemical and/or hydrodynamic conditions are favourable for a particular metal at that time.

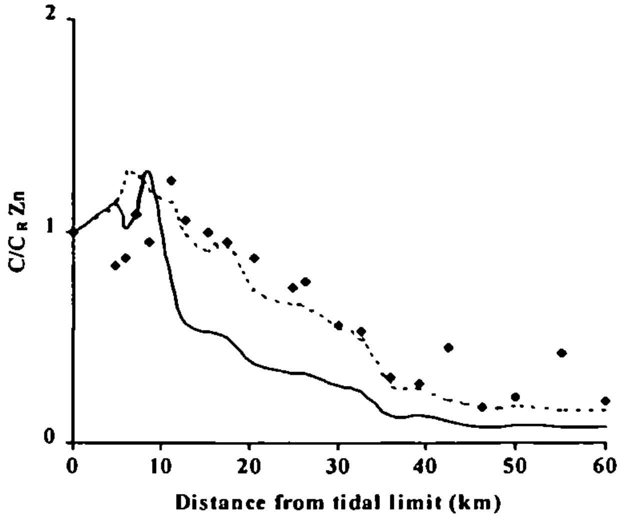


Figure 5.10 The extent of desorption of Zn from resuspending sediments (—) and seaward-fluxing PSPM (----) as a function of distance along the estuary in June 1998. Measured C/C_R ratios are also given (◆).

Unfortunately, application of the sorption models could not be extended to include Hg. This was because EA measurements of dissolved Hg in the estuary are sparse and the REM is not sampled at all during their routine surveys (see Figures 5.1 and 5.5a). Hence C/C_R ratios cannot be calculated at the present time. Further work could therefore assess the relative importance of mechanisms (2) and (3) in relation to Hg in the Mersey.

5.2.4 Model sensitivity testing

Results of the previous section indicate that desorption from SPM traversing the salinity gradient is predicted to be virtually non-existent in the Mersey. However, there are limitations to the model, four of which are described in the following text.

The model relies on an assessment of the equilibrium partitioning of trace metals between the dissolved and particulate phase. Using a similar approach to describe trace metal partitioning in other energetic, tidally influenced estuaries, Turner (1996) proposed that the inability to adequately reproduce metal distributions in some environments was due to subsidiary metal contributions (including porewater inputs), chemically different resuspending SPM populations and disequilibrium between sorbed and dissolved components. It was argued that good fits between field and modelled K_D distributions in the Weser for example, were due to reduced extraneous trace metals from anthropogenic, porewater and tributary sources and a high flushing time of up to 50 days (Grabemann *et al.*, 1990) which would allow chemical equilibria to be approached. Whilst the mean water residence time of the Mersey Estuary is 32 days, it can increase to over 50 days at times of low freshwater flow (Jones, 1978) and it is envisaged that near equilibrium conditions are reached in the Mersey, particularly during the summer. Unlike the Weser however, additional trace metal sources are probable in the Mersey, including that from tidally disturbed sediments releasing elevated metal concentrations from interstitial waters. As Turner (1996) suggested, it is important to accurately define two key partitioning variables, K_D^0 and *b*, if a more predictive framework for the study of trace metal behaviour in estuaries is to be developed.

Martino (2000) investigated the effect of pre-equilibrating ^{63}Ni with dissolved organic ligands on the reactivity of ^{63}Ni. Freshwater was collected from above the tidal limit of the River Mersey during the June 1998 survey and pre-equilibration times of 0, 24 and 120 hours were used prior to radiotracer uptake experiments. A longer pre-equilibration time would be expected to result in increased complexation of ^{63}Ni with dissolved organic ligands, thereby increasing the resistance of Ni to association with the particulate phase. Interestingly, and significantly for Ni, pre-equilibration time made virtually no difference to the value of K_D which was shown to be independent of salinity (Figure 5.11). Whilst seemingly unimportant for Ni, the pre-equilibration of other metals over a suitable period may be necessary in incubation experiments in order to produce values of K_D^0 and *b* that are capable of adequately describing and replicating measured dissolved metal concentration ratios. Further investigations could therefore be made to determine the seasonal effects of pre-equilibration time on the value of *b* and to see how the importance of this varies between metals.

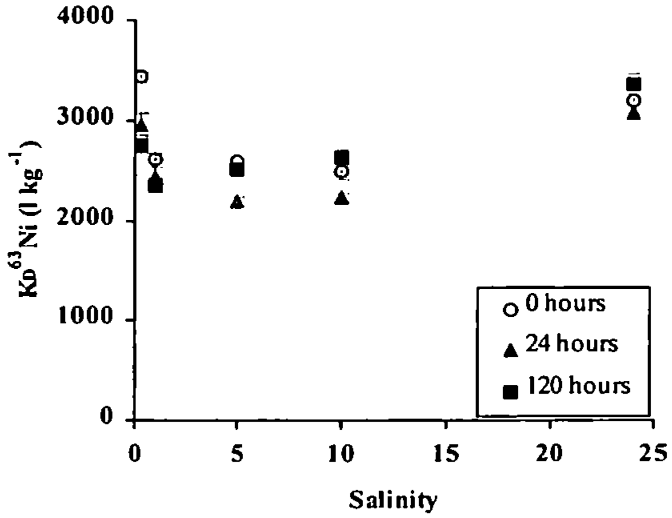


Figure 5.11 The effect of pre-equilibrating ^{63}Ni with dissolved organic ligands on the sorption of ^{63}Ni to Mersey SPM.

The salinity-dependent constant, *b*, is found by the use of linear trendline equations describing the best fit between K_D and salinity data. However, deviations from linearity naturally occur due to changes in particulate and water chemistry along the full salinity gradient which (as this work has shown) are induced by alterations in such variables as pH, DO, DOC, POC and particulate Fe+Mn. Thus *b* relates to an 'averaged' change in partitioning with salinity. In reality therefore, the rate of increase/decrease in equilibrium metal partitioning is likely to vary at several locations along the estuary axis.

The effect of changing the magnitude of *b* is demonstrated in Figure 5.12, where the relative change in C/C_R is again assessed for Zn. Here, the same empirically derived values for $K_D{}^0$ in both June and October are used as in Figure 5.9, but the value of *b* is increased by factors of 5 and 10. The influence of high/low flow conditions is clearly identified. In the summer (Figure 5.12a), reduced riverine input allows chemical equilibria to be approached and the effect of increasing *b* is to induce significantly greater desorption. Conversely, during periods of high runoff (Figure 5.12b), a shorter flushing time does not allow sufficient progression toward equilibrium conditions and *b* is reduced by an order of magnitude compared to summer low flow conditions. Subsequently, more significant increases in *b* are required (exceeding 10 times the original radiochemically-derived value) if model calculations are to be commensurate with measured C/C_R in the mid-outer estuary. Desorption of Zn from PSPM is inhibited when flows are high but is predicted under summer low flow conditions. The importance of this demonstration is that if suspended particles in the Mersey underwent future compositional changes due to continued improvements in water quality and also became more heterogeneous over distance then in theory, values of *b* would be increased. This would mean that desorption from seaward-fluxing SPM could become a more significant mechanism for metal loss than is observed at present.

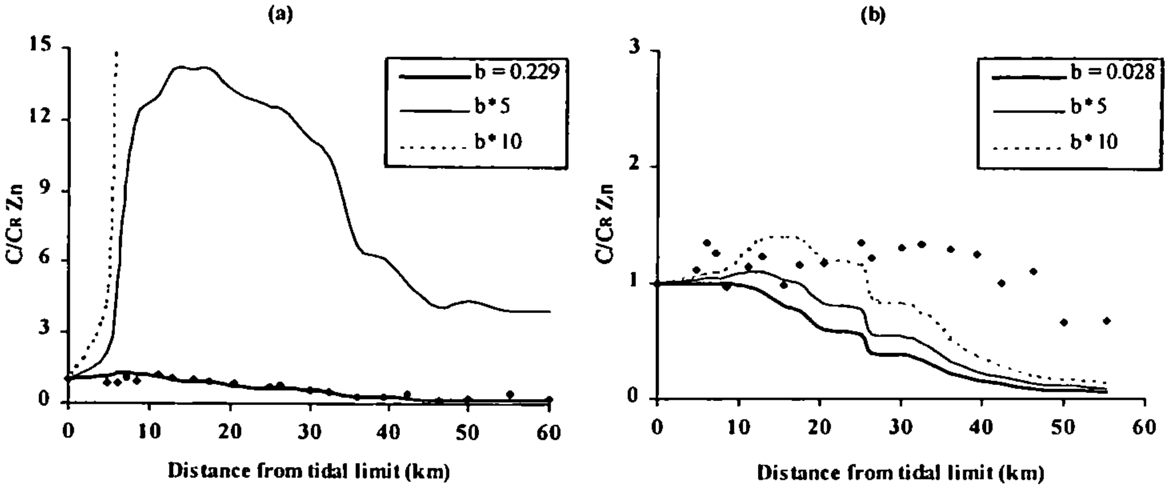


Figure 5.12 The effect of changing the value of *b* on the extent of salinity-induced desorption (expressed as C/C_R) of (a) Zn in June 1998 and (b) Zn in October 1998. Measured C/C_R ratios are also given (◆).

5.3 Summary

Due to large, historical discharges and a strong affinity for particulate matter, mercury is the most persistently measured and reported trace metal contaminant occurring in the Mersey Estuary. Radiotracer uptake experiments have been used to examine the phase partitioning of this element in order to ascertain the major factors affecting its geochemical behaviour within the estuary. As for other metals in Chapter 4, the main controls exerted on the phase distribution of Hg were salinity and turbidity. At least 70% of Hg (rising to 100%) was present in the particulate phase at all times of sampling. The importance of turbidity was highlighted, with Hg concentrations rising when associated with a strong increase in SPM concentration. A significant association exists between particulate carbon and Hg in line with the findings of many other researchers and this exerts a third restraint on Hg availability. Organic ligands, some of which may be highly specific to the Mersey, are believed to be salted out of solution by either electrostriction or destabilisation-coagulation at higher salinities. The presence of sewage-derived organic matter may also be implicated in the process of salting out. By this mechanism, organic carbon and associated Hg are both retained very effectively in the particulate phase. This supports the findings of other researchers who have demonstrated that despite drastic reductions in Hg inputs in the last 20 years, the loss of Hg from bed sediments is not proceeding as rapidly as expected.

Bed sediments remain substantially enriched for carbon and some metals (by up to a factor of 6) compared to SPM. There is no pronounced removal of dissolved metals in the TMZ; indeed addition of a number of metals is consistently observed. The magnitude and location of peaks in dissolved metal concentrations vary depending on fluvial flow and differences in chemical reactivity. Broad peaks in dissolved metal concentrations may in part be due to slow desorption kinetics induced by elevated DOC concentrations. It is proposed that the cause of consistent addition of dissolved metals throughout the mixing zone may arise from three routes, listed below in order of perceived significance:

1. Desorption from particles resuspending from the bed, which are rich in trace metals compared to ambient SPM in the water column. Values for α (defining the extent of metal depletion in particles at equilibrium in the water column compared to those resuspending from the bed) suggest that sediments need to be contaminated by as little as 7% (and often as low as $\leq$ 2%), in order for desorption to occur. Contaminated sediments could therefore supply a persistent source of dissolved metals for as long as a suitably high concentration gradient exists between metals in SPM and metals in bed sediments. Decontamination of the most heavily metal-polluted bed sediments in the upper and mid estuary by this mechanism is anticipated to take decades.
2. The release of metal-rich porewaters upon tidal disturbance of bed sediments. This mechanism is possible if early diagenesis, ameliorated by the presence of sufficient organic matter, is allowed to occur in the upper estuary during neap tides. Under suitably quiescent conditions of low tidal energy, low flows and reduced DO (particularly in the summer months) degradation of organic detritus by large bacterial populations would release labile metals to interstitial waters in the sediment. Vigorous tidal stirring during spring tides would cause porewater infusion of dissolved metals to the overlying water column. Estimated porewater concentrations are comparable to other moderately contaminated UK estuaries and would be sufficient to produce the

dissolved metal maxima determined by Martino (2000).

3. A third contribution to dissolved metal addition could arise from metals desorbing from seaward-fluxing SPM although this source currently appears to be of minor importance in the Mersey. Based on the data available, desorption from PSPM is only indicated for Zn for one survey. However, the release of dissolved metals *via* this mechanism may become more prevalent if compositional changes to Mersey SPM occur in the future (e.g. further increases in Fe or Mn combined with reductions in organic carbon). These alterations could favour an overall increase in sorptive capacity and allow the accommodation of metals in more readily exchangeable forms. This would help to reduce the potential for the long-term accumulation of metals by aiding their release at higher salinities. Suggestions have also been made for refining the derivation of salinity- and metal-dependent constants used in predicting dissolved metal distributions. This is vital for the correct application of chemical partitioning codes and subsequent interpretation of empirical model results, particularly if applications such as these are to be incorporated into numerical models.

This chapter has allowed further insights into seasonal factors affecting trace metal behaviour and mechanisms of both metal retention and loss have been proposed. Together with the findings from the previous two chapters, these results will be used to provide conclusions regarding the current and future status of the estuary in Chapter 6.

Chapter 6

Conclusions: The Current and Future Status of the Mersey Estuary

6 Conclusions: the current and future status of the Mersey Estuary

The purpose of this chapter is to draw together the findings of previous sections and illustrate how a combination of hydrodynamic, sedimentary and biogeochemical processes may be determining the present outcome of ongoing remediative measures to improve water quality in the Mersey Estuary. Implications of these mechanisms in terms of further progress in recovery from trace metal contamination will also be given.

6.1 Predictions of metal loss from upper estuary bed sediments

Sediment metal residence times have been calculated for Cd, Cu, Hg, Pb and Zn using the 25-year data set in Harland *et al.* (2000) and are provided in Table 4.12, Section 4.3.3. The results are derived from data for sediments sampled in the inner and outer estuary. However, higher concentrations of some metals exist in sediments in the upper estuary, which have not been accounted for in the aforementioned study. Sediments in the top 5 km are enriched with metals compared to those from the inner and outer estuary zones (by only 1.6x for Zn but by 9x for Pb, see data for 1997 and 1999 for this study in Table 4.11). A clear requirement therefore exists for an additional assessment of sediment metal residence times in the upper reaches. As there is no available long-term time series of metal concentrations in sediments for the upper estuary, an alternative calculative approach is required.

The capacity of part of an estuary to be cleansed of metals may be alternatively established by calculating a sediment renewal time. The method is based on estimating the amount of dissolved metal released from bed sediments of known contaminant concentration in the region of interest and subsequent transport out of the estuary. The plausibility of porewater infusion from contaminated sediments has already been established in Chapter 5 and could represent a significant means of dissolved metal addition in the upper estuary, at least at the onset of large spring tides. Three major assumptions have been made here: (1) the absence of additional inputs and/or scavenging of dissolved metals by particles, (2) the complete downestuary advection of dissolved metals for two tidal cycles per day with no return of dissolved metals into the estuary and (3) the homogeneous distribution of metals in bed sediments throughout a given area. Relevant information pertaining to the calculations are listed below:

- Distance from the tidal limit to EA station 22: 4 800 m

Estimated width of section:	100 m
Mixing depth of sediment:	0.2 m
Estimated depth of water:	5 m
Sediment density:	2 500 kg m^{-3}
Volume of sediment:	96 000 m^3
Porosity of sediment:	80%
Mass of sediment:	192 000 t
Estimated volume of water per tide:	2.4 x 10^9 l

Mean sediment metal concentrations relate to sediments normalised to 40% silt content collected as part of this study in 1999. Dissolved metal data are from the companion study by Martino (2000) and refer to concentrations that give maximum deviations from the theoretical dilution line. Results are presented in Table 6.1 and have been calculated as follows, taking the data for Cd as an example:

If the mean Cd concentration in surface sediments equals 1.49 μg g^{-1} and the total mass of sediment amounts to 192 000 tonnes, then the total mass of Cd in sediment = 1.49 * 192 000 / 1 x 10^6 = 0.29 tonnes. The maximum observed deviation from the TDL for Cd was 0.45 μg l^{-1}. If 2.40 x 10^9 l of water are exchanged per tide, then the mass of dissolved Cd potentially advected per tide equals 0.45 * 2.40 x 10^9 / 1 x 10^{12} = 0.00108 tonnes and the mass of dissolved Cd advected per year = 0.00108 * 2 * 365.25 = 0.79 tonnes. The half life is determined as the mass of particulate Cd (0.29 t) divided by the mass of dissolved Cd lost per year (0.79 t) and equates to 0.37 years. Finally, the sediment renewal time is equivalent to 6 half lives, which for this metal amounts to 2.22 years.

Table 6.1 Renewal times for metals in grain size-normalised sediments from the upper reaches of the Mersey Estuary.

	Metal					
Parameter	**Cd**	**Co**	**Cu**	**Ni**	**Pb**	**Zn**
Mean particulate concentration (μg g^{-1})	1.49	14.3	38.0	55.9	476	284
Mass of metal in sediment (t)	0.29	2.75	7.30	10.7	91.4	54.5
Maximum dissolved concentration (μg l^{-1})	0.45	1.47	1.27	2.94	0.84	9.81
Mass of dissolved metal advected per year (t)	0.79	2.58	2.23	5.15	1.47	17.2
Half life (y)	0.37	1.07	3.28	2.08	62.1	3.17
Sediment renewal time (y)	**2**	**6**	**20**	**13**	**372**	**19**

As a consequence of the assumptions made, the sediment renewal times probably represent the minimum amount of time required for complete metal removal from sediments at the head of the estuary providing this is the only mechanism in operation. Renewal times imply the following trend of decreasing affinity of metals with particulate matter: Pb > Cu ~ Zn > Ni > Co > Cd. The data suggest however, that decontamination of sediments in the region may be achieved relatively soon if there are no additional inputs of Cd, Co and Ni into the estuary. Similarly, substantial reductions in bed sediment concentrations of Cu and Zn could occur within the next 20 years. The notable exception is for Pb, a highly particle-reactive element occurring in very high concentrations in bed sediment located in the first 5 km of the Mersey. It is suggested that a relatively minor amount of dissolved Pb is evacuated from the estuary each year compared to the other metals, contributing to a sediment renewal time for Pb in excess of 350 years.

This work has shown (Section 5.2) that both the injection of metal-laden interstitial waters and desorption from tidally-resuspended particles are the two most likely processes that could be responsible for the generation of dissolved metal maxima reported by Martino (2000). Higher dissolved metal concentrations relative to those occurring in freshwater regularly occur in the first 5 km of the estuary (see Figure 5.8). Desorption from resuspending particles is likely to proceed as long as a gradient exists between metal concentrations in bed sediments and SPM that is at equilibrium with ambient dissolved metals in the water column. This work has shown that such gradients do occur, as bed sediments are loaded with metals (except for Zn) compared to SPM, particularly in the upper estuary (Figure 5.7). As a result, the renewal times given in Table 6.1 could be substantially reduced if desorption from metal-rich resuspending particles in the low salinity zone and TMZ is also taken into account. However, the approach required to quantify the effect that the two mechanisms operating in tandem would have on the renewal times in Table 6.1 is at present unclear.

Comparing the two sets of data in Tables 4.12 and 6.1, it can be seen that equivalent sediment renewal/metal residence times are reached for Cu whilst values for other metals differ widely. The estimated time for recovery of sediments from Cd contamination is an order of magnitude lower in the upper estuary than for sediments located significantly downestuary. Similarly, reduction of Zn is predicted to take half the time in the upper estuary compared to the inner and outer estuary. This is a little surprising considering that upper estuary sediments generally have higher burdens of these metals than those sampled by Harland *et al.* (2000). The opposite tendency is exhibited for Pb however, as loss of Pb from sediments near the weir is estimated to take 14 times longer than in other regions.

The reasons for these discrepancies possibly relate to differences in the level of sediment enrichment, which is partly controlled by grain size, and also the relative affinity of individual metals for particulate matter and POC. This is demonstrated in two ways. Firstly, with a K_D of ~10^5, Pb is highly particle reactive and exhibits substantially elevated concentrations in upper estuary sediments. Persistent dissolved Pb peaks occur in the low salinity zone (see Figure 5.8d) but the release of Pb, either through desorption or porewater infusion is minor compared to the amount of Pb present in the particulate phase, which could be held strongly on binding sites of higher energy. Conversely, the magnitude of dissolved Cd and Zn maxima relative to their concentrations in bed sediments is considerably greater (e.g. see Figure 5.8a for Cd). These metals have low (Cd) to moderate (Zn) affinities with estuarine particles and are likely to be present in more readily exchangeable forms. Correspondingly, evacuation of these metals from sediments is achieved more quickly. The erratic axial profiles for dissolved Cd imply that Cd is largely lost through salinity-induced desorption, whereas the behaviour of dissolved Zn is effectively moderated by fluctuations in organic carbon along the salinity gradient.

6.2 Particle retention

Sediment dynamics in the Mersey are complex. The Crosby and Queens channels are constrained by extensive training walls and navigability is maintained by dredging (Price and Kendrick, 1963). In the past, dredging was performed upstream as far as Widnes, but with declines in traffic, the upstream limit for dredging is now at the entrance to Eastham locks on the southern shore and at the corresponding point on the North shore at Garston Docks (Taylor, 1986). However, a large percentage of dredged fines are returned directly back into the estuary (O'Connor, 1987). The position of the low water channel is continually changing (P. Jones, pers. comm.) and the presence of strong tidal currents leads to considerable redistribution and hydraulic sorting of sediment in the estuary (Harland *et al.*, 2000; Turner, 2000). Sand is transported landward through the Narrows from Liverpool Bay to be deposited in the inner estuary (Price and Kendrick, 1963) and the estuary is believed to be gradually accreting sediment (Liverpool Bay Study Group, 1975). Murdock (1995) described the exchange of fine sediments of the estuary with that of Liverpool Bay and the Irish Sea as follows:

> *'Fine sediments entering or leaving the estuary tend to oscillate with the ebb and flow of tidal movements and may only disperse into Liverpool Bay during exceptionally wet weather and large spring tides. As a result of this physical process the estuary may be described as an accretion zone for sediments.'*

An accretion rate of 1.0 x 10^6 t a^{-1} was estimated by Price and Kendrick (1963) which has since been amended by Taylor (1986) to a gross value of 4.0 x 10^6 t a^{-1} to also account for significant dredging operations. In an investigation of metal and SPM fluxes through the Mersey Narrows, Cole and Whitelaw (2001) demonstrated that for the majority of tidal and river flow conditions, a net seaward transport existed. However, during spring tides of high tidal range ($\geq$ 8.14), calculations indicated a tendency for a reduction or even reversal of this seaward transport. Harland *et al.* (2000) hinted that the retention time of fine sediment was likely to be of the order of decades, although no exact figure had yet been proposed, and concluded that even if metal loads to the estuary were lowered further, a considerable time would be required for the reduction of many metals to background concentrations.

The high surface areas and long residence times exhibited by fine-grained deposited and suspended particles means that their geochemical composition may reflect both contemporary and historical inputs into an estuary system (Turner, 2000). Evidence from this work has consistently pointed to the possibility that SPM in the Mersey is aged and has become relatively uniform in terms of its geochemical reactivity and physical characteristics. In light of this and the presumed high sediment retention capability of the Mersey, it is therefore pertinent to consider the derivation of a 'particle residence time'.

The particle residence time is calculated by dividing the weight of suspended material present in the water column throughout the estuary (in tonnes) by the sediment yield (tonnes per annum). The total mass of SPM in the Mersey can be estimated by multiplying the volumes of 2 km estuary segments by the actual turbidities measured in this study at each EA sampling station. For a limited number of sections where a suitable EA station cannot be readily identified, linear interpolation has been used to estimate SPM concentration. The data produced for the March 1998 survey are given as an example in Table 6.2. Sediment yield due to catchment erosion was calculated according to the method used by Wilmot and Collins (1981), producing a value of 4.6 x 10^4 t a^{-1} (see Table 1.7). In addition, a substantial amount of material (3 x 10^6 t a^{-1}) is regularly removed from the estuary (Camacho-Ibar *et al.*, 1992) and also needs to be accounted for in the calculations. Particle residence times have only been calculated for surveys where complete axial coverage of the estuary was achieved and the findings are displayed in Table 6.3.

Thus, for the March 1998 survey:

Total estimated mass of SPM in the estuary = 77 348 tonnes.

Table 6.2 Segment volumes and an estimation of SPM tonnage in the Mersey Estuary on 30/03/1998.

Distance from tidal limit (km)	Volume (l) *	SPM (mg l^{-1})	SPM in segment (t)
0 – 2	8.00E+07	36	2.88
2 – 4	1.20E+08	105	12.6
4 – 6	1.70E+08	107	18.2
6 – 8	2.10E+08	343	72.0
8 – 10	2.70E+08	579	156
10 – 12	5.40E+08	115	62.1
12 – 14	1.26E+09	287	362
14 – 16	1.63E+09	430	701
16 – 18	2.08E+09	275	572
18 – 20	3.59E+09	414	1 486
20 – 22	7.10E+09	303	2 148
22 – 24	7.96E+09	247	1 964
24 – 26	1.07E+10	191	2 040
26 – 28	1.75E+10	150	2 624
28 – 30	2.08E+10	88	1 826
30 – 32	3.48E+10	109	3 795
32 – 34	2.99E+10	121	3 615
34 – 36	3.20E+10	133	4 251
36 – 38	3.28E+10	163	5 330
38 – 40	3.55E+10	177	6 285
40 – 42	3.48E+10	185	6 416
42 – 44	3.20E+10	192	6 142
44 – 46	4.43E+10	167	7 403
46 – 48	5.10E+10	142	7 236
48 – 50	6.17E+10	208	12 827
			TOTAL = 77 348

* Segment volumes based on calculations for mean tides (Jones, 1978)

Catchment erosion supplies 4.6 x 10^4 t a^{-1} of sediment to the estuary.

Dredgings equate to 3 x 10^6 t a^{-1}. If 40% of this is silt, then the mass of silt removed each year = 1.2 x 10^6 tonnes.

The particle residence time is then calculated by dividing the total amount of resuspendable material present both in the water column during the survey and that physically removed through dredging, by the catchment sediment yield, *i.e.*:

$(77\,348 + 1.2 \times 10^6) / 4.6 \times 10^4 = 27.8$ years.

Consistent estimates for particle residence time are produced despite variations in tidal range and river flow generating large differences in the amount of SPM present in the estuary at the time of sampling. This is because the incorporation of dredged sediment confers a substantial control on the calculation. The resulting value is of the order of 27 years. Residence times for suspended particles of 18 months and 17 years have previously been calculated for the Tamar and Humber estuaries, respectively (Turner, 1990) and 2 days for the Sabine-Neche Estuary in the United States (Baskaran *et al.*, 1997). Whilst the retention of particulates within the Mersey exceeds that of the other estuaries mentioned, this value is likely to be underestimated, for several reasons. Firstly, surveys were performed on spring tides when segment volumes will be larger than those used in the calculations. Secondly, it has been assumed that surface turbidities could be extended throughout the water column. Whilst these turbidities will be approaching maximal concentrations for the above spring tide surveys, and the waters of the estuary are generally well mixed, some vertical heterogeneity would exist with higher SPM loads occurring nearer the bed. Prandle *et al.* (1990) estimated that an extreme spring tide could produce an SPM tonnage (~ 205 000 t) that is 80 times greater than during an extreme neap tide (~ 2 560 t). Values for spring tides in Table 6.3 are up to 7 times lower than those produced in the literature. Bearing these factors in mind, it is suggested that a more realistic residence time for suspended particles in the Mersey may be around 40-50 years, a timescale that is in apparent agreement with the recent (2002) findings of other researchers (D. Prandle, Proudman Oceanographic Laboratory, pers. comm.).

Table 6.3 Estimates of SPM tonnage and suspended particle residence times for the Mersey Estuary. Q = river flow for the River Mersey at Howley Weir.

Survey	**Q (m^3 s^{-1})**	**Tidal range (m)**	**SPM (t)**	**Residence time (y)**
March 1998	47.2	10.9	77 348	27.8
June 1998	29.1	9.2	39 793	27.0
October 1998	82.4	8.2	65 442	27.5
May 2000	10.1	9.4	27 842	26.7

Given such a considerable timescale, it would appear reasonable that particle character (e.g. C content and SSA) is relatively constant throughout the estuary and that trace metal concentrations in suspended particles are largely independent of the time of sampling. Thus, the long particle residence time would seem to be implicated in the buffering process. Adequate assessments of estuarine pollution should therefore not only rely on particulate metal measurements but also the degree of internal cycling within the system including turbidity and particulate variability in terms of geochemical reactivity. Thus, in dynamic macrotidal estuaries such as the Mersey, Humber and Thames, contemporary pollution is somewhat masked by high suspended particle concentrations, the dynamic exchange of historically contaminated particles between bed sediments and the overlying water column and the relatively high levels of POC and DOC. The net result is a retention of current and historical inputs into the system, at least in the medium term, which would assist in explaining the slow-down in trace metal decontamination reported by Laslett (1995), Fox *et al.* (1999) and Harland *et al.* (2000).

Newly published research (Thomas *et al.*, 2002) suggests the Mersey has recently evolved towards a morphologically steady state. Computational hydrodynamic model results and the analysis of bathymetric data indicate that peak accretion occurred between 1906 and 1977. This has been related to training wall construction and dredging in Liverpool Bay causing changes in sediment transport patterns outside the estuary which both acted to increase the supply of non-cohesive sediment to the estuary mouth. In particular, flood tidal flow over a large sandbank (the Great Burbo Bank) in Liverpool Bay became increasingly dominant and enhanced the transport of fine sands towards the estuary mouth. The authors derived the Dronkers parameter for the estuary upstream of New Brighton for a number of individual years spanning the period 1871-1997. The Dronkers parameter (γ) is a method of relating estuarine geometry to theoretical tidal asymmetry using 1-D tidal equations (Dronkers, 1998): a value of 1 signifies an approximate balance between ebb and flood tides, figures < 1 indicate ebb dominance and figures > 1 indicate flood dominance. In 1871, γ was found to equal 1.41, rising to 1.58 in 1906 and declining to 1.34 in 1977 and 1.31 in 1997. Bathymetric adjustment in Liverpool Bay changed hydrodynamic flow patterns and reduced flood tidal transport of offshore sands over Great Burbo Bank thereby diminishing the capacity for sediment importation into the estuary. In the period 1977-1997, a net sediment flux of approximately zero was calculated.

Reduced fluxes of non-cohesive marine sands into the estuary implies that the mixing in of marine particles with metal-contaminated estuarine particles could be lessened over time and to some extent, could slow down the observed trends of reducing sediment metal concentrations. Conversely, if morphological changes are induced that serve to reduce flood dominance further, then net exports of particulate matter and a lowering of suspended particle residence times could occur which would assist metal decontamination.

6.3 Overall Conclusions

The increased regulation of effluent discharges entering the tidal and non-tidal Mersey has produced slow but consistent improvements in the water quality of the estuary in terms of basic water chemistry, biology and aesthetics. Significantly, in 2000 no part of the estuary was any longer classified as being of bad quality. Previous researchers have documented fairly rapid declines in dissolved and particulate trace metal concentrations since restorative measures were initiated to control the magnitude and quality of metal inputs in the 1970s. This study has established that particulate and dissolved contaminant metal concentrations have now stabilised and that a combination of prevailing hydrodynamic, sedimentary and biogeochemical conditions are responsible for maintaining trace metals at present-day levels in the Mersey Estuary. The major objectives of this research have been accomplished, in particular:

- A co-ordinated and extensive seasonal field sampling programme and controlled analytical experimentation have allowed a comprehensive insight into the processes affecting trace metal biogeochemistry in the Mersey Estuary. Measurements of SSA, particulate metal concentrations, the differentiation of particle size (sediment granulometry and the separation of sub-populations of SPM based on variations in their settling characteristics) and carbon content have enabled compositional changes in SPM and bed sediments from the entire mixing zone to be evaluated. Access to archival data held by the EA and results from companion studies performed by Martino (2000) and Le Roux (2000) have further assisted in the interpretation of trace metal transport and behaviour in the Mersey. This work is therefore the first study of the estuary to offer a holistic assessment of how chemical and physical processes operating within it are affecting its recovery from a legacy of historical trace metal contamination.

- Estuarine dissolved nutrient concentrations are high and as such no obvious seasonal depletion by phytoplankton was displayed. Limited non-conservative behaviour was demonstrated for dissolved nutrients, with slight removal occurring for NH_4^+ accompanied by addition of NO_2^- in June 1998 and July 2000. Nitrate displayed alternating patterns of removal and addition along the estuary axis. It is postulated that the trapping of particulate material and the accumulation of substantial amounts of organic matter in the region of the TMZ/estuarine null point supports the growth of high numbers of nitrifying bacteria (~ 10^{10} cells). The oxygen demand exerted by these bacteria creates a DO sag, which is present at all times of the year and extends for almost the entire length of the estuary. Depression of DO becomes particularly evident during the summer months (the lowest value recorded during the axial surveys being

42% saturation in the upper estuary in July 2000) and the most pronounced region of the sag corresponds with peaks in dissolved NO_2^-. Long-term monitoring by the EA and its predecessor the National Rivers Authority has proved that the Mersey has changed from a denitrifying system to one where partial nitrification exists, although estuarine NO_3^- concentrations do not pose any significant environmental concern at the present time. This shift has largely been the result of improved oxygenation and reduced ammonia loads. Seasonal variations in riverine phosphate concentrations result from changes in fluvial inflow, with point sources assuming greater importance during periods of low flow and diffuse sources such as agricultural runoff dominating during higher flow events. Phosphate concentrations are consistently high in the estuary and are undoubtedly implicated in the current GQA designations of poor/fair water quality. Dissolved silicate shows little seasonality but removal in May 2000 and addition in July 2000 could be indicative of the respective growth and decay of diatomaceous blooms during those periods. Dissolved nutrient ratios indicate that N may become limiting in the spring and summer whilst P could become limiting in autumn and winter. CSTT (1997) guidelines are exceeded for winter concentrations of DAIN (12 µM) and DAIP (0.2 µM) and, apart from in December 1997, chlorophyll *a* concentrations also transcend the recommended value of 10 µg l^{-1} as set down under the EC Urban Waste Water Treatment Directive. In addition, winter molar N:Si ratios > 2 occur for the majority of sites along the estuary at different times of year and together, these facts point to hypernutrification in the Mersey.

- Freshwater concentrations of DOC are high compared to many other estuaries. Axial distributions of particulate organic carbon in bed sediments and SPM tend to reflect changes in sediment granulometry and position relative to fluvial inputs and the null point. The total carbon content of SPM has reduced by 75% between 1987 and 1998 in line with the increased control of sewage inputs. Data for TOC, when obtained as a function of inhabitants/discharge ratios, indicate that the estuary shows evidence of organic decontamination approaching that seen in the Rhine and Elbe. As a consequence of declines in particulate C, the mean SSA of SPM has increased by up to 57% during the same timeframe but SSAs are still low compared to those of SPM in other major estuaries and this has implications for metal sorption processes.

- Analyses of the POC and N contents of estuarine particles reveals that atomic C:N ratios approaching that of the Redfield ratio occurred most consistently in May and July 2000 (and less frequently in March and June 1998) and confirm the existence of phytoplankton blooms. During these surveys, algal contributions to total POC in SPM ranged from 20 – 99% in waters of low turbidity but became progressively reduced due to poor light availability when SPM concentrations exceeded ~ 100 mg l^{-1}. At other times/locations, C:N and POC:Chl a ratios were elevated, implying that the organic carbon pool is comprised of a mixture of other natural as well as anthropogenic ligands. The amount and type of POC in the estuary varies throughout the seasonal cycle in response to changes in freshwater runoff, vegetative die-off, the relative magnitude of waste inputs compared to the dilution capacity of the estuary as well as the incidence of bacterial and photosynthetic activity.

- Estuarine POC concentrations show limited axial variation compared to other systems. A long average flushing time (32 days) and partial nitrification alter the buffering capacity of the estuary and calculations indicate that 35 - 60% of seston POC is rapidly mineralised. Ratios of POC:Chl *a* and C:N indicate that the efficiency of this process can also be attributed to the type of POC predominant at any given time. For example, the high flow conditions in the River Mersey in October 1998 delivered significant inputs of terrestrial organic matter to the mixing zone and mineralisation was reduced. Mineralisation efficiency rose however, when increasingly labile sources of organic carbon such as sewage, bacteria and phytoplankton assumed more prevalence in the estuary.

- Metal partitioning has been elucidated by analysis of field and laboratory distribution coefficients (K_Ds). The phase distributions of Cd, Co, ^{203}Hg, Ni and Pb are largely controlled by salinity and particle concentration. However, additional control on partitioning was mediated by cyclic variations in organic C (especially for Hg) and bacterial and photosynthetic production producing localised changes in water and particulate chemistry. For Co co-associated with Mn, this occurred through axial changes in DO causing reductive dissolution in the upper estuary followed by progressive re-adsorption of Fe-Mn hydroxides in the inner and outer estuary. The phase partitioning of Cu and Zn were largely independent of the time of sampling, although removal of both metals in the upper estuary in March 1998 (Martino, 2000) suggests phytoplankton uptake. The salting out of metal-organic complexes at higher salinities is believed to be a major factor contributing to the retention of metals in the particulate phase. For Hg (and possibly other metals) this process could be assisted by the presence of sewage, as experiments involving the uptake of ^{203}Hg showed an increase in K_D with salinity at a time when C:N ratios consistently identified the association of sewage-related material with SPM throughout the estuary (March 1998). The same effect was not observed in either June 1998 or October 1998 when natural POC ligands were predominant.

- Bed sediments remain substantially enriched in carbon and most of the metals studied relative to pre-industrial concentrations. The extent of enrichment is partly dependent on sediment location, which itself reflects the action of physical mechanisms such as dispersal and hydraulic sorting and supports the findings of previously published research. Sediment trapping produces an essentially well mixed suspended particle population which has become substantially (physically and chemically) modified over time due to repeated cycles of Fe-Mn (hydr)oxide dissolution and reprecipitation and the presence of large quantities of organic C in the system. This culminates in the generation of an SPM pool, which has relatively uniform chemical reactivity and significantly different bulk characteristics (e.g. SSA and the relative proportions of Fe, Mn and C) to that occurring in other moderately contaminated macrotidal estuaries. A residence time of ~ 40-50 years has been estimated for SPM in the Mersey and it is anticipated that only very small contributions of particulate metals are permanently flushed out of the estuary into the surrounding coastal zone.

- The results of settling experiments showed that overall, PSPM possesses higher concentrations of trace metals (Cd, Co, Fe, Mn, Ni and Pb) than TSPM. The largest variance occurred for Co and Fe but for other metals the differences, whilst statistically significant, were much smaller. Data for Cu and Zn revealed a lack of distinction in geochemical reactivity between the two particle types. Thus, evidence suggests that PSPM and TSPM in the Mersey are not as geochemically or physically dissimilar as in other macrotidal estuaries such as the Humber and Tamar and that this is probably linked to the long residence time of SPM in the Mersey and the magnitude of past discharges. Metal concentrations in unsettled (bulk) SPM were shown to be almost exclusively the result of mixing naturally varying quantities of PSPM with TSPM and this demonstrates that separation and measurement of the two settling populations is both procedurally and analytically viable.

- Relatively invariant suspended particulate Cd, Cu, Ni, Pb and Zn concentrations throughout the Mersey mixing zone suggest that salinity-induced desorption of these metals is largely repressed at present. This is possibly to be expected since the adsorptive capacity of PSPM is not significantly enhanced over that in resuspending particles. The data also imply that complex and significant changes in sorptive control may be exerted by the relative presence of Fe, Mn and POC in Mersey particles and that this is important in the regulation of contaminant metal concentrations along the salinity gradient. However, desorption of metals at high salinity may become more prevalent in the future if restorative measures are continued which enable further increases in Mn and/or reductions in C in PSPM than those already observed to date.

- There is no pronounced removal of dissolved metals in the TMZ. Instead, broad peaks in dissolved metals occur in the region of the FSI and TMZ which may in part be due to slow desorption kinetics induced by elevated concentrations of DOC. The use and refinement of empirical sorption models has demonstrated that the cause of consistent dissolved metal addition is likely to be dominated by desorption of metals from tidally resuspended sediments. This is possible because resuspending particles are rich in metals compared to ambient SPM that is at equilibrium with dissolved metals in the water column and because the flushing time of the Mersey is sufficiently long to allow chemical equilibria to become established. A secondary source of dissolved metals has been identified. It is thought that infusions of metal-rich porewaters from sediments in the upper extremes of the estuary could arise during the onset of spring tides following the occurrence of sediment diagenesis during more quiescent neap tides, especially during the summer months when DO saturation is most repressed.

- Calculations of future metal loss from bed sediments have been made by two independent methods. The resulting data indicate that decontamination may be achieved for Cd, Co, Cu, Hg, Ni and Zn within the next 2-3 decades or even less, provided that metal inputs continue to decline or at least remain at present-day levels. The rate at which this proceeds will vary between metals due to differences in for example, particle reactivity, their affinity for organic matter and redox-sensitive elements such as Fe and Mn and speciation and will also vary depending upon the location and physical characteristics of the sedimentary material. The prevalence of high concentrations of Pb in upper estuary bed sediments means that elimination of this element is likely to proceed at a far slower rate and may take as long as ~350 years. In contrast, the loss of Pb from intertidal sediments located further downestuary is only predicted to take up to 20-30 years.

6.4 Suggestions for further work

An integrated scientific approach is necessary in order to gain a suitable understanding of the physical, biological and chemical processes operating in dynamic estuarine systems. Furthermore, from an estuarine management viewpoint, appropriate identification of contaminant sources and sinks and how these are influenced over a range of timescales is critical for reliable assessments of historical and future trends and the modelling of estuarine fluxes.

This study has established an effective baseline against which further progress in restoration of the Mersey Estuary can be assessed. Other areas of work that could warrant future study are:

1. The settling of particulate trace metals requires further investigation. It has been shown that bulk SPM comprises particles of various origins at different times of year. Settling experiments were performed for four seasonally distinct periods but settling times were not varied. The inclusion of plankton, sewage-derived and riverine particles are all likely to affect the settling characteristics and metal contents of PSPM and TSPM. It would be useful to identify the trace metal contribution that each particle type makes to each of the two settling fractions and how this may vary according to alterations in the settling time employed.

2. Porewater concentrations of trace metals in sediments in the uppermost 5 km of the estuary have been estimated based on observed deviations of dissolved metals from conservative mixing. There are no known porewater metal data for the Mersey and the existing gap in present knowledge would therefore be bridged by performing these measurements. Such data could confirm or deny the existence of sediment diagenesis in the extreme upper estuary during neap tides and indicate the relevance of conservative calculations made in this work.

3. In the absence of any other data, contemporary metal concentrations determined for surface sediments in this study have briefly been compared to 'pre-industrial' concentrations from the base of saltmarsh cores taken from the upper estuary by Fox *et al.* (1999) in Section 4.3.1. The cores however only extended to a depth of 1 m and are unlikely to have reached horizons exhibiting true background levels. Since 1999, significantly more core sampling has been undertaken by the British Geological Survey but the results are as yet unpublished (J. Ridgway, BGS, pers. comm). These samples have penetrated to a depth of 9 m and metal concentrations determined at this depth therefore are more likely to represent background concentrations from which more realistic enrichment factors can be estimated once the data becomes available.

4. Pre-equilibration of ^{63}Ni by Martino (2000) prior to laboratory incubation studies did not show any appreciable differences in the partitioning of the radioisotope with respect to salinity. However, this may not be true for other metals in the Mersey and should be investigated. Experimental protocols of this kind should be refined to match the prevailing conditions in the estuary under study (e.g. adjustment for long or short flushing times, those experiencing high/low DOC concentrations) in order to generate more accurate coefficients for modelling purposes.

5. The continuance of measurements made in this study would enable further quantification of the ongoing restoration of the Mersey. Analyses of particulate carbon, SSA and Mn for example, could determine how further declines in organic inputs would affect the sorptive capacity of estuarine particles. Salinity-induced desorption of metals may become more prevalent over time if organic coatings on particles are further reduced and this should be monitored. The effect of slow changes in estuarine morphology such as a continued reduction in flood-dominance and how this may assist or prolong the clean up of the estuary also warrants investigation.

An impacted ecosystem may require several decades at least before noticeable progress in restoration is achieved. Charting the recovery of marine ecosystems to acute incidents or chronic contamination sustained over long periods inevitably requires long-term monitoring. All too often, concern over a short-term accidental release fades very quickly. Similarly, once improvements are established in the control of one polluting material, the regulatory authorities are under pressure to switch their attention to other forms of chronic inputs. It is appropriate therefore to echo the sentiments of Hawkins *et al.* (2002) and call for the extended monitoring of impacted water bodies like the Mersey. More specifically, long-term observational programmes like that of Harland *et al.* (2000) should be performed in tandem with the types of measurements made herein so that a more holistic picture of the efficacy of legislation can be attained.

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