

Trace Metal-Particle Water Interactions in the Western North Sea

by

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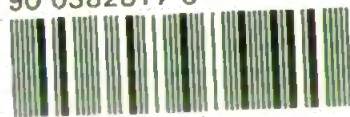
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Joanna Lee Dixon

Abstract

The distribution of trace metals (Fe, Mn, Cu, Cd and Pb) has been determined in dissolved and particulate phases, along with relevant hydrographic parameters, from the nearshore coastal zone of the western North Sea (between 52°N and 56°N) during four Land Ocean Interaction Study (LOIS) surveys covering the seasonal cycle (autumn 1994 to summer 1995). The behaviour of the redox-sensitive metals, Fe_p and Mn_p, in the western North Sea were strongly correlated ($r \geq 0.44$ for all seasons, $P < 0.05$) in all surveys and exhibited maximum concentrations in winter (16 mg g⁻¹ and 700 µg g⁻¹ respectively) which progressively decreased throughout the year. Distinct seasonal variations were also observed for particulate Cu, Cd and Pb. For example, enhanced concentrations of Cu_p (36 ± 39 µg g⁻¹) and Cd_p (0.36 ± 0.42 µg g⁻¹) in the Humber coastal zone during summer were attributed to preferential particulate organic/biogenic-metal interactions. In contrast enhanced, though diffuse, atmospheric inputs of Pb from continental winds were considered to have contributed to the elevated Pb_p concentrations (82 ± 27 µg g⁻¹) observed offshore during winter. Results from radio-tracer incubation experiments suggest that biological activity makes a significant contribution to the removal of dissolved Mn and Cd to the particulate phase. However, a phase lag of two to three months between maximum primary productivity and maximum particulate metal adsorption ($K_D = 2 \times 10^4$ & 5×10^2 for Mn and Cd respectively) indicates a decoupling from the spring plankton bloom. In general metal distributions in the Humber coastal zone were significantly influenced by freshwater discharge, tidal regime at the mouth of the estuary and prevailing wind conditions. Total trace metal fluxes across the mouth of the Humber Estuary were highest during spring (311, 8.96 & 1045 kg day⁻¹, for Cu, Cd and Pb respectively) and lowest during summer (25.7, 1.12 & 33.4 kg day⁻¹, for Cu, Cd and Pb respectively). They were dominated by variations in freshwater outflow and the tidal range during sampling. On an annual basis comparison to estuarine inputs (rivers, industry and sewage sources) suggested retention of Cu (25%) and Cd (56%). Estimates of partitioning (K_D) were derived from the dissolved and particulate data for Cu, Cd and Pb over the seasonal cycle. Copper was dominated by the particulate phase (73-80%) in all seasons but summer, whilst Cd showed particulate phase dominance (54-70%) in autumn and winter only. The Pb distributions were dominated by the particulate phase (94-99%) independent of season. Trace metal settling velocities implied that the Humber Plume was acting as a sink for Cu, Cd and Pb in winter and spring. However settling velocities calculated for Cd and Pb (flood tide) in summer were similar to background suspended particulate matter (SPM) suggesting long range transport with the residual circulation. Modelling of Pb isotopic ratios in the Humber Plume suggested that on average 32-39% of the extracted Pb_p originated from anthropogenic sources. The data from this study has given unique information concerning the concurrent seasonal distributions of particulate trace metals in the western North Sea and have yielded new insights into mechanisms affecting trace metal cycling and transport, essential in the development and refinement of coupled hydrodynamic-geochemical models.

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Declarations

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A program of advanced study was undertaken which included guided reading in topics related specifically to Marine Chemistry and generally to advances in Marine Science. Advanced training was undertaken in a range of analytical techniques appropriate in the biogeochemical cycling of trace metals including flame and flameless atomic absorption spectrometry, inductively coupled mass spectrometry, gamma spectroscopy and liquid scintillation counting.

Relevant scientific seminars and conferences were regularly attended at which work was often presented; external institutions were visited for consultation purposes, and several papers prepared for publication.

Publications

Dixon, J.L., 1997 Trace metals in Bermuda inshore waters. *Estuarine and Coastal Shelf Science*, Bulletin Number 24, February 1997, pp14-19.

Dixon, J.L., Nimmo, M., Morris, A.W. and Millward, G.E. 1998 The biogenic interactions of particulate Cd in the western North Sea. *Land Ocean Interaction Study Newsletter*, Number 12, pp8-9.

Dixon, J.L., Nimmo, M., Morris, A.W. & Millward, G.E. Copper, lead and cadmium in the Humber Coastal Zone, UK. *Estuarine and Coastal Shelf Science*, (in prep)

Dixon, J.L., Nimmo, M., Morris, A.W., Millward, G.E. and Jago, C. Trace element concentration in suspended particulate matter fractionated according to the settling velocity: Implications for trace metal transport in the Humber coastal zone. *Journal of Marine Systems* (in prep)

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Dixon, J.L., Millward, G.E. & Morris, A.W. Fluxes of trace metals from the Humber Estuary and along the Holderness coast. Poster presentation, *ECSCA Local Meeting on the Humber Estuary and adjoining Yorkshire and Lincolnshire Coasts*, Hull, April 1996.

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Regular meetings and discussions were held with colleagues at Plymouth Marine Laboratory in order to discuss cruise plans and obtain advice and assistance with data.

Signed Jordan

Date 1st November 1998

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1 Introduction

1.1 Setting The Background

The coastal zone is of great socio-economic value directly and indirectly to society, providing space and resources for living, agriculture, industry, recreation, waste disposal and transport. Interaction between human and natural factors is causing the physical, chemical and biological environments of the coastal zone to change rapidly. The contaminants that pose the greatest threat to the marine environment are, in variable order of importance and depending on differing national or regional situations, sewage, nutrients, synthetic organic compounds, sediments, litter and plastics, metals, radionuclides, oil/hydrocarbons and polycyclic aromatic hydrocarbons (UNCED, 1992). Trace metals alone have been shown to exhibit deleterious effects on ecosystems even at relatively low concentrations (Salomons *et al.*, 1988). Those originating from anthropogenic land based sources are of particular concern since they exhibit toxicity, persistence and bioaccumulation in the food chain (UNCED, 1992) making estuaries and receiving coastal areas particularly vulnerable to anthropogenic disturbance. The North Sea has been a focus of concern due to the numerous highly industrialised countries bordering its coastline (Tappin *et al.*, 1995). The North Sea Community Research Project (NSP, 1987-92) provided an extensive set of high quality measurements of trace metals in seawater, sediment and atmospheric reservoirs. This was in an effort to quantify the sources, sinks and to enhance the understanding of the factors influencing the distributions of trace metals in the central and southern North Sea. However the complex trace metal interactions, estuarine fluxes and seasonally active controlling biogeochemical processes in nearshore coastal environments are still not well quantified

(Millward & Turner, 1995). Therefore carrying out subsequent impact assessment of trace metals to the wider shelf seas is difficult.

The Land Ocean Interaction Study, Rivers, Atmosphere and Coast component (LOIS RACS) aimed to bridge this apparent 'gap' with an intensive seasonal sampling campaign of the estuarine-coastal interface of the western North sea. Complimentary surveys up to 100 km offshore were additionally investigated to examine contaminant gradients away from land. LOIS is an ongoing Community Research Project whose collaborative, multidisciplinary approach aims to provide an integrated, holistic view of how coastal ecosystems work, and how they are likely to respond to future environmental changes caused by natural or anthropogenic processes (Morris & Allen, 1993). The current work formed an integral part of the chemistry component of LOIS RACS.

The metals investigated in the present study were chosen to represent a variety of biogeochemical reactivities. Manganese (Mn), iron (Fe) and lead (Pb) are particle reactive metals (Burton *et al.*, 1993). The aquatic chemistry of Mn in estuarine waters is dominated by the oxidation of the relatively soluble Mn(II) to insoluble MnO_x ($1.5 < x < 2$) (Yeats & Strain, 1990), where MnO_2 is thermodynamically more stable than Mn(II) in oxic environments. Coastal and estuarine sediments are often enriched in solid manganese oxides (Yeats *et al.*, 1979; Sundby *et al.*, 1981; Shiller *et al.*, 1985; Sundby & Silverberg, 1985) which under anoxic conditions reduce to form soluble Mn(II) which subsequently enters the water column by diffusion or turbulent mixing processes (Dehairs *et al.*, 1989). Iron has a similar redox chemistry, but Fe(II) is more rapidly oxidised than Mn(II). The chemistry of lead is known to be dominated by its affinity with the particulate phase (Balls, 1985; Valenta *et al.*, 1986; James *et al.*, 1993; Statham *et al.*, 1993; Tappin *et al.*, 1995) but under low suspended particulate matter (SPM) concentrations, Pb(II) shows strong complexation to hydroxide and carbonate anions (Turner *et al.*, 1981). Furthermore thermodynamic equilibrium speciation calculations have indicated the possibility of the complexation of Pb by humic acids (Mantoura *et al.*, 1978). However experimental investigations on dissolved humic material of marine and estuarine origin (Raspor *et al.*, 1980; Raspor *et al.*, 1984a & b; Valenta *et al.*, 1986) have found that for Pb rather large concentrations of dissolved humic material (above $0.3-0.8 \text{ mg l}^{-1}$) are required to obtain a 10% complexation. In agreement, recent studies

of the interactions of Pb with the dissolved, colloidal and particulate components of estuarine and coastal waters in southern England by Muller (1996) concluded that Pb mostly interacts with particulate and colloidal components. In contrast to the above findings Capodaglio *et al.* (1990) showed that between 50-80% of total dissolved Pb in coastal areas was complexed by organic ligands (2-5 nM in coastal waters) that were associated with biological activity. Lead is also potentially toxic to marine organisms (Scarponi *et al.*, 1996).

Copper (Cu) and cadmium (Cd) are less particle reactive (Burton *et al.*, 1993) due to their complexation with organic material (Turner *et al.*, 1981; Bourg, 1983; van den Berg *et al.*, 1987; Chester *et al.*, 1988; Kuwabara *et al.*, 1989; Nimmo *et al.*, 1989; Hirose, 1990; Gardner & Ravenscroft, 1991a & b; Hirata, 1992; Paulson *et al.*, 1994a & b and all references therein; Hall *et al.*, 1996; Owens *et al.*, 1997) and chloride anions (Salomons & Kerdijk, 1986; Bourg, 1987; Comans & van Dijk, 1988; Turner *et al.*, 1992a; Comber *et al.*, 1995) respectively, although their concentrations in the stratified open ocean are influenced by down-column transport in association with biogenous particulate material (Boyle *et al.*, 1976; Bruland, 1983; Bruland & Franks, 1983; Burton *et al.*, 1983:1993). Cadmium is on the UK Priority Red List of substances of concern in relation to discharges to the North Sea (Department of the Environment, 1987). Langston (1990) concluded that Cu is potentially one of the most hazardous metals present in marine environments due to its potential ecotoxicological effects e.g. sensitivity of macroalgae (Gledhill *et al.*, 1997) and nitrogen fixation (Suter, 1993) to Cu exposure.

However it is the speciation, or relative proportion of the bioavailable form of the metal that is of environmental importance, not the total concentration of trace element (Phinney & Bruland, 1994; Campbell, 1995; Millward & Turner, 1995). Speciation can mean both the grouping of the physical form of the element i.e. particulate/dissolved phase or the categorisation of the chemical species present i.e. chloro complex. Changes in physical and chemical forms may have significant impact on the bioavailability and geochemical reactivity of the element (Bourg, 1988). Physical speciation has been shown by Bourg (1988) to be ultimately controlled by the concentration of solid surface sites (SPM type and concentration). Chemical speciation is dominated by the

concentration and composition of organic matter and inorganic complexing ligands and respective element-ligand complex formation constants (Bourg, 1988; Gledhill *et al.*, 1997). Mantoura *et al.* (1978) calculated that dissolved humic acid complexes of trace metals were only important for Cu (and possibly Pb & Ni) and that increases in salinity were accompanied by a rapid decrease in the proportion of humic-bound metals (except Cu) due to; a) competition for humic material from Ca and Mg and b) an increase in the proportion of chloro species e.g. Cd at salinities >10. Evidence from electrochemical analysis has even suggested that for some estuaries, e.g. the Scheldt, the total organic Cu fraction represents more than 99.99% of total dissolved metal (van den Berg *et al.*, 1987). Whilst Paulson *et al.* (1994a & b) concluded that in the absence of biotic particles the partitioning of ionic copper in suspensions was controlled by chemical processes dominated by complexation with particulate and dissolved organic matter.

1.2 Study Sites

The study site chosen for LOIS RACS extended from Great Yarmouth to Berwick-upon-Tweed on the east coast of Britain and is from herein referred to as the western North Sea or LOIS coastal zone (see Figure 1.1). A considerable diversity of river catchments and coastal types are displayed within this region which in terms of river flows and prevailing winds, are subject to the effects of major industrialised conurbations. More intensive studies were also performed in the Humber coastal zone which encompassed the Wash embayment, the Humber Estuary and Holderness Cliff nearshore environments in a box varying between the latitudes 52.7°N and 54.1°N, and longitudes 0.1°W and 2.4°E. The following sections outline the current knowledge of the prevailing hydrodynamics and inputs of freshwater, SPM and trace metals in both the western North Sea and more specifically the Humber coastal zone.

1.2.1 *The western North Sea*

Few studies have specifically focused on the western North Sea (Dutton *et al.*, 1973; Preston, 1973; Taylor, 1979; Jones & Jefferies, 1983; Balls, 1985) so when reviewing

the available literature on the hydrodynamics and trace metal distributions of the western North Sea, data from the whole North Sea has often been included and subsequently discussed.

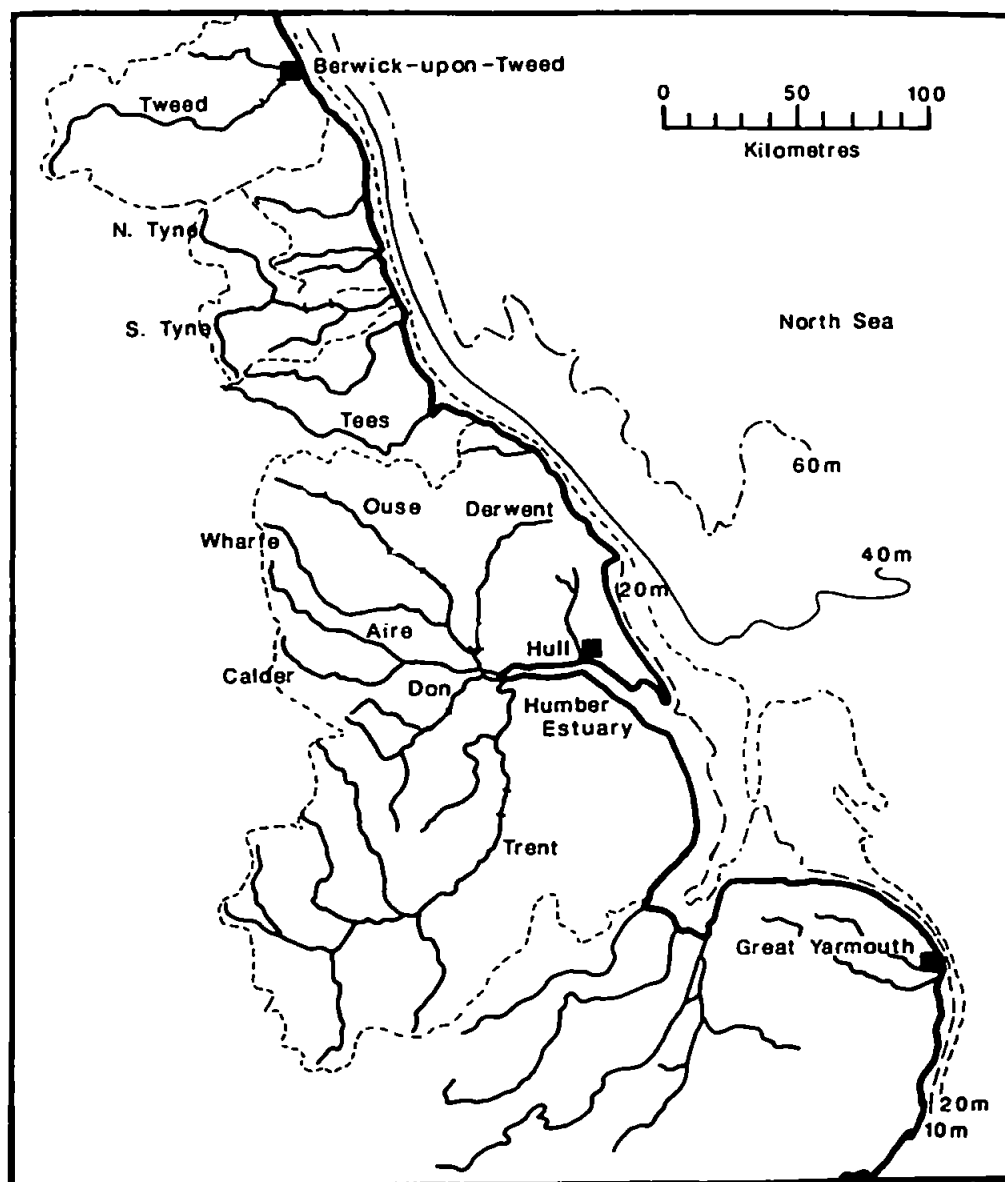


Figure 1.1 The LOIS RACS study site on the east coast of Britain showing the river catchment systems. Sampling was focused on the coastal boundary layer between Berwick-upon-Tweed and Great Yarmouth extending up to 100 km offshore (from LOIS Science plan for a Community Research Project, 1992).

1.2.1.1 Hydrodynamics

The North Sea is a shallow (30-200 m), rectangular-shaped basin with a shelving topography from south to north and a deep (up to 600 m) trough, the Norwegian Rinne,

on its eastern margin (Reid *et al.*, 1988). It is a relatively enclosed system with a total volume estimated at about 47 000 km³ (Department of Energy (DOE), 1987b). The basic physical structure and circulation of the North Sea is illustrated in Figure 1.2.

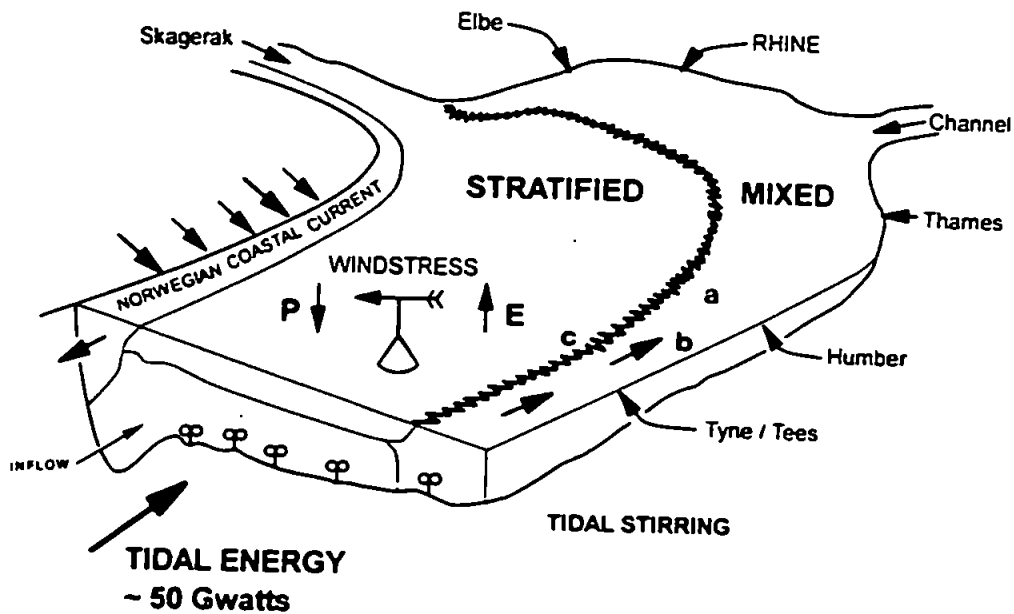


Figure 1.2 Schematic of basic physical processes in the North Sea (from Simpson, 1994). The letters a, b and c represent the location of the depth profiles illustrated in Figure 1.4 which serve to illustrate summer thermal stratification as shown above.

The energetic motions of the North Sea are forced by several different mechanisms namely the tides, winds and seasonal forcing from surface heating and cooling (Simpson, 1994). The tides are the most important (for a thorough review the reader is referred to Huntley, 1980) such that energy enters the North Sea at a rate of 50 GW across the northern boundary from the Atlantic. This tends to produce motions that dominate the kinetic energy budget and induce strong frictional stresses which have a stirring effect. Indeed tidal stirring by the interaction of the seabed with the tidal stream is the dominant process governing the downward mixing of solar heat input and the development of seasonal thermal stratification (Simpson & Hunter, 1974; Pingree & Griffiths, 1978). Other important water density differences arise from freshwater inputs from rivers. The other major source of mechanical energy the wind, along with changes in atmospheric pressure, is responsible for driving storm surge conditions (Simpson, 1994).

The combined effects of freshwater inputs, wind stress forcing and tidal rectification tend to induce a weak anticlockwise circulation (exemplified in Figure 1.3) that is typically only a few cm s^{-1} , i.e. long flushing times up to 3 years.

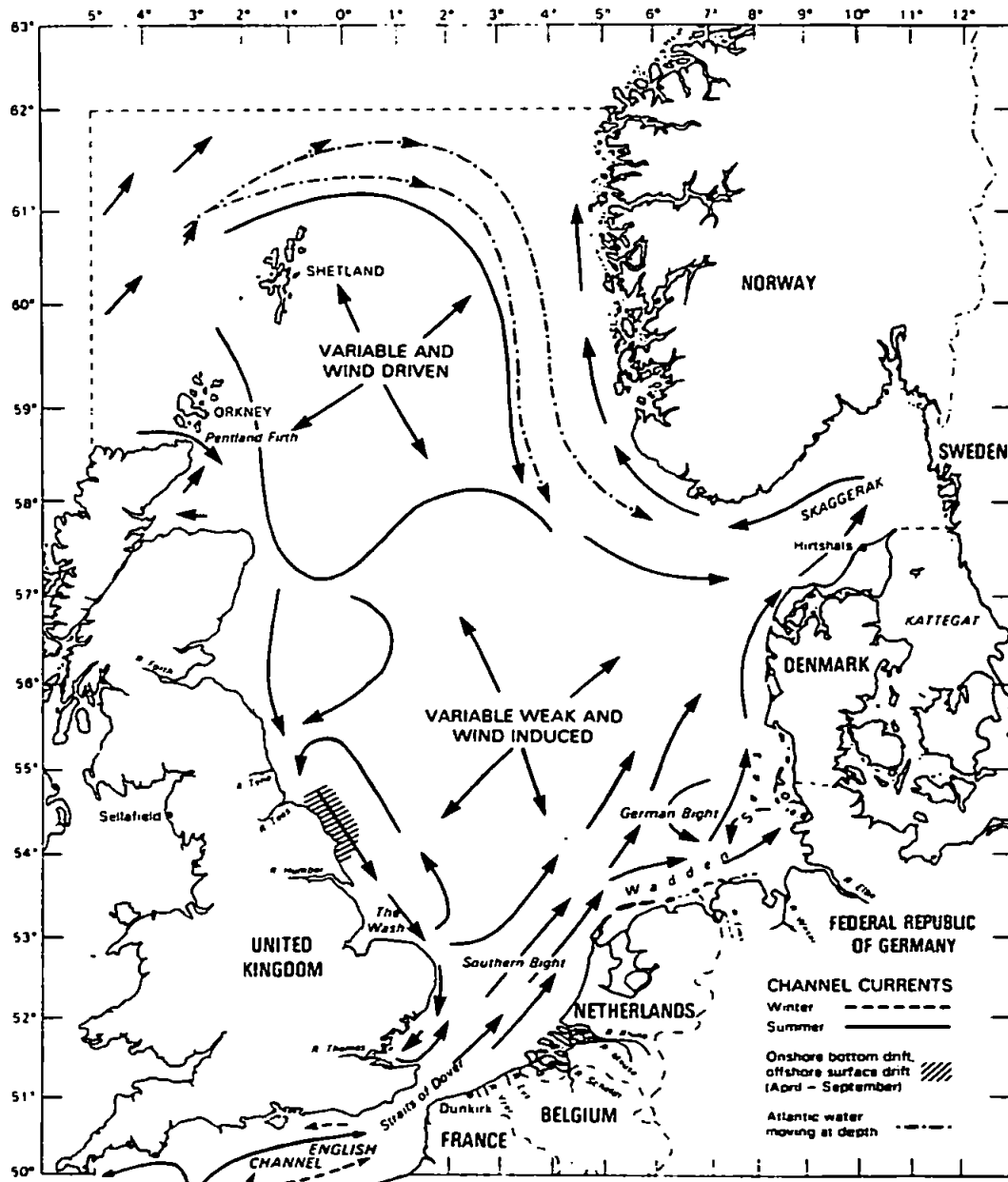


Figure 1.3 Surface current system of the North Sea (from Lee, 1980).

The weak advection means that the thermal structure is mainly controlled by local vertical exchange which, in turn, is closely related to tidal stirring. In the Southern Bight (see Figure 1.3) strong tidal currents maintain a highly turbulent regime which ensures complete vertical mixing throughout the year. In contrast the stirring in the northern North Sea is much weaker and stratifies in response to seasonal heating. Between these

two distinct regimes is an important frontal region (Figure 1.2) whose position varies little throughout summer. This phenomena is clearly illustrated by the temperature depth profiles from the summer LOIS survey (see Table 2.1) in Figure 1.4. The physical oceanography of the North Sea has been further reviewed in detail by Lee (1980), Eisma (1987) and Otto *et al.* (1990).

1.2.1.2 Freshwater inputs

Various attempts have been made in the past to subdivide the water bodies of the North Sea according to their source or properties (Lee, 1980; International Council for the Exploration of the Sea (ICES), 1983; Reid *et al.*, 1988; Tappin *et al.*, 1995) For example Tappin *et al.* (1995) defined the following water masses based on their surface salinity distributions; English Coastal Waters (ECW), English Channel/Thames Waters (ECTW), Continental Coastal Waters (CCW) and Central North Sea Waters (CNSW). The subdivision by the ICES study group took into account hydrographic and biological conditions to consider the flushing times of the North Sea (ICES, 1983). The mean transport of water through the ICES defined coastal boxes are summarised in Figure 1.5 where the subdivision 3'' most closely corresponds to the western North Sea nearshore coastal region of this study. Indeed freshwater inputs calculated by the method of Taylor *et al.* (1981;1983) for the period 1948-81 were $541 \text{ m}^3 \text{ s}^{-1}$ for subdivision 3''. However the western North Sea encompasses the plumes of the Tweed, Tyne, Tees, Humber estuaries and the outflow from the rivers discharging into the Wash. The Wash is not really an estuary with a full salinity gradient but should be considered as a coastal lagoon (Eisma & Irion, 1988). A summary of the physical properties for each of the previously mentioned freshwater inputs into the western North Sea are given in Table 1.1.

A considerable range in physical characteristics are displayed by the main estuaries (including the Wash) that discharge into the western North Sea. The main freshwater flux to the western North Sea comes from the Humber Estuary ($246 \text{ m}^3 \text{ s}^{-1}$, Gameson, 1976) which drains the largest catchment area of $27\,000 \text{ km}^2$. The physical and chemical characteristics of this estuary will be considered in more detail in section 1.2.2.

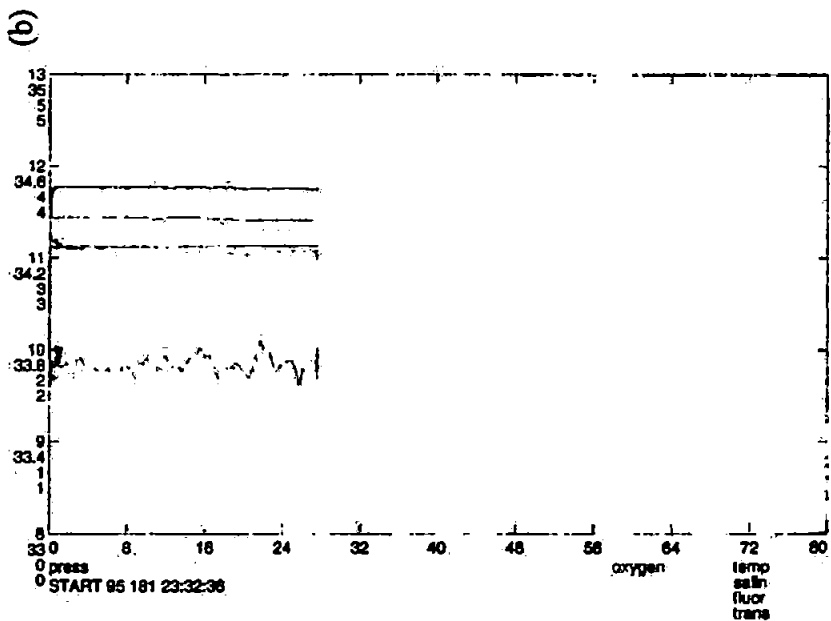
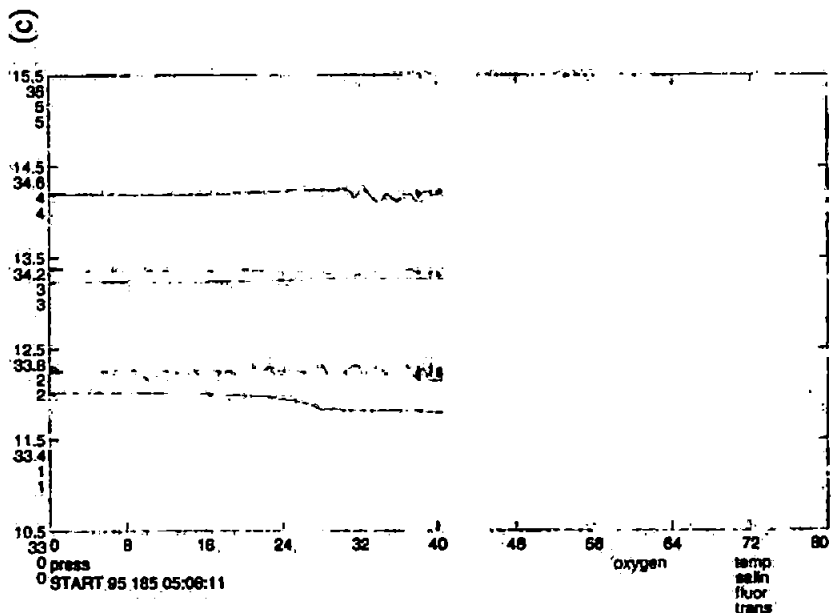
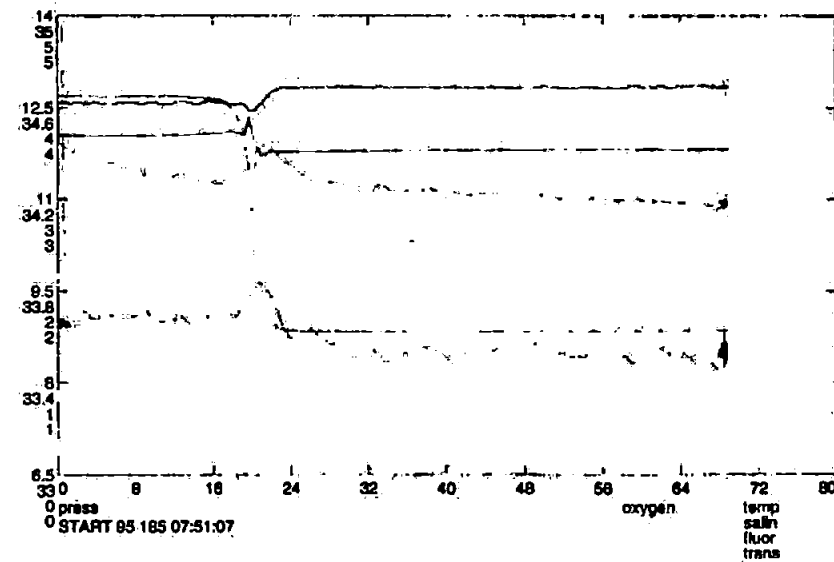


Figure 1.4 Depth profiles of temperature (red), salinity (light blue), fluorescence (green) and transmission (dark blue) from the down cast of a conductivity, depth, temperature (CTD) profiler deployed during the summer '95 survey. The locations of the profiles a, b and c are illustrated in Figure 1.2.

Table 1.1 Physical properties of the main estuaries including the Wash that discharge into the western North Sea.

Property	Tweed	Tyne ^f	Tees ^f	Humber ^f	Wash ^f
Catchment area (km ²)	4900 ^a	2927	2210	27000	12500
Mean river outflow (m ³ s ⁻¹)	78 ^b	45	20	246	48
	(35-140) ^c	(7-120)	(2-70)	(60-450)	
Tidal range mouth (m)	2.5-4.1 ^a	2.1-4.3	2.3-4.6	3.5-6.2	3.6-6.5
Salinity mouth	10-35 ^a	<33	32.5-33.5	27-30	33-34
Circulation type	partially mixed/ strongly stratified ^a	stratified	stratified	well mixed	well mixed
Residence time (days)	≤1 ^a	4 (average)	≤5	40	100
[SPM] mouth (mg l ⁻¹)	<0.3-0.5 ^c	16	7	65	10-100
	(2-20) ^d	(11-27)	(6-10)	(30-108)	
Fluvial SPM flux (x 10 ⁴ t a ⁻¹)	4.5 ^c	1.5-9.8	2.-2.4	17.2-22.5	10 (4.3-17.3)

^aUncles & Stephens, 1996; ^bWilliams, 1995; ^cUncles & Stephens, 1997; ^dBalls, 1994; ^eCalculated from $y=60x^{0.78}$ (Wilmot & Collins, 1981) where y = sediment flux (t a⁻¹) and x = catchment area (km²); ^fZwolsman, 1994 and all references therein; ^gFox & Johnson, 1997.

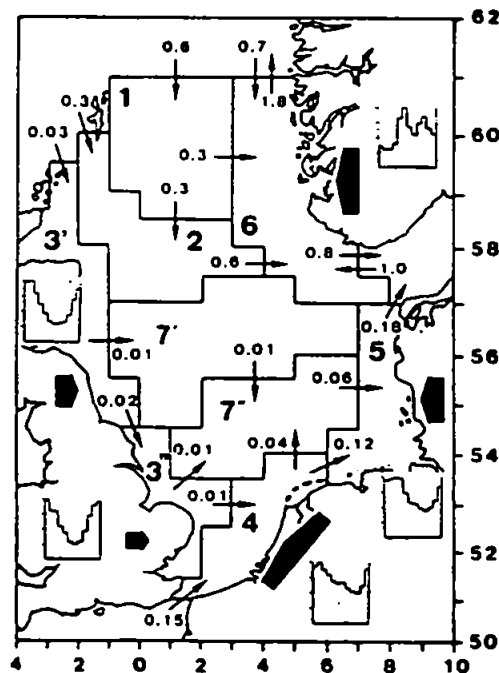


Figure 1.5 Subdivisions (1-7) of the North Sea where the arrows depict net water fluxes ($\times 10^6$ m³ s⁻¹) between the boxes (ICES, 1983). Large filled black arrows represent the size of the freshwater flows from the coasts (largest arrow is 2889 m³ s⁻¹). Seasonal cycles are also depicted for the runoff into each box; the divisions on each histogram represent 25% of the largest monthly runoff from that box (modified from Reid *et al.*, 1988).

The Tweed Estuary has the second highest water discharge (Fox & Johnson, 1997). However the river Tweed and its tributaries drain a sparsely populated (less than one tenth of the UK average (Tweed Foundation, 1992)), mainly agricultural area (Laslett, 1995; Uncles & Stephens, 1996). This is in contrast to the predominantly industrial catchments of the Tyne and Tees estuaries (Zwolsman, 1994). The Tyne river basin contains part of the Northern Pennine orefield, which has been mined extensively for Pb and Zn since medieval times whilst the river Tees catchment area includes the industrial cities of Stockton, Middlesbrough and Redcar (Zwolsman, 1994). The banks of the Tyne Estuary have undergone major canalisation and subsequently the intertidal areas have almost completely disappeared (Pomfret *et al.*, 1991) which is one of the factors leading to the strong stratification and ultimately short residence time of the river water (Cassie *et al.*, 1962). The nature of the outflows (plumes) of the Tyne, Tees and Humber into the North Sea are described in detail by Lewis (1990). Briefly vertical mixing of SPM and associated contaminants in the Tyne Plume are likely to be too slow for regions of minimum dilution to form before discharge plumes are cut off from the estuary mouth by reversal of the tidal flow. In comparison, modelling of the outflow from the Tees Estuary has suggested that regions of minimum dilution at the sea bed occur between 1.5 and 4.0 km from the estuary mouth (Lewis, 1990). The variation in the extent of the 'freshwater plumes' of the estuaries discharging into the western North Sea is illustrated by the surface salinity contours of the LOIS winter survey (see Table 2.1) in Figure 1.6a. The plumes of the UK estuaries initially stay close to the coast and are transported approximately south east with the weak residual circulation until being caught by inflow water from the Channel upon which they change direction towards the continental coast (see Figure 1.3).

1.2.1.3 Suspended matter and sediment transport

The suspended material consists of single mineral particles and aggregates of mineral particles and organic matter. The actual concentrations in the water are very much influenced by the seasonal and short term variations in water movement and primary productivity (Eisma & Irlon, 1988). Numerous field studies in the North Sea have

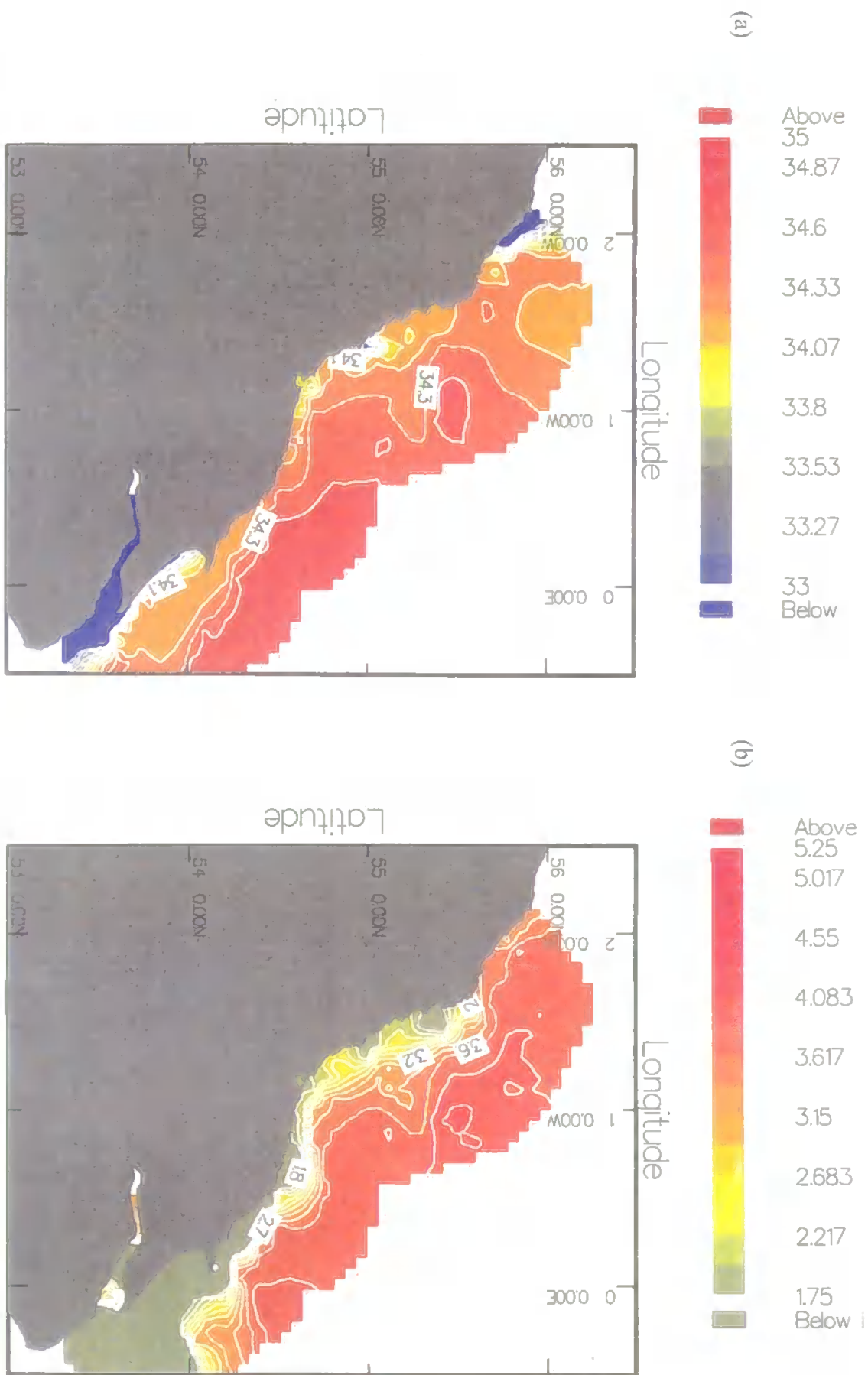


Figure 1.6 Surface contours of (a) salinity and (b) transmission in the western North Sea obtained during the winter '95 survey (volts, raw ship time data, arbitrary units).

provided information on the composition, concentration, origin and budgets of the suspended matter (summarised by Eisma & Kalf, 1987; McCave, 1987; Nolting & Eisma, 1988; Jago *et al.*, 1993; Howarth *et al.*, 1994; McManus & Prandle, 1996). The total supply of SPM to the North Sea is summarised in Table 1.2 (fluvial SPM fluxes from the Tweed, Tyne, Tees, Humber estuaries and the Wash to the western North Sea were previously given in Table 1.1).

Table 1.2 Sources of SPM to the North Sea ($\times 10^4 \text{ t a}^{-1}$).

Origin	Eisma (1981)	Eisma & Kalf (1987)	Eisma & Irion (1988)
English Channel	1000	1000	2200-3000
Atlantic Ocean	1000	1000	1040
Seafloor erosion	500	600-750	900-1350
Rivers	450	480	480
Coastal erosion	70	70	220
Atmosphere	160	160	160
Primary Production	100	100	100
Baltic	50	50	50
TOTAL	3300	3500-3600	5200-6400

However inputs of SPM from coastal erosion are probably substantially larger than those listed in Table 1.2. Data by McCave (1987) and Dyer & Moffat (1992) suggest that erosion of the Holderness Cliffs alone provide between $140\text{-}261 \times 10^4 \text{ t a}^{-1}$ to the North Sea which subsequently dominates the SPM budget of the Humber coastal zone. However fluvial SPM (from the Humber Estuary and the Wash) despite its relatively low contribution to the total SPM budget ($<10\%$ McCave, 1987; Dyer & Moffat, 1992) is a major carrier for contaminants i.e. anthropogenically derived trace metals whereas marine SPM and that of the Holderness Cliffs can be considered to be relatively depleted in comparison (Salomons & Eysink, 1981; Turner *et al.*, 1991; Zwolsman & Van Eck, 1993).

In general the SPM in the North Sea is transported through the same anticlockwise circulation as described in section 1.2.1.1. Typical concentrations of SPM, dispersal and subsequent deposition locations of mud and sandy mud are indicated in Figures 1.7a, b & c. However the estuary outputs of the western North Sea do not mix with the

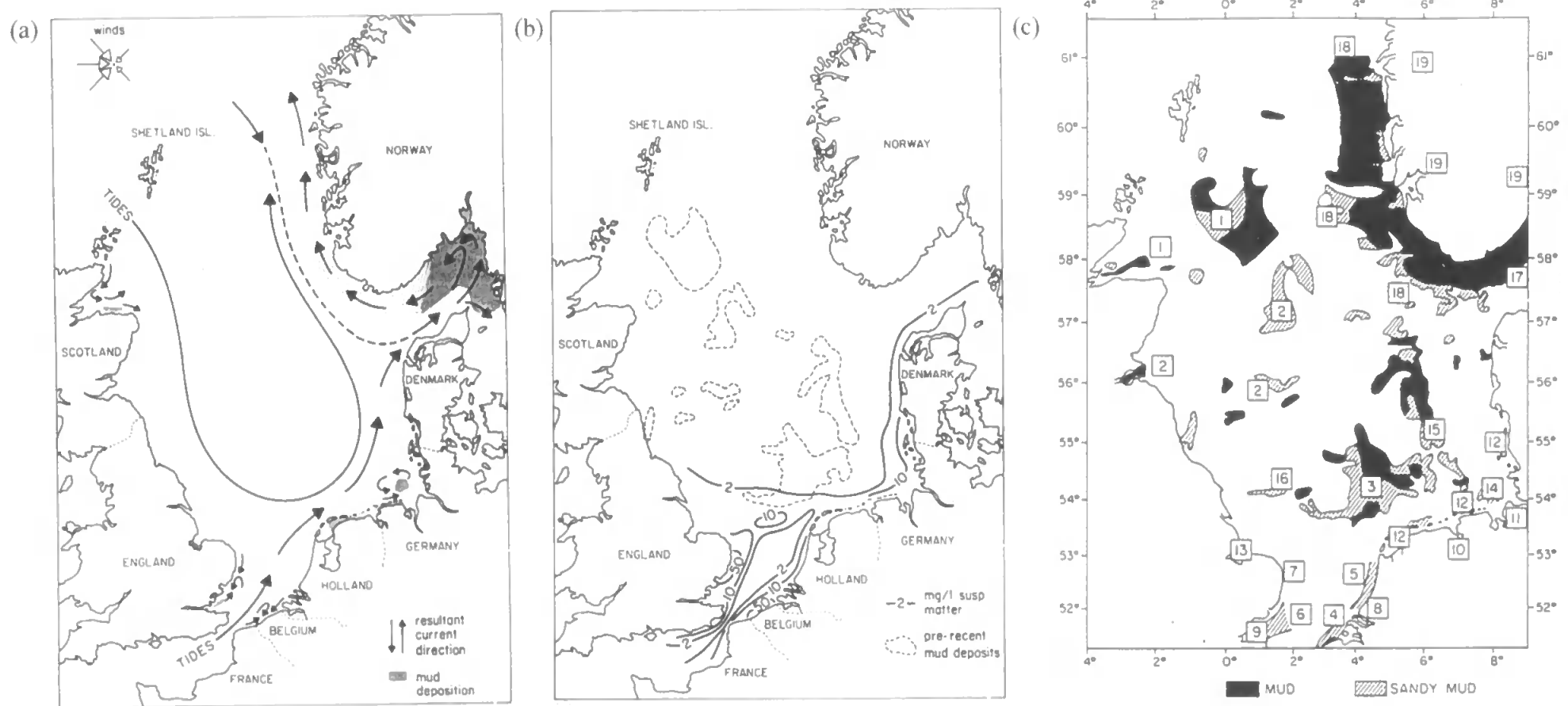


Figure 1.7 (a) & (b) Dispersal and deposition of SPM in the North Sea (from Eisma, 1981 & Eisma & Kalf, 1987); (c) Distribution of mud and sand in the North Sea (from Eisma, 1981). 1 Northern North Sea (chiefly Fladen Grounds); 2 Central North Sea; 3 Oyster Grounds; 4 Flemish Banks; 5 Dutch coastal area; 6 East Anglia coast; 7 Yarmouth-Lowestoft; 8 Rhine-Meuse-Schelde estuaries; 9 Thames estuary; 10 Ems estuary; 11 Elbe-Weser estuary; 12 the Waddensea; 13 the Wash; 14 German Bight; 15 Elbe-Rhine; 16 Outer Silver Pit area; 17 Skagerrak; 18 Norwegian Channel; 19 Norwegian and some Swedish fjords.

entire volume of the North Sea and hence have a major impact on the nearshore coastal zone for all contaminants i.e. trace metals. The surface transmission (reflecting relative differences in SPM concentration) of the western North Sea obtained during the LOIS winter'95 survey in Figure 1.6b also serves to illustrate the high concentration of suspended material emanating from the estuary mouths and from the erosion of the Holderness Cliffs.

1.2.1.4 Trace metals

Trace metals exist in a variety of different chemical and physical forms in the marine environment. A schematic review of the major pathways and reservoirs of trace metals in a marine ecosystem is depicted in Figure 1.8. For a more in depth discussion of trace metal behaviour in marine environments the reader is referred to Chester (1990). In general trace metal inputs to the North Sea can be classified as either point sources e.g. estuarine outputs, dump sites etc. or diffuse e.g. the atmosphere. Table 1.3 presents an overview of the data available in the literature on the synthesis of trace metal inputs (Cu, Cd & Pb) to the North Sea.

Table 1.3 Summary of the inputs of Cu, Cd and Pb into the North Sea.

Source	Inputs to the North Sea (t a ⁻¹)		
	Cu	Cd	Pb
River Inputs	1290-1330 ^a	46-52 ^a	920-980 ^a
Direct Discharges	≤400 ^a	40 ^a	≤165 ^a
Atmospheric			
Dry	350 ^b , 873 ^c	33 ^b	350 ^b , 1354 ^c
Wet	194 ^d	15 ^d	688 ^d
Dumpings			
Dredgings	≤1000 ^a	≤20 ^a	≤2000 ^a
Sewage Sludge	≤100 ^a	≤3 ^a	≤100 ^a
Industrial Waste	≤160 ^a	≤0.3 ^a	≤200 ^a
TOTAL	3494-4057	157-163	4423-5487

^aKersten *et al.*, 1988; ^bOttley & Harrison, 1992; ^cBradshaw, 1992; ^dChester *et al.*, 1993.

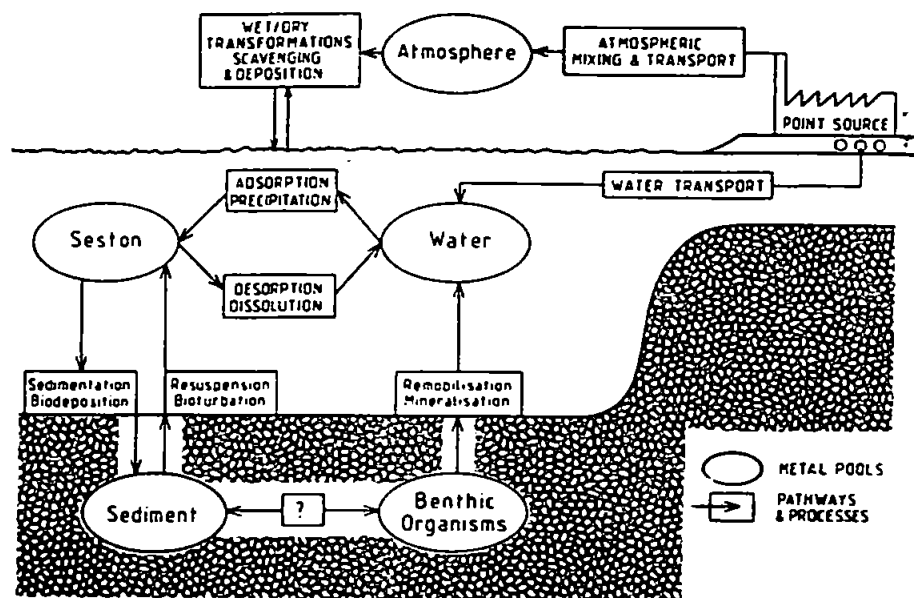


Figure 1.8 Schematic review of the major pathways and pools of trace metals in a marine ecosystem (from Kersten *et al.*, 1988).

Particles in seawater play a major role in regulating the chemical forms, distributions and deposition of trace metals released into marine waters (Hart, 1982; Wollast, 1982; Salomons & Förstner, 1984). Indeed such is the extent to which the behaviour of dissolved trace metals is dominated by suspended solids that Turekian (1977) referred to the phenomenon as the *great particle conspiracy*. Balls (1989) likewise suggested that the dynamic nature of the marine environment with its constant throughput of water and particles acts to reduce the magnitude of changes in dissolved trace metal concentrations arising from increased anthropogenic inputs. This 'buffering' effect he reported to be greatest in turbid waters ($> 5 \text{ mg l}^{-1}$) especially for particle reactive metals such as Pb (Balls, 1988). The highly turbid waters of the western North Sea and Humber coastal zone (refer to Figure 1.6b) highlight the importance of the solid phase when considering trace metal behaviour and dynamics. Indeed Balls (1989) concluded that (a) trend monitoring of dissolved trace metals was only valuable in areas of low turbidity and for metals such as Cd which have a low particle reactivity and (b) effort and resources were better directed towards process orientated research in order to better understand the transport and cycling of trace metals in the marine environment. Hydes & Kremling (1993) similarly reported that sediment exchange reactions play a significant role in controlling the dissolved concentration of trace metals but also concluded that '*an understanding of the direction in which mans activities may be shifting the system*

requires more detailed studies than have yet been carried out!' implying that more intensive studies specific to a region are required.

Several authors have reported the concentration of trace metals in the North Sea (for example, Baeyens *et al.*, 1987, SPM and dissolved; Kersten *et al.*, 1988, SPM; 1991, SPM and surface sediments; Kremling & Hydes, 1988, dissolved; Nolting & Eisma, 1988, SPM; Dehairs *et al.*, 1989, SPM and sediments; Turner, 1990, SPM and sediment; Turner *et al.*, 1991, SPM; Burton *et al.*, 1993, SPM and dissolved; Hydes & Kremling, 1993, dissolved; Rowlett & Lovell, 1994, sediment; Laslett, 1995, SPM and dissolved; Millward *et al.*, 1996, SPM; Tappin *et al.*, 1995; SPM and dissolved; Williams, 1995, SPM and sediments; Slomp *et al.*, 1997, sediments and pore water) which have been summarised for the trace metals Cu, Cd and Pb in Table 1.4. However there is still no internationally agreed standard analysis procedures for the determination of particulate trace metals in marine ecosystems. The compilation of results in Table 1.4 are derived from the application of different analysis techniques i.e. Graphite furnace atomic absorption spectrophotometry (GFAAS), Flame AAS, Inductively coupled mass spectrometry (ICP-MS) etc. More importantly the adoption of different dissolved trace metal pre-concentration steps (if required) and applied leachates to extract various particulate fractions e.g. total particulate load, reducible fraction, Fe and Mn Oxides, carbonates etc. may lead to operational systematic differences. Therefore any subsequent comparison of data sets from different laboratories is often hampered by the adoption of different analytical protocols.

In addition Balls (1985) questioned the accuracy of trace metal data collected in British waters as reported in Preston (1973) and further suggested, that in some instances, data reflected the extent of contamination during sampling, storage and analysis. Notwithstanding the above caveats dissolved concentrations obtained post 1983 in the North Sea show close agreement with dissolved Cu (Cu_d) concentrations ranging between 0.120-0.830 $\mu\text{g l}^{-1}$, dissolved Cd (Cd_d) concentrations between 0.004-0.060 $\mu\text{g l}^{-1}$ and dissolved Pb (Pb_d) between 0.013-0.135 $\mu\text{g l}^{-1}$. It is noticeable that in comparison data from the Belgian and Dutch coasts (Baeyens *et al.*, 1987) displayed elevated concentrations of all the aforementioned dissolved trace metals presumably reflecting enhanced anthropogenic disturbance in this estuarine coastal zone interface.

Table 1.4 Summary of previous determinations of particulate and dissolved Cu, Cd and Pb in the North Sea.

Form	Reference	Cu	Cd	Pb	Region	Details
Dissolved ($\mu\text{g l}^{-1}$)	Dutton <i>et al.</i> (1973) ¹	0.300-2.00	<0.100-1.60		North Sea	
	Preston (1973) ¹	0.240-1.90	0.010-1.40	<0.050-0.800	western North Sea	
	Jones & Jefferies (1983) ²	0.200-1.00	0.025-0.200		North Sea	
	Balls (1985) ³	0.120-0.580	0.010-0.060	0.015-0.135	western North Sea	July'83
	Baeyens <i>et al.</i> (1987) ³	0.280-2.50	0.014-0.110	0.045-0.260	Belgian & Dutch coasts	October'82
	Baeyens <i>et al.</i> (1987) ³	0.380-1.80	0.030-0.170	0.090-0.660	Belgian & Dutch coasts	March'83
	Kremling & Hydes (1988) ⁴	0.229	0.016		North Sea	July'84
	Hydes & Kremling (1993) ⁴	0.155	0.013		North Sea	February'88
	Burton <i>et al.</i> (1993) ⁴	0.178	0.019	0.023	central & southern North Sea	Dec'88-Jan'89
	Laslett (1995) ⁴	0.240-0.830	0.010-0.032	0.021-0.055	North Sea	June-July'91
		0.200-0.740	0.004-0.051	0.013-0.071		June-July'92
	Tappin <i>et al.</i> (1995) ⁴	0.318	0.025	0.037	English coastal zone	August'88
		0.413	0.022	0.041		Dec'88-Jan'89
	0.508	0.028	0.052		April-May'89	
	0.318	0.017	0.033		Sept-Oct'89	
SPM ($\mu\text{g g}^{-1}$)	Murray <i>et al.</i> , (1980) ⁵	23	<2	90	North Sea	
	Balls (1985) ⁶	5-115	0-0.27	3-152	western North Sea	July'83
	Nolting & Eisma (1988) ⁷	<100	<2	50-300	southern North Sea	January'80
		>100	>2	>500	central & northern North Sea	January'80
	Baeyens <i>et al.</i> (1987) ⁸	18-34	~1.0	~50	Belgian & Dutch coasts	October'82

continued.

Form	Reference	Cu	Cd	Pb	Region	Details
	Turner <i>et al.</i> (1991) ⁹	27			southern North Sea	July'88
	Kersten <i>et al.</i> (1991) ¹⁰	14	0.35	57	North Sea	Jan-March'87
	Laslett (1995) ⁶	18-43	0.10-1.4	16-88	North Sea	June-July'91
	Tappin <i>et al.</i> (1995) ¹¹	10	3.0	~100	English coastal zone	August'88
		30	2.0	~300	English coastal zone	Dec'88-Jan'89
		20		<50	English coastal zone	April-May'89
		30	1.0	~50	English coastal zone	Sept-Oct'89
	Williams (1995) ¹¹	<10-60	0-7.5	0-200	western North Sea	November'93
Surface Sediment (µg g ⁻¹)	Nicholson & Moore (1981) ⁵	0-410	0-7.0	0-320	North Sea	
19	Turner <i>et al.</i> (1991) ⁹	3		25	Wash	<63 µm
	Kersten <i>et al.</i> (1991) ⁶	19	0.17	36	North Sea	6.3-20 µm
		32	0.28	96	North Sea	<2 µm
	Rowlatt & Lovell (1994) ¹²			3-110	England & Wales coast	<2 mm
	Williams (1995) ¹¹	<10-60	<0.50-3.0	25-150	western North Sea	<63 µM
	Balls <i>et al.</i> (1997) ¹²	<10	<0.10	<50	north west North Sea	<2mm

¹Ammonium pyrrolidine dithiocarbamate (APDC) complexation, extraction into chloroform and analysis by tantalum boat technique GFAAS; ²Methyl isobutyl ketone (MIBK)/APDC complexation, extraction into chloroform and analysis by tantalum boat technique GFAAS; ³Differential pulse anodic stripping voltammetry (DPASV); ⁴APDC/diethylammonium diethyldithiocarbamate (DDDC) complexation, extraction into freon and analysis by GFAAS; ⁵Nitric acid/hydrogen peroxide digestion and analysis by flame AAS; ⁶Nitric acid digestion and analysis by GFAAS; ⁷Hydrofluoric acid/nitric acid/hydrochloric acid digestion and analysis by GFAAS; ⁸Hydrofluoric acid/Nitric acid/hydrogen peroxide digestion and analysis by DPASV; ⁹Hydroxylamine-hydrochloride in acetic acid digest and analysis by flame AAS; ¹⁰Hydrofluoric acid digestion and analysis by GFAAS; ¹¹Hydrochloric acid digestion and analysis by GFAAS; ¹²Microwave digestion with hydrofluoric acid/nitric acid/hydrochloric acid and analysis by GFAAS.

The concentration of Cu, Cd and Pb obtained in particulate matter of the North Sea displays some relative variations reflecting (a) the different mineralogy of drainage basins discharging into the North Sea, (b) varying degree of anthropogenic contamination and (c) differences in composition of the SPM. Surveys were also carried out during different times of the year. Indeed results from the first seasonal survey of the southern North Sea (Tappin *et al.*, 1995) showed that the concentrations of particulate Cd (Cd_p) during the summer were higher in all zones apart from the CNSW (see section 1.2.1.2) compared to those observed in winter. This was attributed to the relatively high affinity of Cd for biogenous particles relative to lithogenic material (Noriki *et al.*, 1985; Turner *et al.*, 1992a; Hall, 1993). This trend was consistent with the observations of Cd_p in the Straits of Dover reported by Statham *et al.* (1993). The highest particulate Cu (Cu_p) values in the ECW (see section 1.2.1.2) were obtained during winter, spring and autumn mainly along the north-east UK coastal zone, and in particular in the vicinity of the industrialised Tees Bay (Tappin *et al.*, 1995) suggesting, in contrast to Cd_p , that anthropogenic signals were having a strong influence on the seasonal variations of Cu_p concentrations. Tappin *et al.* (1995) also reported a distinct seasonality in particulate Pb (Pb_p) concentrations noting that they were markedly higher during the winter over the entire southern North Sea and were of similar value to those reported by Nolting & Eisma (1980) for surface SPM samples collected during winter'80 (see Table 1.4). The reader is referred to Tappin *et al.* (1995) for a thorough review of the seasonal distributions of dissolved and particulate Cd, Co, Fe, Mn, Ni, Pb and Zn and the processes giving rise to the observed concentrations in the central and southern North Sea of the NSP survey area.

The trace metal results of the NSP indicated the importance of establishing high quality measurements of seasonal distributions when trying to unravel the complicated biogeochemical pathways of many contaminants in dynamic shelf regimes. Further reviews of the literature on trace metals have been provided within each chapter as it was considered to be either more appropriate or beneficial to be discussed alongside the results of the present study.

1.2.2 The Humber coastal zone

1.2.2.1 Hydrodynamics

The prevailing hydrodynamics of the Humber coastal zone have previously been discussed in section 1.2.1.1 in the context of the whole North Sea. However a hydrodynamic model of the Humber coastal zone has been developed from the general purpose hydrodynamic model produced by the Natural Environmental Research Council (NERC) NSP (Prandle, 1984; Morris & Allen, 1993) and is illustrated in Figure 1.9. Residual tidal velocities over an M2 tidal cycle were calculated and used to drive the model. The model was forced by the seasonal variations in the freshwater input from the Humber and Wash rivers but variations due to wind stress were neglected.

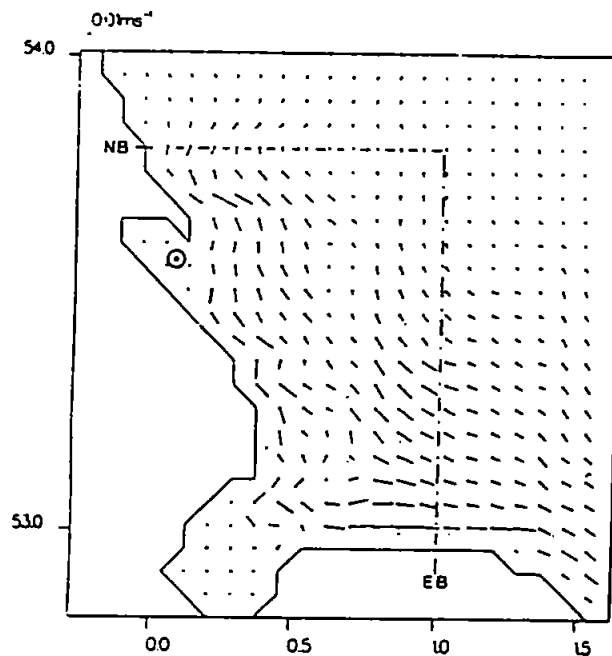


Figure 1.9 The residual (non-tidal) flow field modelled for the Humber coastal zone where NB and EB refer to northern and eastern boundaries used in flux budget calculations as mentioned in section 1.2.2.4 (originally from Morris & Allen, 1993 and modified by Millward *et al.*, 1996).

The dominant flow in the Humber coastal zone is south-easterly (as in Figure 1.3) along the Yorkshire/Lincolnshire coast and then eastwards along the Norfolk coast. The strongest currents ($0.05\text{-}0.10\text{ m s}^{-1}$) occur in relatively shallow water close to the coast. Offshore currents are much slower at $0.01\text{-}0.02\text{ m s}^{-1}$ i.e. weak advection current as

previously mentioned in section 1.2.1.1. Morris & Allen (1993) calculated that a dissolved constituent entering the coastal zone at the Humber mouth would take 10-15 days to be transported out of this region.

1.2.2.2 Freshwater inputs

The two main freshwater inputs into the Humber coastal zone are from the rivers of the Humber Estuary and the Wash lagoon. The Humber is the largest estuary in the UK and drains approximately one fifth of the land area of England (see Table 1.1). Eleven million people live in the catchment which includes much of the country's coal output, electricity generating capacity and manufacturing industry¹. An historic review on the development of industrial activity around the Humber Estuary is given by Bellamy (1988) and Jones (1988). Freshwater into the Humber Estuary is supplied by the Yorkshire Ouse and River Trent systems. The Trent flow to the estuary includes the non-tidal Trent and a few relatively small tidal tributaries. The freshwater flows to the Lower Ouse originate from the rivers Don, Aire, Derwent and Wharfe, and the rivers forming the Upper Ouse are the Swale, Nidd and Ure. The rivers Aire and Don, which drain industrial areas of Yorkshire contribute the greatest quantity of freshwater to the Ouse. The river Hull is the only major river that discharges directly into the estuary (Wulffraat *et al.*, 1993). The Humber Estuary runs for 62 km in an easterly to south easterly direction until it reaches the North Sea at Spurn Head (Zwolmann, 1994). The main physical parameters of the Humber Estuary have previously been summarised in Table 1.1. Typical tidal currents range between 0.9-1.9 m s⁻¹ for spring ebb and flood tides respectively.

The Wash is a macrotidal embayment or lagoon (Eisma & Irion, 1988) bordering the Lincolnshire and Norfolk coastlines. The physical characteristics have been previously summarised in Table 1.1. Freshwater is supplied by the rivers Great Ouse, Nene,

¹ <http://www.hull.ac.uk/HumberNet/humber.htm>.

Welland and Witham in the interior part of the embayment (Zwolsman, 1994). The mean combined average river flow is $48 \text{ m}^3 \text{ s}^{-1}$ which is small (approximately 20%) in comparison to that of the Humber Estuary. The Wash is different from the Humber, Tees and Tyne estuaries in that its drainage basin is neither densely populated nor heavily industrialised (Balls, 1985; Schofield *et al.*, 1992). The main function of the hinterland is agricultural, for which large areas of salt marsh have been reclaimed (Zwolsman, 1994). Tidal current speeds in the mouth typically range from $0.2\text{-}0.6 \text{ m s}^{-1}$ (Collins *et al.*, 1981).

1.2.2.3 Suspended matter and sediment transport

In the Humber coastal zone there is a complex and energetic mixing of SPM from seasonally active sources. The most recent estimate for the fluvial discharge of predominantly lithogenic SPM from the Humber Estuary is $22.5 \times 10^4 \text{ t a}^{-1}$ (Dyer & Moffat, 1992). A second source of fine SPM originates from the rapid erosion of Holderness Cliff 'boulder clay' material located due north of the estuary. The latter process provides between $140 \times 10^4 \text{ t a}^{-1}$ (McCave, 1987) and $260 \times 10^4 \text{ t a}^{-1}$ (Dyer & Moffat, 1992) which is approximately ten times the annual flux of material discharging from the adjacent Humber Estuary into the receiving coastal waters (Wilmot & Collins, 1981). The cliff material comprises almost 70% of particles with grain size $<63 \mu\text{m}$ (McCave, 1987). The residual circulation (see section 1.2.1.1) carries the cliff material southwards where it is mixed in various proportions with estuary derived material (Grant & Middleton, 1990; Turner *et al.*, 1991). Seabed drifter experiments released at the mouth of the Humber Estuary by O'Connor (1987) have indicated that only 7% of the eroded cliff material is actually retained by the Humber Estuary and consequently contributes to siltation within the estuary itself. However estimates by Millward & Glegg (1997) suggested that particles retained within the estuary have a residence time of 18 years. This is long when compared to the flushing time of the estuary of about 40 days (see Table 1.1) and has important implications for the retention of particle associated contaminants, such as some trace metals. Other sources of suspended matter to the Humber coastal zone include the North Sea (O'Connor, 1987), the resuspension of surface bed sediments which will be greatest during times of maximum current shear

(Jago *et al.*, 1993) and, during spring and summer months, the production of phytoplankton (Joint & Pomeroy, 1993).

The fluvial SPM in the Wash (see Table 1.1) according to Dyer (pers comm) is likely to be retained almost quantitatively. Indeed it is widely acknowledged that the Wash is an area of mud deposition (see Figure 1.7). For extensive studies of the mechanisms involved in sediment deposition and the origin of the sediment supply to the Wash the reader is referred to Collins and his co-workers (Evans & Collins, 1975:1987; Collins *et al.*, 1981; Wilmot & Collins, 1981). Based on sediment composition, there is evidence to suggest that Humber SPM is also deposited in the Wash to a very great extent (Turner, 1989; Dyer, pers comm). According to McCave (1987), about 80% of the mud supplied to the UK east coast is deposited in the Wash and some smaller depositional areas. Although based on the sediment budget quoted by Dyer & Moffat (1992) only 16% of the total mud supply to eastern England is retained by the Wash, a consequence of higher estimated cliff erosion rates.

1.2.2.4 Trace metals

As previously mentioned the Humber Estuary catchment area drains heavily industrialised areas of the west Midlands and Yorkshire (Zwolsman, 1994). There are about 1600 factories of all sizes in Humberside. These large factories include industries that manufacture pharmaceuticals, fertilisers, dyes and pigments e.g. titanium dioxide and man made fibres. The trace metal distribution in sediments from the Humber Estuary clearly indicate the presence of 'hot spots' near the mouth (Barr *et al.*, 1990), probably associated with the effluents from the titanium dioxide plants (Tioxide Europe Ltd) discharged into the Humber. Indeed Grant & Middleton (1990) reported enrichments of Cu and Pb between 3.5-6.0 relative to a pre industrial sediment sample taken in the Humber Estuary. However once the effect of grain size is taken into account metal concentrations in the Humber Estuary have been reported to be rather uniform throughout the whole estuary with two exceptions (Grant & Middleton, 1990;1993). A single sample from the north bank of the estuary showed elevated Cu and Pb levels in addition to an industrialised area on the south bank receiving effluents from the titanium

dioxide processing factories. Typically reported levels of Cu and Pb in Humber sediments range between 70-206 and 127-469 $\mu\text{g g}^{-1}$ respectively (Grant & Middleton, 1990;1993). Interestingly a report by Barnett *et al.* (1989) on the metal content in *Fucus vesiculosus* collected from the Humber also showed relatively elevated Cu levels of $\geq 50 \mu\text{g g}^{-1}$ on the lower south shore compared to baseline concentrations of the order $30 \mu\text{g g}^{-1}$. This report also demonstrated that Cu and Cd levels in the fronds of the seaweed had approximately doubled in concentration to 70 and $6.5 \mu\text{g g}^{-1}$ respectively in samples collected during February'87 compared to those collected during September'81, indicating enhanced inputs into the estuary. The total (particulate and dissolved) inputs of Cu, Cd and Pb into the Humber Estuary during 1985-92 (PARCOM, 1991; Oslo Commission, 1992; National Rivers Authority, 1993a & b;1995) are shown in Table 1.5. The figures indicate between 26-52% decrease in trace metal inputs in 1992 compared to 1985-89 figures, although more recently the reduction in inputs has slowed with Cd showing an increase in 1992 compared to 1991 figures.

Table 1.5 Total fluxes of Cu, Cd, Pb and Fe into the Humber Estuary.

Metal	Source	Flux (kg day^{-1})				
		1985-89	1990	1991	1992	1993
Cu	Riverine, sewage & industrial	420 ^a	269-280 ^b	225 ^c	205 ^c	
	Dredged		860 ^c			
Cd	Riverine, sewage & industrial	16.6 ^a	2.1-10.1 ^b	7.91 ^c	9.72 ^c	
	Dredged		5.4 ^c			
Pb	Riverine, sewage & industrial	350 ^a	198-231 ^b	540 ^c	258 ^c	
	Dredged		1390 ^c			
Fe	Industrial	175000 ^d				137000 ^f

^aNational Rivers Authority (1993a); ^bPARCOM (1991) low and high loads respectively; ^cNational Rivers Authority (1993b); ^dNewell *et al.* (1984) data for the major source only; ^eOslo Commission (1992); ^fNational Rivers Authority (1995) data for major industrial source only.

A summary of the typical concentrations of Cu, Cd and Pb found in the water and sediments of the Humber Estuary are shown in Table 1.6. Dissolved Cu has shown close to conservative behaviour in the estuary (Gardiner, 1982; Jones & Jefferies, 1983; Balls, 1985; Morris & Allen, 1993; Comber *et al.*, 1995) and is generally present in a complexed form (van den Berg *et al.*, 1987; Gardiner & Ravenscroft, 1991a & b;

Table 1.6 Summary of previous determinations of Cu, Cd and Pb in the Humber Estuary.

	Ref.	Cu	Cd	Pb	Location
Dissolved ($\mu\text{g l}^{-1}$)	1	4.3	0.160	0.5	Spurn Head
	2	0.1-0.9	0.080-0.230		Humber mouth
	3	8.0	0.500		Upper Humber
	4	0.3-3.3	0.026-0.600	0.010-0.055	Humber Estuary
	5	2-10	0.050-0.450		Humber Estuary
	6	0.8-3.6	0.049-0.220	0.023-0.620	Humber Estuary
	7	0-2.9	0.000-0.170		Humber Estuary
SPM ($\mu\text{g g}^{-1}$)	8	21-110		29-43	Humber Estuary
	7	0-110	0.00-2.0		Humber Estuary
	6	36-55	0.11-0.40	140-190	Humber Estuary
	9	29	3.70	128	Humber mouth
Surface	9	30	0.80	155	Humber mouth
Sediment ($\mu\text{g g}^{-1}$)	10	17		36	Humber, north bank
	10	11		25	Humber, south bank
	11	70-206		127-469	Humber Estuary

1 <http://www.hull.ac.uk/HumberNet/humber.htm>; 2 Murray *et al.* (1980); 3 Gardiner (1982); Balls (1985); 5 Comber *et al.* (1995); 6 Laslett (1995); 7 Morris & Allen (1993); 8 Turner *et al.* (1990); 9 Williams (1995) surface sediment analysis of <63 μm fraction; 10 Turner *et al.* (1991); 11 Grant & Middleton (1990;1993).

Comber *et al.*, 1995) that is less harmful to marine organisms than 'free' ionic copper (Sunda & Guillard, 1976). Copper is known to bind strongly to natural organic ligands (Comber *et al.*, 1995). The concentration of such ligands in the dissolved phase has been shown to decrease with increasing salinity for the Humber Estuary (Apte *et al.*, 1990) which may help to explain decreasing Cu_d concentrations with increasing salinity.

Dissolved Cd has been similarly shown to display conservative behaviour in the Humber (Balls, 1985; Morris & Allen, 1993) although recent results by Comber *et al.* (1995) consistently showed broad peaks in dissolved concentrations within the estuary which were attributed to diffuse discharges and inputs from the Trent and/or desorption from particulate matter as a consequence of dissolved phase chloro complexation. Cadmium is not very particle reactive and is thus not easily removed from the dissolved phase (Oakley *et al.*, 1981; Balls, 1985; Laslett, 1995). However Cd does form highly stable soluble complexes with dissolved chloride ions which are more abundant in seawater compared to river water which often leads to an increase in Cd_d concentrations with

salinity in some estuaries e.g. Gironde, Rhone and Huanghe (Elbaz-Poulichet *et al.*, 1987), Changjiang (Edmond *et al.*, 1985; Elbaz-Poulichet *et al.*, 1987), and the Forth and Tay (Laslett, 1993) although this has not been reported for the Humber (Balls, 1985; Morris & Allen, 1993). The Humber Estuary has previously been established as a significant source of Cd_a to the North Sea (Balls, 1985; Laslett, 1995; Tappin *et al.*, 1995) as it often exhibits some of the highest concentrations observed in European macrotidal estuaries (Laslett, 1995). The uptake of Cd_a by plankton has previously been demonstrated by Turner *et al.* (1992) using radiotracers, but the relatively high 'background' levels of Cd_a in shelf waters have previously been thought to mask the sufficient depletion of stocks and hence the typical development of nutrient-like profiles (Bruland, 1980; Bruland & Franks, 1983; Burton *et al.*, 1993).

Unlike Cu and Cd the distribution of Pb is strongly governed by its association with the particulate phase (see section 1.1). Dissolved Pb has not previously shown any linear relationship with salinity for the Humber Estuary (Balls, 1985), although Tappin *et al.* (1995) reported a significant positive relationship for the more extensive Humber coastal area. In general the concentration of Pb_a in the Humber Estuary and the North Sea are very close to values reported for surface waters of the North Atlantic (e.g. Mart *et al.*, 1983; Schaule & Patterson, 1983; Boyle *et al.*, 1986; Tappin *et al.*, 1995) due to the efficient scavenging of Pb from solution onto particle surfaces (Mart *et al.*, 1982; Balls, 1985:1988).

The estuary is also a primary source of Fe because the riverine supply (approximately $0.2-1.2 \times 10^4$ kg day⁻¹) is augmented by large anthropogenic inputs (up to 1.75×10^5 kg day⁻¹) of Fe dissolved in 2% sulphuric acid from the discharge of the Tioxide Group Plc into the river Humber (Newell *et al.*, 1984; Greenpeace, 1992). Subsequent mixing of Fe-rich effluents with sea water eventually results in Fe removal to the particulate phase by precipitation and/or flocculation (Millward *et al.*, 1996). Mixed Fe oxides typically have relatively high specific surface areas (Turner *et al.*, 1991) which possibly account for their extremely high adsorption capacities for trace metals (Hem, 1978, Millward & Moore, 1982; Drever, 1988). Particulate Cu, Cd and Pb generally demonstrate highly scattered trends with salinity for the Humber Estuary (Balls, 1985; Morris & Allen, 1993) although earlier work by Balls (1985) did suggest more conservative mixing of

Cu_p along the estuarine salinity gradient. 'Black box' type calculations of the seasonal fluxes of dissolved and particulate metals in the Humber coastal zone (for boundaries used please refer to Figure 1.9) have been carried out and reported by Morris & Allen (1993) and Millward *et al.* (1996). They concluded that further development of such models required reliable field data sets in order to both force and validate the models. Specifically an improved knowledge of the (1) spatial and seasonal variations of partition coefficients and related kinetic parameters and (2) seasonal changes in freshwater inputs of SPM, dissolved and particulate trace metals were required which themselves form primary objectives of the current study.

1.3 Aims Of The Current Study

1. To provide an extensive seasonal set of high quality measurements of particulate Fe, Mn, Cu, Cd and Pb in the nearshore coastal environments of the western North Sea encompassing the Tees, Tyne, Tweed and Humber estuaries and hence define the seasonal contaminant gradients away from the coast.
2. To provide an intensive seasonal set of high quality measurements of particulate Fe, Mn, Cu, Cd and Pb in the Humber coastal zone in an effort to quantify their sources and sinks within the estuarine-coastal interface and to develop an understanding of the effects of seasonal cycles on particulate trace metal distributions.
3. To calculate fluxes of both dissolved and particulate trace metals across the mouth of the Humber Estuary to the nearshore receiving environment of the Humber coastal zone.
4. To investigate the change in the reactivity of trace metals with particle type in order to improve the understanding of the various pathways/cycling of trace metals in the marine environment. Particle types were differentiated on the basis of their;
 - a) settling velocity,
 - b) spatial location and

- c) biogenic character (refer to section 4.1).
5. To examine the isotopic ratios of Pb in nearshore sediments and SPM of the western North Sea in an attempt to assess the anthropogenic proportion of the extracted concentrations. Similar analysis was performed on particles distinguished by their settling characteristics in order to investigate whether anthropogenically derived Pb was associated with a specific settling particle population.
 6. To identify key processes affecting trace metal behaviour in the Humber coastal zone and to provide concurrent seasonal measurements for the development and parameterisation of a conceptual model describing particulate trace metal transport in nearshore environments.

The fulfilment of these aims will contribute significantly to the further development and refinement of coupled hydrodynamic-biogeochemical models of this coastal region (Morris *et al.*, 1995; Millward *et al.*, 1996) e.g. NOSTRADAMUS (Tappin *et al.*, 1997). A well refined model will be essential for future coastal management, protection and sustainability, these being overall objectives of the LOIS project.

2 Sampling and Analytical Methods

2.1 Sample Collection

2.1.1 Overview of sampling strategy

Sampling surveys were carried out during four LOIS RACS cruises onboard RRS *Challenger* from stations along the Humber-Wash and Humber-Tweed tracks (Figure 2.1) on the western coast of the North Sea, and from herein will be referred to as the autumn, winter, spring and summer cruises as detailed in Table 2.1.

Table 2.1 Summary of research cruises onboard RRS *Challenger*

Cruise	Date	Season
CH115C/94	1-16 November 1994	Autumn
CH117A/95	7-22 January 1995	Winter
CH118A/95	1-14 April 1995	*
CH118B/95	14-26 April 1995	Spring
CH119C/95	30 June- 13 July 1995	Summer

*Productivity cruise only

The overall objective of the chemistry component of the surveys was to study the geochemical behaviour and subsequent transport of trace metals (Fe, Mn, Cu, Cd, Pb) in the nearshore region of the western North Sea between 52° N and 56° N. The emphasis of the work being on the flow of energy and related contaminants from the land to the receiving waters of the coastal zone and subsequent changes with concurrent season. A consistent sampling strategy was implemented on all cruises to ensure data

comparability, both within LOIS and other international community research initiatives namely, the NSP. The latter project focused on the entire central and southern North

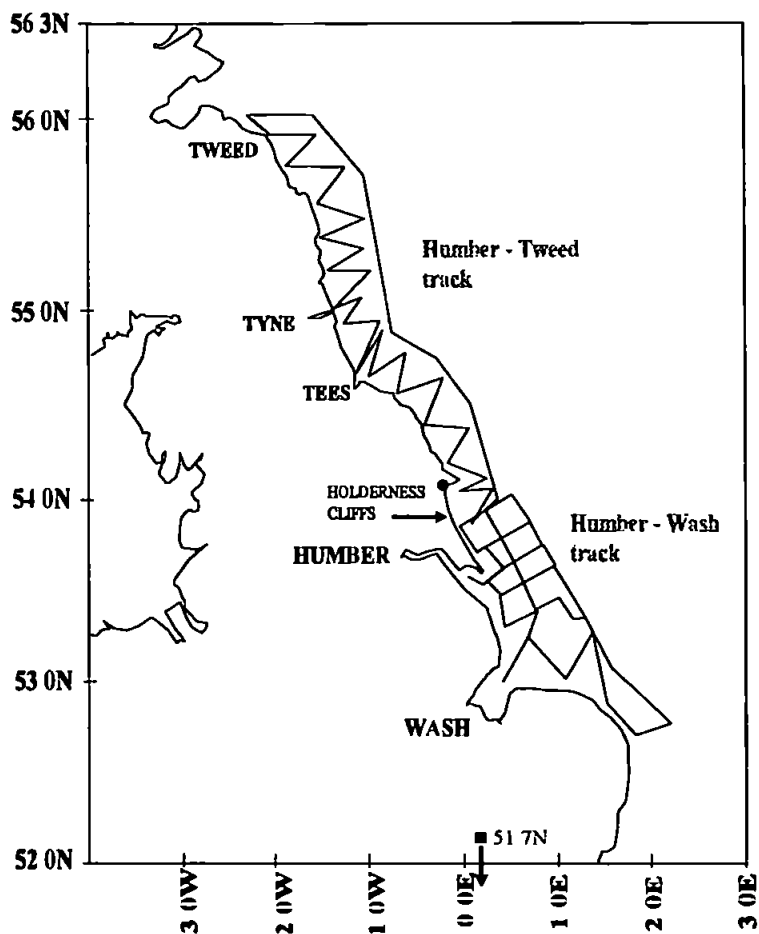


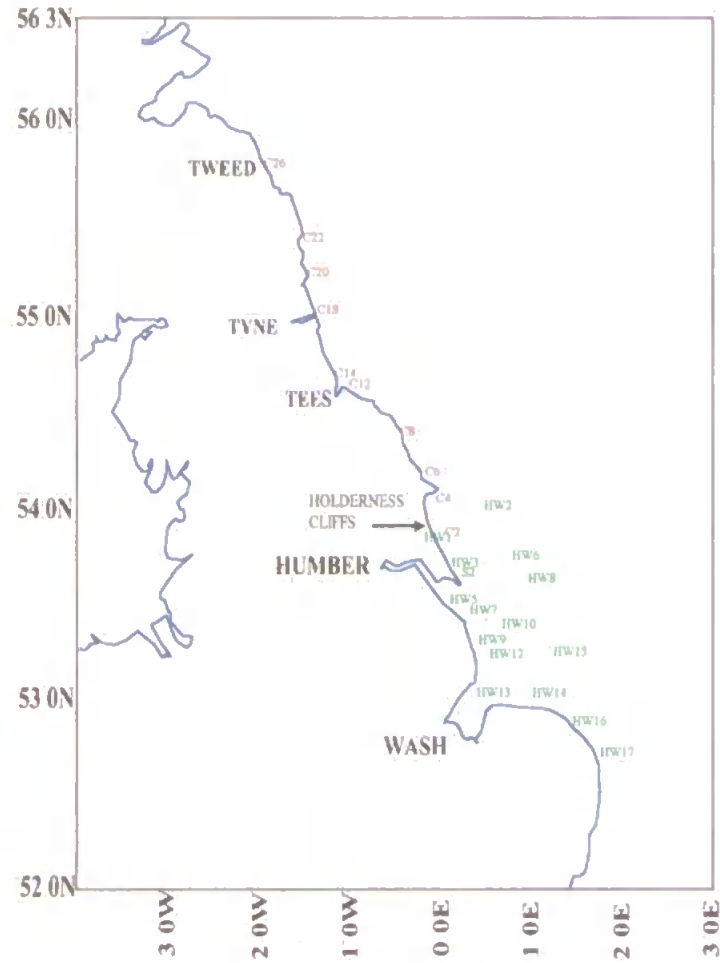
Figure 2.1 The western North Sea showing the Humber-Tweed and Humber-Wash cruise tracks. All sampling locations were along the cruise tracks. The location of the meteorological stations at Bridlington and Donna Nook are indicated by the symbols (●) and (■) respectively.

Sea but nevertheless provided invaluable reference levels for the long term monitoring of the trends of trace metals in the North Sea as the reductions of metal inputs are implemented (Tappin *et al.*, 1995). The adopted sampling strategy involved the following;

- I. The spatial collection of SPM in both the Humber-Tweed and Humber-Wash coastal zones¹ (refer to Figure 2.2),

¹ During autumn'94 and winter'95 cruises sample coverage along the cruise tracks (see Figure 2.2) was restricted owing to adverse weather and time constraints.

(a)



(b)

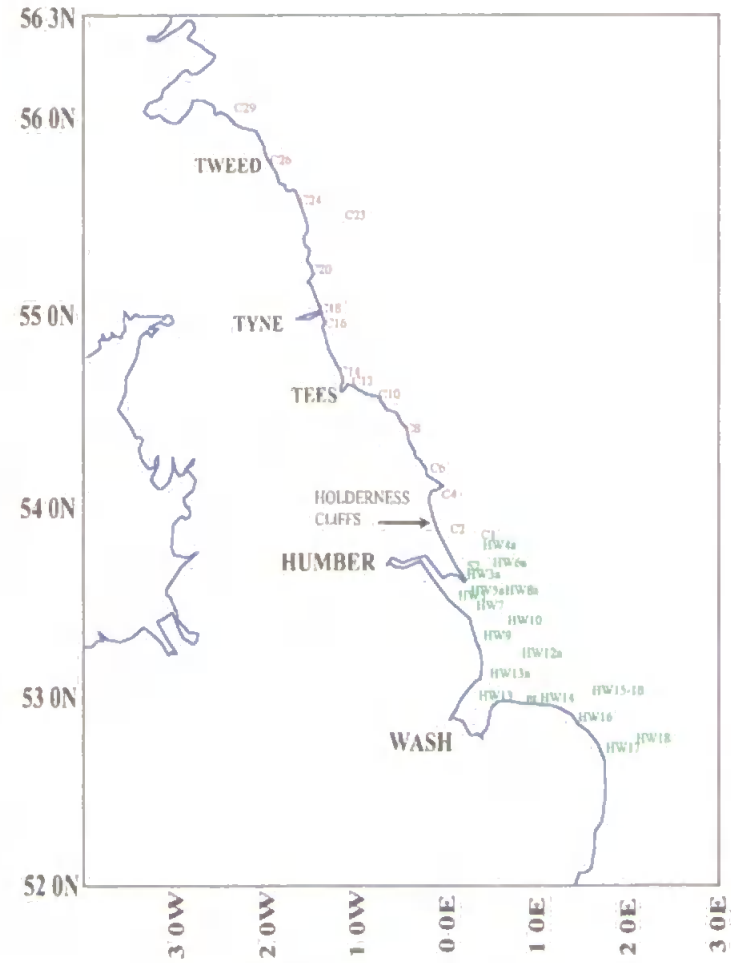
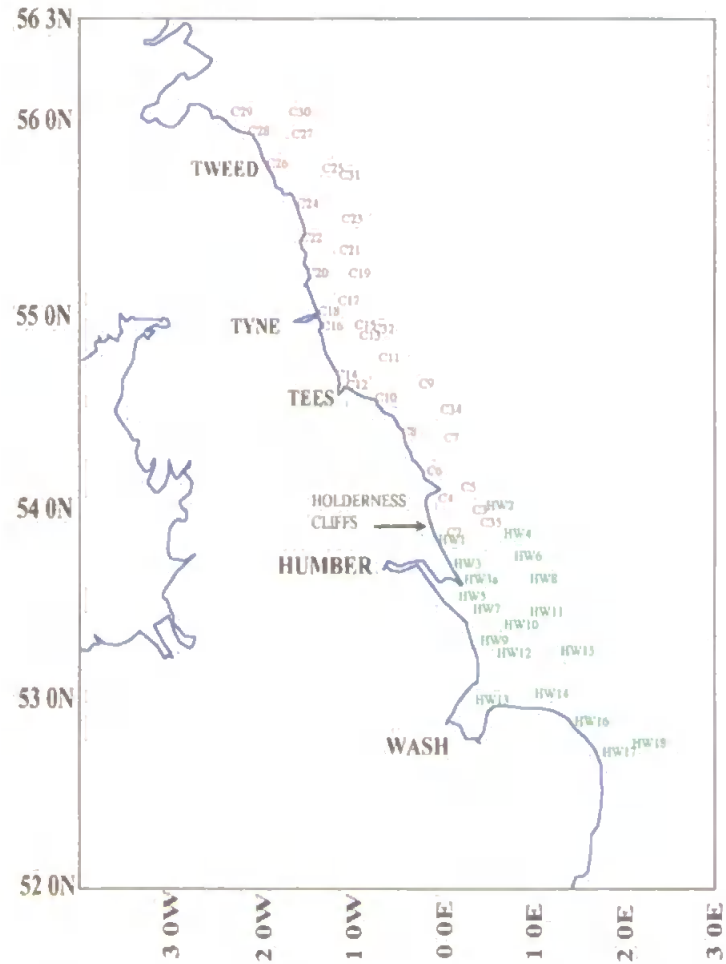


Figure 2.2 Sampling locations along the Humber-Wash (HW - including the anchor station S2, see Figure 2.3) and Humber-Tweed (C) cruise tracks during (a) Autumn '94 and (b) Winter '95.

(c)



(d)

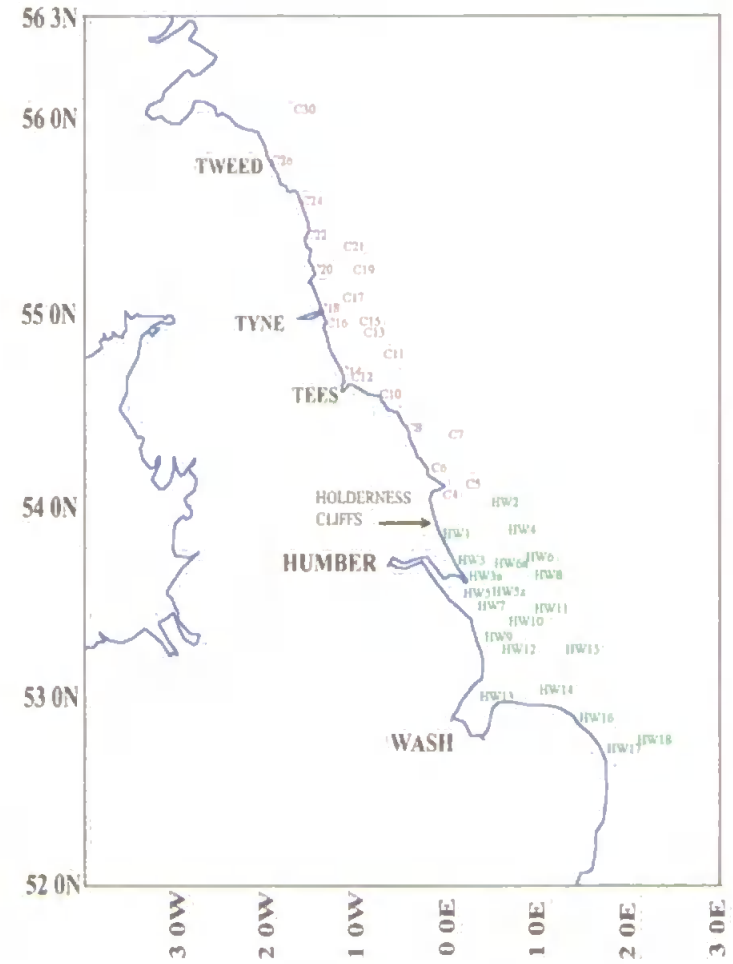


Figure 2.2 continued. Sampling locations along the Humber-Wash (HW - including the anchor station S2, see Figure 2.3) and Humber-Tweed (C) cruise tracks during (c) Spring '95 and (d) Summer '95.

- II. The temporal collection of SPM and simultaneous water samples for dissolved trace metal (Cu, Cd & Pb) analysis from the Humber Plume over complete tidal cycles (greater than 12 hours duration, sampling every hour, for locations refer to Figure 2.3),
- III. The collection of surface sediment samples (see section 2.1.4 for sample locations),
- IV. The onboard incubation of water samples with a gamma emitting radio-isotope cocktail containing ^{109}Cd , ^{137}Cs and ^{54}Mn (see Section 2.5) in order to assess the sorptive properties of different particle populations, as defined by the partitioning between the solid and solution phases (γ -incubations),
- V. The collection of seawater samples for settling experiments with QUISSET (Quasi In Situ Settling velocity) tubes.

For a summary of sample collection see Table 2.2.

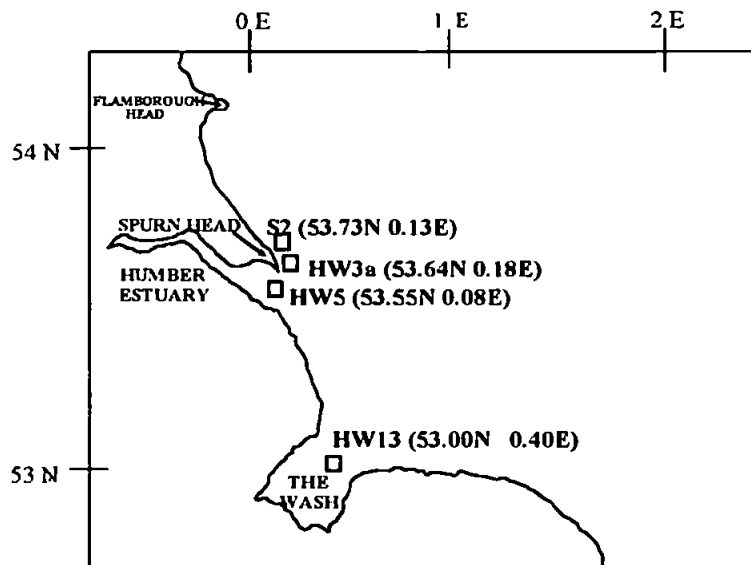


Figure 2.3 Location of anchor stations for temporal SPM and water sampling

Care was exercised throughout all sample collection to minimise contamination from the ship. Sample manipulations were carried out in a clean container situated on the after deck of RRS *Challenger* adopting 'ultra clean' ship board procedures as detailed by Morley *et al.* (1988). The clean container was provided by Research Vessel Supplies (NERC) and was fitted with a laminar flow hood (Class-100) for filter handling and a Milli-Q water system.

Table 2.2 Summary of samples collected during the LOIS cruises

Cruise	Spatial SPM		Temporal SPM		γ -Incubations	Surface Sediment	POC
	Humber-Tweed track	Humber-Wash track	Anchor Stations	Settling Velocity Experiments ^c			
CH115C/94	✓(10)	✓(16)	HW5 ^d , S2 ^d	HW5-High water S2-Flood Tide S2-Ebb Tide	-	✓(9)	-
CH117A/95	✓(15)	✓(18)	HW5 ^d , S2 ^d , HW3a	HW5-Flood Tide ^a HW5-Ebb Tide ^a	✓	-	✓(18)
CH118A/95	-	-	-	-	✓	-	-
CH118B/95	✓(33)	✓(19)	HW5 ^d , HW3a ^d , HW13	HW5-Flood Tide ^a HW5-Ebb Tide ^a	✓	✓(8)	✓(38)
CH118C/95 ^b	-	-	-	-	-	✓(6)	-
CH119C/95	✓(21)	✓(21)	HW5 ^d , HW3a ^d	HW5-Flood Tide ^a HW5-Ebb Tide ^a	✓	-	✓(33)

Figures in brackets refer to number of samples; For location of anchor stations refer to Figure 2.3; ^acomplimentary particulate organic carbon (POC) data; ^bsediment samples were kindly collected by Plymouth Marine Laboratory; ^cwith QUISSET tubes; ^dwith corresponding water samples for Cu_d, Cd_d & Pb_d analysis

2.1.2 Suspended particulate matter (SPM)

Seawater samples were obtained using 10 litre, acid rinsed (see Appendix A for detailed procedures), Go-Flo (General Oceanics, Florida) sampling bottles mounted on a stainless steel, 12 bottle rosette fitted with a Neil Brown Conductivity/Temperature and Depth (CTD) probes. The bottles were designed to enter the air-sea interface closed to avoid contamination during deployment from the surface micro-layer. They were opened at approximately 10 m below the sea surface by a pressure-release mechanism and then closed when tripped by a hydroline messenger (Hunter *et al.*, 1996). Transmissometer (Sea Tech), fluorometer (Chelsea Instruments) and PAR (photosynthetically available radiation) sensors were also mounted on the rosette frame. The retrieved Go-Flo bottles were inverted to ensure sample homogenisation and subsequently mounted on the exterior of the clean chemistry container. The water samples were subsequently filtered under positive nitrogen gas pressure (0.5 bar), through teflon filter presses containing pre-weighed, acid washed, 142 mm diameter, 0.4 μm pore size, Nuclepore polycarbonate filters (the reader is referred to Yeats & Brüggmann, 1990 for a discussion on the merits of different filter types). Between 2-20 litres of water was filtered in order to obtain between 10-100 mg of SPM. The suspended solids were then washed with approximately 20 ml of Milli-Q water in a laminar flow hood to remove sea salts, although it is acknowledged that this may potentially desorb loosely bound metals (Millward & Turner, 1995), dried under vacuum, and stored frozen in individual Petri dishes at -18°C until shore based analysis.

The above on-line filtration procedure was not used in the highly turbid waters of the Humber anchor station (HW5, Figure 2.3), where the concentration of SPM often exceeded 500 mg l^{-1} , as it was anticipated that direct filtration would have resulted in an underestimate of the true suspended matter concentration due to settling of particles in the Go-Flo bottles (Yeats & Brüggman, 1990; Turner, 1990). An aliquot, typically 1-2 litres of unfiltered water was immediately withdrawn from the recovered sampling bottles into an acid cleaned, low density polyethylene (LDPE) container and thoroughly agitated to ensure that all material remained in suspension. The water sample was then filtered

through a pre-weighed, acid washed, 47 mm diameter, 0.4 μm pore size, Nuclepore polycarbonate filter.

2.1.3 Water sampling

Water samples subsequently analysed for Cu_d , Cd_d & Pb_d were collected at the anchor stations in the Humber Mouth and Plume (Figure 2.3). The filtrate from the SPM sampling was collected in 500 ml, pre-acid cleaned, LDPE bottles (Nalgene). Samples were subsequently acidified to *c.* pH 2 by the addition of nitric acid (AristaR 69%, BDH, 1 ml per litre of seawater) in order to prevent hydrolysis of the metal ions, minimise microbial action and help prevent adsorption onto the container walls (Millward & Turner, 1995). It is important to remember that the distinction between the particulate and dissolved phases is operationally defined by the nominal pore size of the filter used i.e. 0.4 μm . It is therefore possible that colloidal sized particles $<0.4 \mu\text{m}$ were not retained by the filter but were incorporated into the 'dissolved' phase. In order to minimise such artefacts the aliquot of filtrate retained for dissolved analysis was taken after approximately 1 litre of seawater had been filtered. It was hoped that this action 'pre-loaded' the filter, effectively reducing the nominal pore size and therefore reducing the amount of colloidal material $<0.4 \mu\text{m}$ incorporated within the dissolved phase (Taylor & Shiller, 1995). Seawater samples were stored cool (2-4°C) and sealed in plastic bags to await further sample manipulation in the shore based laboratory.

2.1.4 Sediment sampling

Surface sediment samples were obtained by the deployment of a Day Grab or from sub-sampling a box core (see Figure 2.4). The Day Grab samples the top 5-10 cm layer but does not preserve the depth structure resulting in a homogeneously mixed surface sample. Upon recovery the collector 'bucket' of the grab was inverted and a sub-sample of sediment taken with an acid cleaned plastic spatula and stored in a 200 ml plastic

(a)



(b)



Figure 2.4 Photographs of (a) a Day grab after the collection of a surface sediment sample and (b) a box corer being recovered after the collection of a sediment sample.

Petri dish. When a box core was deployed a surface scrape took a mixed surface sample down to a similar depth. The samples were labelled, put into plastic bags and immediately stored frozen at -18°C . Sediment samples were taken in the Humber coastal zone and near to the mouths of the main estuaries that discharge into the western North Sea (see Figure 2.5). In addition to samples taken during LOIS cruises a number of sediment samples were analysed from an earlier cruise in the same area (CH99 in the winter of 1992, see Williams, 1995). Table 2.3 summarises the sediment collection details.

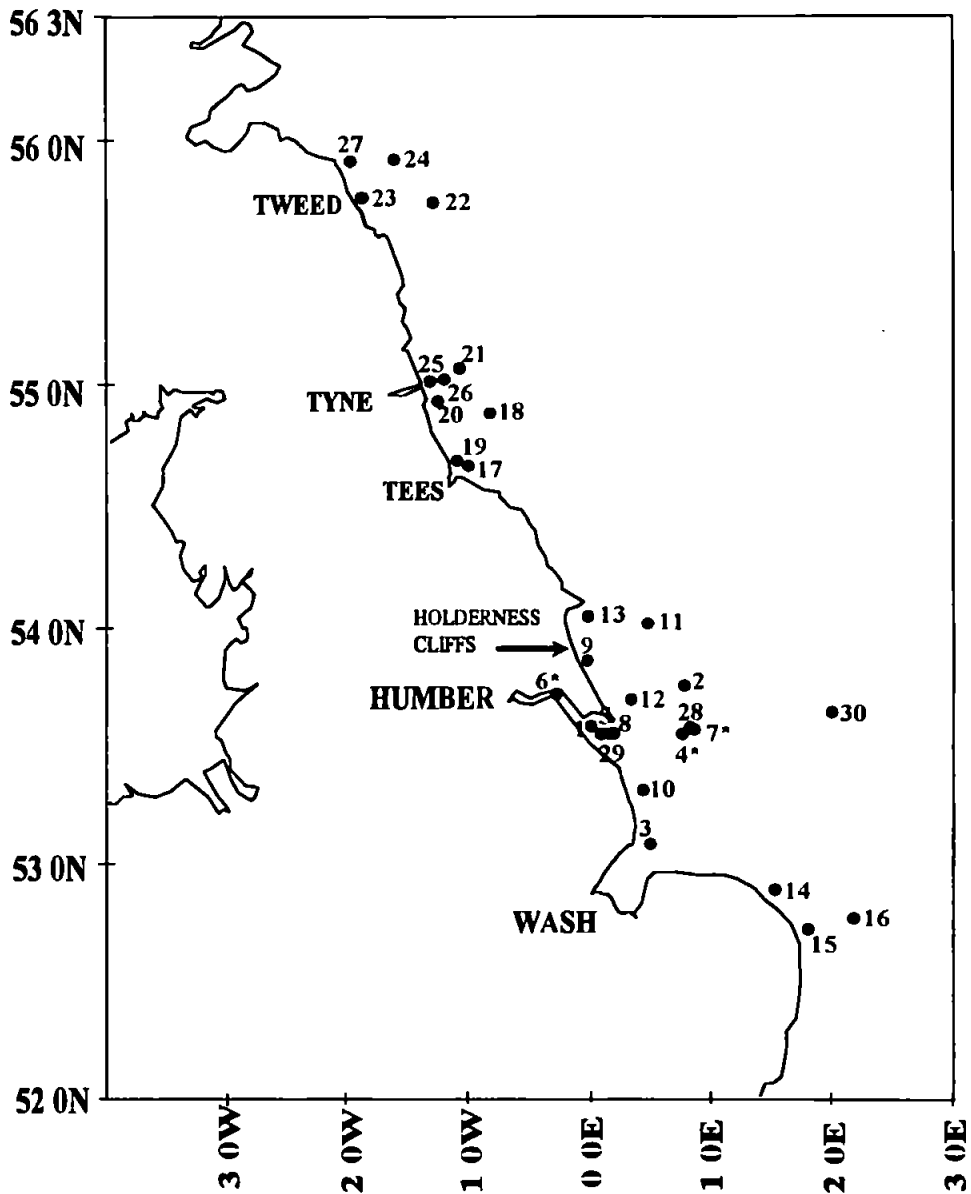


Figure 2.5 Location of sediment samples. * denotes sample taken from a box core.

Table 2.3 Summary of surface sediment collection.

Cruise / Location	Date collected	Depth /m	Position		Ref Fig 2.5
			Lat	Long	
CH99/92					
Humber-Wash	16/12/92	9	53.595 N	0.035 E	1
	8/12/92	27	53.769 N	0.831 E	2
	15/12/92	31	53.135 N	0.558 E	3
	8/12/92	26	53.546 N	0.721 E	4
	9/12/92	8	53.546 N	0.100 E	5
	10/12/92	-	53.722 N	0.249 W	6
	8/12/92	-	53.583 N	0.889 E	7
CH115C/94					
Humber-Wash	7/11/94	14	53.549 N	0.133 E	8
	9/11/94	15	53.859 N	0.033 E	9
	9/11/94	15	53.308 N	0.372 E	10
	10/11/94	48	54.034 N	0.517 E	11
	11/11/94	14	53.780 N	0.231 E	12
	12/11/94	22	54.050 N	0.050 W	13
	12/11/94	18	52.898 N	1.520 E	14
	13/11/94	35	52.715 N	1.817 E	15
	13/11/94	45	52.783 N	2.200 E	16
CH118B/95					
Humber-Tweed	19/4/95	-	54.665 N	1.009 W	17
	19/4/95	-	54.873 N	0.842 W	18
	19/4/95	-	54.687 N	1.119 W	19
	19/4/95	-	54.933 N	1.291 W	20
	19/4/95	-	55.085 N	1.049 W	21
	20/4/95	-	55.750 N	1.251 W	22
	20/4/95	-	55.757 N	1.905 W	23
	20/4/95	-	55.919 N	1.577 W	24
CH118C/95					
Tyne	28/4/95	40	55.153 N	1.419 W	25
Tyne	2/5/95	57	55.148 N	1.294 W	26
Tweed	3/5/95	71	55.916 N	2.080 W	27
Humber	5/5/95	24	55.588 N	0.881 E	28
Humber	6/5/95	16	53.547 N	0.101 E	29
Humber-Wash	7/5/95	47	53.696 N	2.303 E	30

- depth not recorded during sampling

2.1.5 Sampling with QUISSET's

A QUISSET is a sampler designed to collect a horizontal section of water. The tube is a modified (Jones & Jago, 1996) version of the bottom withdraw tube (an Owen Tube) as described by Owen (1976). The QUISSET (see Figure 2.6) is placed horizontally, pulled back, as indicated in Figure 2.6a and lowered into the water column to the required depth. The tube is closed manually via a 'trigger line' which releases the tube from the open position and snaps it shut trapping a 1 m horizontal section of water. Prior to the first cruise the closing velocity of the tubes had been damped as previous laboratory experiments had shown the development of a shock wave that could have disaggregated fragile flocculated particles (Jones, pers comm). Upon recovery the QUISSET tube is inverted to the vertical position after thorough sample homogenisation by tube inversion and rotation. A thermal insulating jacket is placed around the tube after it is placed in a 2 m stainless steel supporting framework in order to maintain the sample at ambient seawater temperature (surface seawater is continuously pumped through the jackets). Upon inversion a timer is started and approximately 1 litre samples are decanted via the bottom tap at selected time intervals of 5, 20, 80 and 300 minutes.

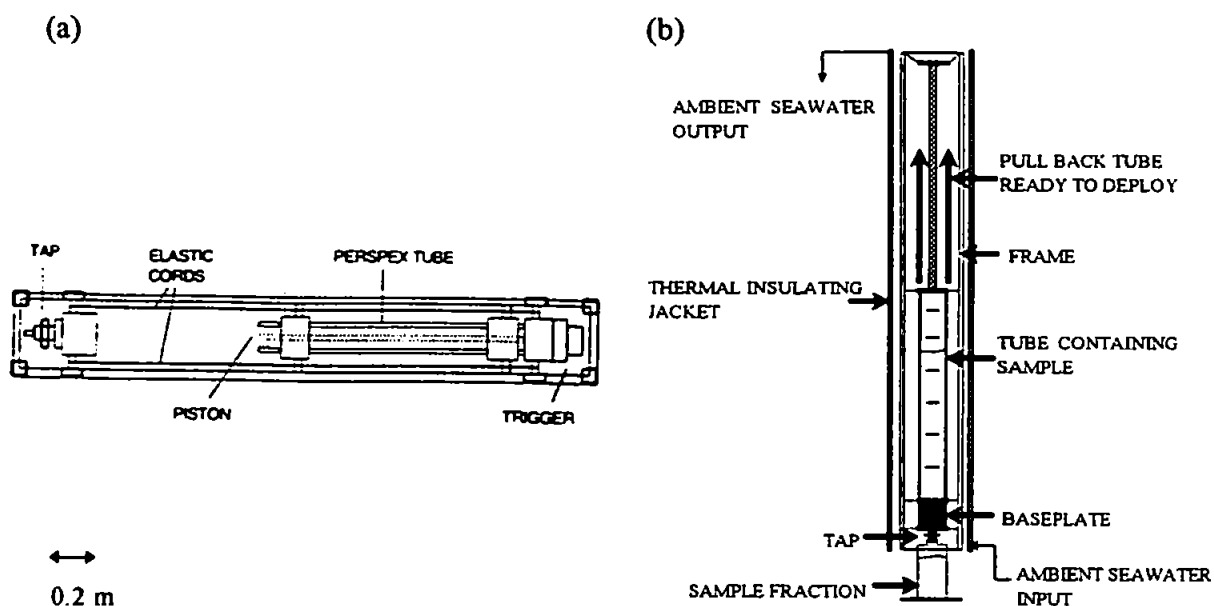


Figure 2.6 Schematic of QUISSET tube in (a) the horizontal position ready for deployment and (b) Stood in the vertical position after deployment. Subsequent sub-samples of seawater are withdrawn through the bottom tap at discrete times and collected as shown in 1 litre LDPE acid cleaned bottles prior to filtration.

The remaining water in the QUISSET tube (300+ minutes) is collected and termed the 'residual' fraction. The samples were subsequently filtered under gravity through acid cleaned, 142 mm diameter, 0.4 μm pore size, Nuclepore polycarbonate filters mounted on acid cleaned teflon filter presses. The samples were stored frozen at -18°C to await further manipulation back in the shore based laboratory. For further details of QUISSET sampling during the present study the reader is referred to Table 2.2.

2.1.6 Particulate organic carbon

Immediately following the collection of seawater samples between 1-6 litres of water were additionally decanted into high density polyethylene (HDPE) containers for filtration and subsequent determination of particulate organic carbon (POC). The seawater samples were filtered through pre-ashed (550°C for 8 hours, Mook & Hoskin, (1982)), 0.7 μm pore size, 47 mm diameter, GF/C filters mounted on an acid cleaned Millipore 47 mm glass filtration apparatus. The volume of seawater filtered varied between 1-6 litres in order to retain sufficient material on the filter for analysis (see section 2.2.5). After filtration the loaded filters were placed in aluminium foil and stored frozen at -18°C (for a summary of the POC samples collected please see Table 2.4).

Table 2.4 Summary of the number and location of the POC samples collected.

Cruise	Humber-Tweed area ¹	HW5		S2 AS	HW3a AS
	Number	QUISSET	AS ²		
CH117A/95	3	flood-5 ebb-5	-	5	-
CH118B/95	6	flood-5 ebb-5	15	-	7
CH119C/95	9	flood-5 ebb-5	14	-	-

¹Refer to Figure 2.1 for area definition & appendix C for sampling sites and %POC values;

²AS denotes anchor station, refer to Figure 2.3

2.1.7 Additional samples

Samples of Holderness Cliff material were collected in December'93 and February'95 (refer to Table 2.5; Figure 2.7) from the shore using an acid cleaned teflon spatula and stored in plastic Petri dishes which were sealed in plastic bags and subsequently stored frozen at -18°C . These samples were taken in order to chemically characterise this end member particle source to the Humber Plume.

Table 2.5 Summary of additional sample collection

Date	Sample type	Site	Fig 2.7 ref.	Position
December 1993	Cliff Material	Moat Farm, Holderness	1	53.80 N 0.07 E
February 1995	Cliff Material	Holderness	2	53.76 N 0.08 E

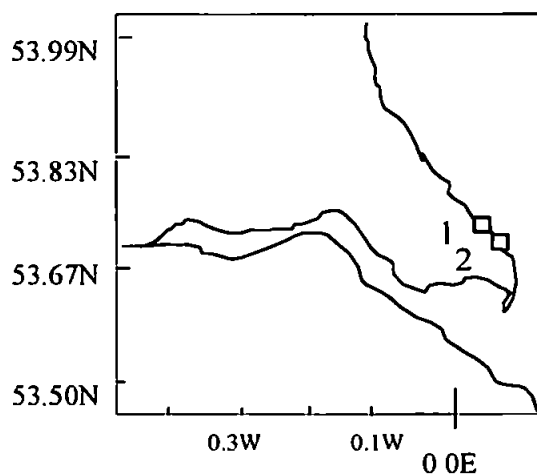


Figure 2.7 Location of Holderness shore based samples

2.1.8 Particle sizing

Recent advances in focused beam reflectance technology have led to the development of the Par-tec 100 which is capable of measuring *in situ* particle sizes (Law *et al.*, 1997). During the LOIS cruises the Par-tec 100 was typically deployed immediately after each CTD or QUISSET for *in situ* particle sizing of the sampled waters. The fragile nature of

large aggregates previously precluded their identification by more conventional means as traditional sampling by pumping or any stirring action provided sufficient energy to fragment large flocs to their component micro-aggregates (Law *et al.*, 1997). The timely development and deployment of the Par-tec 100 therefore provided unique data on the particle size distribution complimenting particulate trace metal data generated from experiments using the QUISSET tubes (see section 2.1.5). The reader is referred to Law *et al.* (1997) for a detailed discussion on the operation, calibration and initial results of the Par-tec 100.

2.2 Sample Pre-treatment

2.2.1 *Particulate matter*

2.2.1.1 Introduction

The ultimate aim of determining the concentration or more specifically the ‘bioavailable’ fraction of trace metals associated with particulate phases is to ascertain whether they pose a significant threat to the quality of the marine environment. However this task is inherently difficult and requires firstly an understanding of;

- a) the individual components that comprise a sediment and an appreciation of phase reactivity or trace metal partitioning with each constituent (Martin *et al.*, 1987),
- b) the geochemical interactions between trace metals in the dissolved and particulate forms and hence the transfer of particulate metals through the ecosystem. A knowledge of the changes in the physico-chemical conditions that the sediment and associated trace metals experience is required in order to predict phase transitions,
- c) the array of extraction techniques commonly adopted to predict particulate trace metal bioavailability and their comparison with natural processes,

in order to make an informed decision of the extraction procedure most relevant to meet the individual aims of the study. The analysis of the particulate material inevitably requires the sample or part of the sample to be brought into solution. This will involve sample manipulations and sample equilibration with added reagents e.g. mineral acids. It is at this stage in the analysis where losses or sample contamination can potentially cause major changes in both the analyte concentration and its species or form. It is therefore imperative that i) all sample manipulations are carried out using acid cleaned apparatus and performed within 'clean' environments e.g. Class 100 laminar flow hoods or a clean room and ii) minimal additional reagents are used and are of AristaR grade or equivalent (Howard & Statham, 1993).

For the current study a one step simultaneous extraction with 1 M Hydrochloric acid (HCl) (AristaR) for 24 hours at room temperature was selected. Hydrochloric acid was used primarily for the following reasons; (i) to enable direct comparison with data from previous studies of the North Sea, (ii) the requirement of a relatively quick and simple methodology owing to the large number of samples and (iii) the inherently greater operationality of multi stage sequential leach schemes. However numerous other extraction procedures have been adopted (Tessier *et al.*, 1979; Förstner *et al.*, 1981; Förstner, 1982:1985; van Valin & Morse, 1982; Luoma, 1983; Tipping *et al.*, 1985; Tessier & Campbell, 1987) each with their associated advantages and disadvantages which are discussed in sections 2.2.1.3 & 2.2.1.4. An overview of the effects that various sample pre-treatments have on preserving particle integrity is also reviewed in section 2.2.1.2. The following discussion expands on the reasoning behind the choice of sample preservation and extraction procedure adopted in this study.

2.2.1.2 Storage Effects

After filtration and collection of SPM samples the filters were folded, loaded surface facing inwards (Yeats & Brüggmann, 1990), placed in a petri-dish and frozen at -18°C as were the collected surface sediment samples. Several review papers (Engler *et al.*, 1977; Thompson *et al.*, 1980; Rapin *et al.*, 1986; Slavek & Pickering, 1986; Kersten & Förstner, 1987) have identified that many problems previously attributed to limitations in

extraction procedures (refer to Sections 2.2.1.3 & 2.2.1.4) are in fact produced by improper sample handling. Thompson *et al.* (1980) and later Rapin *et al.* (1986) stressed that extractions should be conducted as soon as possible after collection as no storage method completely preserves the initial physical and chemical characteristics of trace metal associations, highlighting the particular urgency when collecting anaerobic sediments as opposed to oxic suspended/surface sediments (Engler *et al.*, 1977; Hirner, 1992). There is general agreement among the literature that drying of sediments by aeration, oven drying at 60°C and freeze drying under vacuum all change the original associations of trace metals between sediment components. The latter two drying methods have been demonstrated by Kersten & Förstner (1987) to particularly affect Fe and Mn bound to carbonate fractions and Zn, Cd, Cu and Pb sulphide/organic phases. In agreement with the above findings Rapin *et al.* (1986) concluded that Cu, Fe and Zn were especially sensitive to sample pre-treatment. The above phase shifts are thought to be a result of 'drying' pre-treatments favouring the formation of new mineral solid phases, accelerating the crystallisation of solids such as Fe and Mn oxides. The metal binding capacity of crystalline Fe oxides are known to be an order of magnitude less than amorphous Fe oxides (Luoma & Davis, 1983) in oxidised estuarine sediments suggesting that such a change in state would be associated by decreasing associated metal concentrations. Indeed Thompson *et al.* (1980) studied the effects of sample storage on the HCl extracts of Cu, Zn, Fe and Mn from oxidised sediments and concluded that as the sample aged, extraction of Cu, Mn and Fe decreased. This was attributed to migration of metal ions into more residual sediment phases possibly as a result of increasing proportions of crystalline Fe oxides with decreased metal binding capacities promoting changes in trace metal phase associations. Similarly, Slavek & Pickering (1986) reported that ageing of Fe oxides even during the course of a few hours was sufficient to prevent their total dissolution.

There is some disagreement amongst authors about the wet storage of oxidised sediments at low but above freezing temperatures i.e. typically 1-2°C. Rapin *et al.* (1986) reported no significant changes in trace metal partitioning in oxic sediments that had been stored wet at 4°C for 20 days, in disagreement with Kersten & Förstner (1987) who concluded that the wet storage of sediments was inadequate due to possible microbial induced shifts from oxidising to more reducing conditions, a view also

supported by Thompson *et al.* (1980). A more acceptable method of sediment preservation by freezing (Rapin *et al.*, 1986; Yeats & Brüggmann, 1990) *cf.* wet storage has been widely accepted as it suppresses, if not effectively prevents, any microbially induced phase shifts and hence its adoption in the present study for storage of all particulate material.

2.2.1.3 Sequential extraction

Solid state speciation governs geochemical fate and biological availability of particle associated trace metals (Nirel & Morel, 1990). Numerous studies have investigated 'solid speciation' (Martin *et al.*, 1987) of trace elements by using sequential extraction techniques (Tessier *et al.*, 1979; Förstner, 1981,1982; van Valin & Morse, 1982; Luoma, 1983; Tipping *et al.*, 1985; Tessier & Campbell, 1987; Chester *et al.*, 1988) and have tried subsequently to relate the solubilised fractions to their 'bioavailability' or selective solid phase e.g. carbonates, Fe oxides etc. Two of the most widely used and documented sequential extraction schemes are outlined in Table 2.6.

However a number of authors (Calmano & Förstner, 1983; Kersten & Förstner, 1987; Kheboian & Bauer, 1987; Nirel & Morel, 1990; Hirner, 1992) have expressed their concerns over the continued use of such extraction schemes as they remain to be successfully validated and actually do not provide particulate speciation but merely phases of the particulate mineral that have been 'operationally' defined by the strength of the leaching agent. The likelihood of trace element redistribution among phases during extraction has also been elucidated (Förstner, 1985; Kheboian & Bauer, 1987; Hirner, 1992). A specific study by Tipping *et al.* (1985) showed direct evidence of redistribution when Mn oxide was selectively separated from Fe oxide by using acidified hydroxylamine hydrochloride. Electron probe microanalysis before extraction indicated that the majority of the Pb was in the Mn phase with none in the Fe fraction. Analysis after the extraction showed that the Pb was now associated with the Fe oxide phase and was not present in the seawater extract as expected. In addition reagents themselves are not as selective as many authors claim (Kersten & Förstner, 1987; Kheboian & Bauer,

1987), extraction efficiencies vary according to leach time used, particulate matter to extractant volume and reabsorption or 'matrix' effects (Martin *et al.*, 1987).

Table 2.6 Examples of adopted sequential extraction schemes

Fraction	Reagents and conditions	
	Tessier <i>et al.</i> (1979)	Förstner <i>et al.</i> (1981)
Exchangeable Carbonate	1 M MgCl ₂ , pH 7 1 M CH ₃ COONa/ CH ₃ COOH, pH 5	1 M CH ₃ COONH ₄ , pH 7 1 M CH ₃ COONa, pH 5
Easily reducible Fe and Mn oxides	0.04 M NH ₂ OH, HCl 25% CH ₃ COOH, 96°C	0.1 M NH ₂ OH, HCl, pH 2
Moderately reducible		0.2 M (NH ₄) ₂ C ₂ O ₄ H ₂ , 0.2 M H ₂ C ₂ O ₄
Organic matter and sulphides	30% H ₂ O ₂ , HNO ₃ , pH 2 85°C + 3.2 M CH ₃ COONH ₄ 20% HNO ₃	H ₂ O ₂ , pH 2 + CH ₃ COONH ₄
Residual	HF, HClO ₄	HNO ₃

However, one undeniable distinction among phases separated by sequential extraction procedures is that the 'residual fraction' (i.e. that which is only solubilised by the final application of strong acid, refer to Table 2.6) remains unaffected by short-term natural, anthropogenic, or experimental changes in the total element concentration (Chester *et al.*, 1986; Statham & Chester, 1988). It thus follows that the residual fraction represents a minimal estimate of the unreactive concentration of the metal in the particles. For predominantly siliclastic sediments this is assumed to be the metals inherently bound to the silicate lattice. Martin *et al.* (1987) also recognised that those elements incorporated into crystalline silicates are largely unavailable by either biological or diagenetic processes over time scales of a year to a decade.

In the application of this work to coastal marine studies it is therefore imperative to carefully choose the extraction strategy taking into account all the above pitfalls. Essentially in environmental applications an appreciation of the 'reactive' components or concentration of an element that is readily available to participate in exchange reactions with abiotic or biotic components present in the aquatic system is required. The use of sequential extraction procedures at best provides a gradient for the physico-chemical association strength between trace elements and solid particles (Martin *et al.*, 1987).

Due to time considerations and inherent problems associated with sequential extractions a one step simultaneous extraction procedure was chosen for this study.

2.2.1.4 One step extraction

Single step extractions have been widely applied to environmental surveys since they emphasise the contrast between anthropogenically modified and natural trace metal concentrations (Martin *et al.*, 1987). The advantages of using a single reagent are that; (i) they are rapid (see section 2.2.1.1) and easy to perform, (ii) have minimal sample manipulations and therefore a lower possibility of contamination from reagents, (iii) often have better reproducibility than their sequential counterparts i.e. smaller coefficient of variation between replicate samples (Dutton, 1991) and (iv) they clearly show the contrast between concentrations associated with the residual silicate lattice and the more labile phases and are generally considered a useful tool in identifying anthropogenic contaminants (Martin *et al.*, 1987). However associated disadvantages of single extraction procedures include the likelihood of trace metal re-adsorption (Malo, 1977) during extraction as discussed in section 2.2.1.3. Rendell *et al.* (1980) reported varying degrees of re-adsorption (Cu 29%, Pb 54% & Cd 3%) of trace metals when particles were extracted for 16 hours with 0.01 M HCl. Also, the use of a single reagent does not permit the dissolution of all organic and inorganic labile forms without also attacking some of the detrital phases, the metal extracted being largely dependant upon the type of sample (Chester & Hughes, 1967; Agemian & Chau, 1977). To investigate the extraction efficiency of 1 M HCl three different certified reference sediments (BCSS-1, MESS-1 & PACS-1) were similarly digested and the relative trace metal percentage recoveries computed (see section 2.4.1.1).

Hydrochloric acid is a strong acid but it is not an oxidising agent *cf.* nitric acid and can generally be considered to dissolve carbonates, some sulphides and electropositive metals, and to extract some metals from silicate lattices without fully destroying the siliclastic lattice (Howard & Statham, 1993). However, despite the above mentioned methodological problems and limitations, partial extractions of sediments have provided significant insight into the physico-chemical factors influencing the bioavailability of

particulate trace metals (Tessier & Campbell, 1987). Indeed trace metal levels in various benthic organisms have been best related to 'relatively easily' extracted fractions or 'weakly bound' metals (Luoma & Bryan, 1978:1979:1982; Diks & Allen, 1983; Tessier *et al.*, 1983:1984; Loring, 1987; Tessier & Campbell, 1987; Loring & Rantala, 1988; Langston, 1990). The use of HCl as the extracting reagent has received various reports in the literature ranging from the ability to;

- a) mineralise the easily soluble components of the mineral matrix (Hirner, 1992),
- b) remove weakly bound metals that might potentially be available to the biota (Loring & Rantala, 1988),
- c) dissolve the metals in exchangeable positions and those associated with carbonate, soluble Fe and Mn oxides phases and weakly attached organic matter fractions (Agemian & Chau, 1977; Malo, 1977; Martin *et al.*, 1987) and,
- d) attack some moderately resistant solid phases e.g. carbonate, gypsum, anhydrite associated metals including severe attack on clay minerals (van Valin & Morse, 1982).

thus indicating that it is an appropriate reagent for extracting the more 'bioavailable' fractions of trace metals. In addition, results from Luoma & Bryan (1982) on two deposit feeding benthic organisms *Scrobicularia plana* and *Nereis diversicolor* showed that the extraction of surrounding sediments with 1 M HCl explained the largest percentage variation in trace metals concentration in the organisms. Similar results were also documented by Langston (1990). Another interesting find by Luoma & Bryan (1979) was that Pb accumulation by *Scrobicularia plana* could be predicted by determining the Pb/Fe ratio in 1 M HCl extracts from the sediment, since a significant correlation was observed between this ratio and Pb in tissue.

It follows that bioaccumulation and subsequent biomagnification up through the food web has been shown to depend not only upon trace metal concentrations within the organism (which are also a function of a range of physiological factors such as age and sexual condition) but also on the levels of Fe oxides and organic matter (Luoma &

Bryan, 1978) in sediments and the particular geochemical phases with which the trace metals are associated. The reservoir of trace metals in sediments are generally an order of magnitude higher than those found in the adjacent overlying water column (Hirner, 1992). Deposit and filter feeding organisms live in the sediment and directly ingest metal-enriched particles and have the potential to transfer any available metals from such particles to higher trophic levels. They are most commonly exposed to oxidised sedimentary particles and most feed non-selectively; mechanically separating particles on the basis of size, or perhaps specific gravity. Tahgon *et al.* (1978) recognised that smaller particles are preferentially ingested, while Luoma & Davis (1983) concluded that the permanent components of fine grained oxidised sediments include hydrous oxides of Fe, Mn and Al, aluminosilicate minerals, organic matter and carbonates thus suggesting that the use of HCl in the extraction procedure is appropriate in the determination of the more 'mobile' and bioavailable trace metal fractions.

Furthermore, several studies of Pb isotope data (Hirner, 1992; Williams *et al.*, 1994; Williams, 1995) have shown that anthropogenic Pb is isotopically light and concentrated in the exchangeable fraction i.e. that fraction solubilised with 1M HCl, whilst isotopically heavy geogenic Pb is found in the silicate residual fraction adding further validity to the use of HCl.

2.2.2 SPM extraction procedure

The digestion of SPM samples was carried out using equipment that had undergone a strict cleaning regime prior to use as summarised in appendix A. Particulate samples were generally digested in batches of twenty. They were firstly removed from the freezer and allowed to air dry in a laminar flow hood (Class 100, BASSAIRE V102) until upon weighing they reached a constant weight (SALTER electronic balance, range 0.00001 - 180 g, calibrated every two weeks). The weight was noted so the concentration of SPM could be calculated. Then the filter and load were placed in acid cleaned Teflon reactors (100 ml volume, BDH) before adding 10 ml of 1 M HCl (AristaR, BDH sp.gr.1.18), ensuring that the SPM was totally emersed in the solution a lid was put over the reactor and the digest left for 24 hours in a laminar flow hood. The filter was subsequently

'crushed' with a plastic spatula and the filtrate and filter washings (in further aliquots of 1-2 ml 1 M HCl) filtered under vacuum through Nuclepore polycarbonate, 47 mm diameter, 0.4 μm pore size filters). The filtration system was washed a further three times with 2-5 ml aliquots of HCl acid to ensure complete recovery of the filtrate. The washings and filtrate were retained and made up to 25 ml in acid washed plastic volumetric flasks before transferring to acid cleaned LDPE 30 ml bottles ready for analysis (see section 2.3).

A blank filter was similarly digested every 10 SPM samples (refer to Table 2.7). The average blank filter weight was 0.14418 ± 0.00001 g. SPM samples weighing less than 5% of the average weight of the blank filter were not accepted. These amounted to 2.5% of the total number of samples.

2.2.3 Sediment extraction procedure

Sediment samples were defrosted to room temperature in a laminar flow hood (as above). Small aliquots of sediment (approximately 2-3 g) were then filtered through a 63 μm acid washed Nylon sieve. The filtrate was subsequently filtered directly onto pre-weighed, acid washed, cellulose acetate, 0.45 μm pore size, 47 mm diameter Sartorius filters. The greater than 63 μm fraction was collected by back rinsing the sieve with Milli-Q water and collecting the particles into pre-weighed plastic boats. The less than 63 μm (but greater than 0.45 μm) particles were retained by the filter.

This protocol ensures the simultaneous fractionation of the sediment into less than and greater than 63 μm diameter particle populations. Wet sieving is assisted with a minimum amount of Milli-Q water (approximately 2-3 ml) which also serves to wash the sediment of major salts. The sediment fractions were then dried in an oven (LEEC) at 40°C and weighed to constant weight so the percentage of each population could be calculated.

In general the smaller the size of the sediment fraction, the larger the concentration of trace metals associated with this fraction i.e. many trace metals are mainly present in the clay/silt particles with grain size less than 63 μm (Krumgalz, 1989 and all references therein). This is attributed to the increase in specific surface area of the smaller fractions and to the surface properties of clay minerals (Förstner *et al.*, 1982) and hence the need to size fractionate surface sediment samples.

Between 0.1-0.3g of dried sediment were then weighed directly into acid cleaned teflon reactors (100 ml volume, BDH). The subsequent extraction procedure used was identical to that adopted for the SPM samples (section 2.2.2) to ensure data comparability. Both fractions of the sieved sediment were digested in the same manner in order to assess metal fractionation as a function of sediment size fraction.

2.2.4 Seawater extraction procedure

Dissolved trace metals often require extraction and pre-concentration from seawater (depending on analytical method adopted) in order to reduce matrix effects from seawater constituents and to ensure sufficient concentrations for accurate and precise analysis. Prior to metal pre-concentration and extraction the seawater samples were allowed to equilibrate to room temperature in a laminar flow hood. The dissolved trace metals were then complexed with a chelating agent solution (1% w/v in both ammonium pyrrolidine dithiocarbamate (APDC, SpectrosoL grade, BDH) and diethylammonium diethyldithiocarbamate (DDDC, SpectrosoL grade, BDH) made up in Milli-Q water), extracted into 1,1,2 trichlorotrifluoroethane (Freon, GPR grade, BDH) and back extracted into nitric acid (AristaR 69% concentrated, BDH), following the method of Danielsson *et al.* (1978), as modified by Statham (1985). For a detailed description of procedure followed see HMSO (1988). The reader is also referred to Batterham & Parry (1996) for details of an improved dithiocarbamate/oxine solvent extraction method for the preconcentration of trace metals from seawater. This method showed that only one single rapid extraction was required compared to the laborious triple extraction procedure required for the quantitative recovery of trace metals from seawater using the

HMSO (1988) method (Danielsson *et al.*, 1978; Statham, 1985) adopted in the present study.

2.2.5 Particulate organic carbon

The percentage POC content of the collected SPM samples (section 2.1.6) were analysed by Loss On Ignition (LOI) (Mook & Hoskin, 1982). Filters were firstly defrosted, air dried in a laminar flow hood and stored in a dessicator prior to combustion, weighed dry (A), placed on aluminium foil and put in a muffle furnace at 550°C for 8 hours. The combusted filters were allowed to cool and re-weighed (B) to a constant weight. The percentage POC was then calculated as follows where C represents the mass of SPM on the filter in grams;

$$\% \text{POC} = \left(\frac{A - B}{C} \right) \times 100 \quad 2.1$$

2.3 Sample Analysis

The sample digests (SPM and surface sieved sediment samples) were analysed for the trace metals Fe, Mn, Cu, Cd and Pb in addition to $^{206/207}\text{Pb}$ isotopic ratios. The filtered seawater samples were analysed only for Cu, Cd and Pb. The mass dominant Fe and Mn metals were analysed by flame atomic absorption spectroscopy (flame AAS). The remaining metals were all analysed by graphite furnace atomic absorption spectroscopy (GFAAS). Lead isotopic ratios were determined by inductively coupled plasma mass spectrometry (ICP-MS). Experiments involving the spiking of samples with gamma emitters (section 2.5) were counted on a high resolution Ge crystal coaxial detector.

2.3.1 Flame atomic absorption spectroscopy

Iron and Mn analysis were carried out on the digests using flame AAS (Varian SpectrAA 300/400 connected to an on-line printer) with a PTFE micro-cup injection system using 200 μ l samples (Berndt, 1981; Statham, 1985). Instead of the usual stationary peak area signal, a transient peak signal is obtained where peak height represents the absorbance of the element. Peak area is not measured as it is sensitive to injection volume. Use of the micro-cup connected to a nebuliser by a short piece of tubing made it possible to use small sample volumes, an important consideration when only small (usually 25 ml) finite volumes of each sample were available. Berndt (1981) investigated the % relative signal height as sample volume varied from 10-1000 μ l and showed that sample volumes greater than 150 μ l produced 100% relative signal height.

Calibration was carried out using acidified standards prepared from Spectrosol stock solutions (BDH). Laboratory analytical precision (Howard & Statham, 1993; Tappin *et al.*, 1995) of the method was less than 10% for both Fe and Mn. The limit of detection and procedural or methods blanks for flame AAS i.e. particulate Fe and Mn analysis are given in Tables 2.7 & 2.8. Full instrument conditions are detailed in appendix B. Samples were reanalysed when either the correlation coefficient of the calibration curve was less than 0.995, or the percentage relative standard deviation (%RSD) of 3 replicate readings of the same sample were greater than 10%.

2.3.2 Graphite furnace absorption spectroscopy

The analysis of many trace elements in the parts per million range (ppm) i.e. typically from extracted SPM samples requires low detection limits. Analysis by GFAAS not only provides appropriate detection limits which, for many elements are lower than other available established and/or novel atomic spectroscopic methods (Sturgeon, 1989) but offers a relatively cheap way to obtain accurate and precise measurements of many dissolved and particulate extracted trace metals e.g. Cu, Pb & Cd. The analysis of marine samples is 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. high salt content of many marine samples compared to acidified standards. The use of matrix modifiers (Tsalev *et al.*, 1990) in combination with optimisation of the GFAAS temperature program (Williams, 1995) often reduces or eliminates such effects. Matrix modifiers work by essentially reacting with the analyte thus stabilising the metal so that higher pyrolysis temperatures can be used. A Pd based modifier was used in the determination of dissolved and particulate Cu and Pb (500 mg l^{-1} Pd with 1% NH_2OH in 1% HNO_3) (Schlemmer & Welz, 1986; Williams, 1995). A phosphate based modifier was used in the determination of Cd ($2000 \text{ mg l}^{-1} \text{PO}_4^{3-} + 10 \text{ mg l}^{-1} \text{MgNO}_3$). Temperature programs for the graphite furnace essentially followed those recommended by Williams (1995) who optimised conditions for the analysis of North Sea particulates but were occasionally optimised as necessary for each metal by cycling through different combinations of char and atomisation temperatures. Peak profiles were printed out for each temperature combination. By consideration of peak profile and maximum absorbance obtained by various temperature combinations, optimal furnace programs were obtained and are detailed in appendix B.

Dissolved and particulate Cu, Cd and Pb were all determined by GFAAS, Perkin Elmer SIM6000 with Zeeman background correction connected to a Perkin Elmer AS-70 autosampler. For the analysis of the SPM and sediment extracts the method of standard additions was used because the exact matrix of many marine samples cannot be identified and matched when preparing associated standards. Standards were prepared from Spectrosol standard solutions (BDH) and made up in 1 M HCl (AristaR). For the detection of dissolved trace metals (section 2.2.4) seawater stripped of trace metals is produced which is subsequently employed in the preparation of standards. In this case straight calibration using the prepared standards can be used because sample and standard matrixes are effectively matched. For the dissolved trace metals inter laboratory precision, quoted as %RSD, was assessed by ten extraction's and subsequent analysis of CASS-3 certified reference seawater and were 9.5%, 10% and 10.5% for Cu, Cd and Pb respectively (for results of extraction efficiencies see section 2.4.1.2). Precision (from replicate sample concentrations) of particulate trace metal analysis by GFAAS were less than 10% for all metals. For calculated limits of detection and procedural blanks for dissolved and particulate Cu, Cd and Pb see Tables 2.7 & 2.8. All samples analysed had

Table 2.7 Summary of procedural blanks \pm 1 standard deviation. Procedural blanks are presented as a % of the average trace metal concentration for each cruise

Metal	Cruise														
	CH115C/94				CH117A/95				CH118B/95				CH119C/95		
		<i>n</i>	%		<i>n</i>	%		<i>n</i>	%		<i>n</i>	%			
Particulate															
Fe (mg l ⁻¹)	0.009 \pm 0.033	6	0.01	0.005 \pm 0.021	9	0.001	0.003 \pm 0.016	9	0.007	0.036 \pm 0.038	6	0.27			
Mn (mg l ⁻¹)	0.003 \pm 0.005	6	0.07	0.003 \pm 0.007	9	0.06	ND	9	0.000	0.001 \pm 0.002	6	0.14			
Cu (μ g l ⁻¹)	0.52 \pm 0.62	6	0.01	4.37 \pm 1.90	9	4.00	3.66 \pm 1.33	9	5.88	3.52 \pm 1.10	6	9.77			
Cd (μ g l ⁻¹)	0.20 \pm 0.11	6	11.8	0.31 \pm 0.19	9	19.0	0.27 \pm 0.13	9	26.1	0.31 \pm 0.10	6	40.7			
Pb (μ g l ⁻¹)	3.16 \pm 1.60	6	0.86	1.66 \pm 1.18	9	0.37	3.53 \pm 1.56	9	1.21	2.97 \pm 0.97	6	3.94			
Dissolved															
Cu (μ g l ⁻¹)	0.324 \pm 0.011	3	30.0	0.345 \pm 0.004	3	18.4	0.295 \pm 0.007	3	15.2	0.230 \pm 0.005	3	13.2			
Cd (μ g l ⁻¹)	0.083 \pm 0.001	3	40.0	0.026 \pm 0.005	3	31.0	0.020 \pm 0.004	3	9.30	0.036 \pm 0.004	3	26.1			
Pb (μ g l ⁻¹)	0.079 \pm 0.004	3	38.5	0.087 \pm 0.005	3	41.6	0.064 \pm 0.004	3	4.63	0.070 \pm 0.003	3	6.00			

Table 2.8 Calculated limits of detection (LOD) for each trace metal based on 3σ of the procedural (method) blank.

Metal	CH115C/94	CH117A/95 ^{C_{miise}}	CH118B/95	CH119C/95
Particulate				
Fe (mg l ⁻¹)	0.10 (1.58:173)	0.06 (0.85:104)	0.05 (2.77:86.7)	0.12 (23.8:208)
Mn (mg l ⁻¹)	0.02 (0.32:34.6)	0.02 (0.28:34.6)	0.01 (0.55:17.3)	0.06 (11.9:104)
Cu (µg l ⁻¹)	1.85 (0.03:3.21)	5.70 (0.08:9.88)	4.00 (0.22:6.93)	3.31 (0.66:5.74)
Cd (µg l ⁻¹)	0.32 (0.01:0.55)	0.57 (0.01:0.98)	0.39 (0.02:0.67)	0.31 (0.06:0.54)
Pb (µg l ⁻¹)	4.79 (0.08:8.30)	3.55 (0.05:6.15)	4.68 (0.26:8.11)	2.92 (0.58:5.06)
Dissolved				
Cu (µg l ⁻¹)	0.033	0.012	0.021	0.015
Cd (µg l ⁻¹)	0.003	0.014	0.012	0.012
Pb (µg l ⁻¹)	0.012	0.014	0.012	0.009

Values indicated in brackets express the minimum and maximum LOD on a w/w basis (µg g⁻¹) calculated using the minimum and maximum weights of SPM retained on the filters during each survey.

to pass quality assurance criteria of %RSD less than 10% and appropriate calibration curves with correlation coefficient greater than 0.995.

2.3.3 Inductively coupled plasma mass spectrometry

The analysis of sediment and SPM samples for stable lead isotopic ratios was achieved by using ICP-MS (VG Plasmaquad PQ2-Turbo ICP-MS, Fisons Instruments). In order to calibrate the instrument a standard Pb isotopic reference solution (NIST-981) was used. The isotopes ^{202}Hg , ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb were counted. The relative interference of ^{204}Hg to ^{204}Pb can be theoretically calculated by knowing the number of ^{202}Hg counts and the % relative abundance of each Hg isotope and were typically less than 2.5%. Laboratory precision (Howard & Statham, 1993) was assessed by replicate measurements (over a 4 hour period) of the same sample and gave a relative standard deviation of 0.6% ($n = 20$) for the $^{206/207}\text{Pb}$ isotopic ratio *cf.* 0.6%, Sturges & Barrie (1987); 0.76%, Hinnens *et al.* (1987); 0.2-3.0%, Hopper *et al.* (1991); 0.3%, Farmer *et al.* (1996).

2.4 Quality Control

The objective of any trace analysis is to obtain accurate and precise data (Howard & Statham, 1993). Accuracy is how close the measurement is to the real value and is normally ascertained by analysing suitable certified reference materials, whereas precision describes the spread of replicate or repetitive measurements i.e. % RSD values quoted in section 2.3. This section firstly summarises the accuracy of both sediment and seawater extractions by looking at recovery of trace metals from certified reference sediments and seawater samples. All certified reference materials used were supplied by the National Research Council, Canada (NRCC) as part of the Marine Analytical Chemistry Standards Program. An inter laboratory comparison of the concentration of SPM obtained is then investigated to ensure data quality.

2.4.1 Accuracy

2.4.1.1 Certified reference sediments

In order to gain a greater insight into the proportion of each metal solubilised by a 1 M HCl leach, three certified reference sediments BCSS-1, MESS-1 and PACS-1 (NRCC) ranging in contaminant concentrations were digested following the same procedure as that adopted for SPM and surface sediment samples. Certified values were obtained only after their complete dissolution in mixtures of various acids with hydrofluoric acid (Krumgalz & Fainshtein, 1989). It was therefore hoped that a comparison with certified values would indicate percentage of the total trace metal content solubilised by HCl attack. A similar study was undertaken by Krumgalz & Fainshtein (1989) who used a hot nitric acid dissolution and these results are included in Table 2.9 for comparison purposes.

Cadmium and Pb were quantitatively recovered from the three certified reference sediments extracted by HCl (1M) at room temperature for 24 hours without total silicate lattice dissolution. These results are in good agreement with those of Krumgalz & Fainshtein (1989) who used a strong oxidising agent and suggest that Cd and Pb are predominantly associated with 'easily extractable' fractions of particulate matter i.e. readily available to the biota. Copper shows interesting differences between the two methods of extraction. The nitric acid digest removes approximately 90% of total Cu in comparison to the hydrochloric procedure which removes between 45-67%. It is interesting to note that extraction efficiency for Cu increases as the certified reference value increases i.e. for more polluted sediments, suggesting that with increasing anthropogenic load relatively more Cu is associated with more surface bound easily extractable fractions as one might intuitively expect. This comparison highlights differences between nitric and hydrochloric acid extracts with respect to the individual components of the sediment particles which are solubilised. It is postulated that the increase in recovery of Cu found when using nitric acid reflects the proportion of Cu associated with more residual organic phases that are oxidised by the acid (i.e. HCl acid is not an oxidising agent and is therefore unlikely to remove anything other than weakly associated surface organic constituents in addition to Fe and Mn oxide phases as

Table 2.9 Trace metal content ($\mu\text{g g}^{-1}$; mg g^{-1} for Fe) in standard reference sediments following a 1 M HCl leach for 24 hours at room temperature.

	Certified Reference Sediments		
	BCSS-1	MESS-1	PACS-1
Fe			
Certified reference value	32.9 ± 1.0	30.5 ± 1.8	48.7 ± 0.84
Mean	7.87 ± 1.63	4.40 ± 0.28	18.1 ± 0.78
Number of values	5	5	5
Average recovery ^a (%)	23.9	14.4	37.2
Average recovery ^b (%)	90.6	84.5	-
Mn			
Certified reference value	229 ± 15	513 ± 25	470 ± 12
Mean	59.4 ± 1.53	83.4 ± 3.5	132 ± 4.45
Number of values	5	5	5
Average recovery (%) ^a	25.9	16.2	28.1
Cu			
Certified reference value	18.5 ± 2.7	25.1 ± 3.8	452 ± 16
Mean	8.23 ± 1.71	12.7 ± 0.45	302 ± 4
Number of values	5	5	5
Average recovery ^a (%)	44.5	50.4	66.8
Average recovery ^b (%)	89.2	92.8	-
Cd			
Certified reference value	0.25 ± 0.04	0.59 ± 0.10	2.38 ± 0.20
Mean	0.26 ± 0.03	0.61 ± 0.04	2.50 ± 0.13
Number of values	5	5	5
Average recovery ^a (%)	105	104	105
Average recovery ^b (%)	100	107	-
Pb			
Certified reference value	22.7 ± 3.4	34.0 ± 6.1	404 ± 20
Mean	23.6 ± 3.4	35.9 ± 1.8	403 ± 25
Number of values	5	5	5
Average recovery ^a (%)	104	106	99.8
Average recovery ^b (%)	116	100	-

^aResults from this study; ^bKrumgalz & Fainshtein (1989)

discussed in section 2.2). Indeed many sequential extraction schemes employ nitric acid to remove organic and sulphide phases (Tessier *et al.*, 1979; refer to section 2.2.1.3). Recovery of both Fe and Mn, the mass dominant phases, is very poor ranging between 14-37%. Krumgalz & Fainshtein (1989) did not analyse leachates for Mn but did report extraction efficiencies between 84-90% for Fe and concluded that approximately 20%

seemed to be incorporated into the silicate lattice i.e. not dissolved by the nitric acid. Following on from this and including recent HCl extraction efficiencies one could conclude that approximately 60% of total Fe appears associated with phases solubilised by hot nitric acid e.g. organics and sulphides but not by cold HCl, while 20% remains incorporated within the silicate core and the last 20% remains associated with 'easily solubilised' components of the sediment i.e. possibly more anthropogenic fractions.

2.4.1.2 Certified reference seawater

The extraction efficiency of dissolved metal extraction and pre concentration from seawater was assessed within each batch by the analysis of a variety of certified reference seawaters (NRCC), ranging from estuarine (SLEW-1) to coastal samples (CASS-2). Dissolved trace metal samples taken ranged between salinities of 24-36. It was therefore hoped that any changes in extraction efficiencies due to different matrix effects (e.g. changing salinity) would be elucidated by the analysis of certified reference seawater samples from the estuarine to offshore coastal continuum. The analysis of nearshore CASS-3 seawater was part of a inter-laboratory calibration exercise within all participating LOIS Institutes/Universities. The results of all the extractions have been summarised by type and are presented in Table 2.10.

The extractions of CASS-3 samples in general (87-100%) showed good agreement with certified values although Cu and Pb were not totally recovered. However recoveries compare well with recent results from Batterham & Parry (1996) who used an improved dithiocarbamate/oxine single solvent extraction procedure. Seawater extractions of CASS-2 samples yielded a 100% recovery for Cu but slightly overestimated Cd and particularly Pb. In contrast estuarine reference waters SLEW-1 demonstrated less than 100% recovery for all metals. The dissolved samples analysed as part of the LOIS study all originated from nearshore coastal waters. The good extraction efficiencies of the above mentioned reference material serve to both validate the dissolved extraction method and provide a way of assessing the accuracy of the procedure.

Table 2.10 Dissolved trace metal concentrations ($\mu\text{g l}^{-1}$) in certified reference seawater.

Certified Reference Seawater	Cu	Cd	Pb
CASS-2 (Coastal Seawater)			
Certified reference value	0.675	0.019	0.019
Mean	0.675 ± 0.115	0.020 ± 0.002	0.022 ± 0.002
Number of values	5	5	55
Average recovery (%)	100	105	116
CASS-3 (Nearshore Seawater)			
Certified reference value	0.517 ± 0.062	0.030 ± 0.005	0.012 ± 0.004
Mean	0.452 ± 0.043	0.030 ± 0.005	0.011 ± 0.005
Number of values	8	8	8
Average recovery (%)	87	100	92
SLEW-1 (Estuarine Water)			
Certified reference value	1.76 ± 0.09	0.018 ± 0.003	0.028 ± 0.07
Mean	1.64 ± 0.09	0.017 ± 0.002	0.027 ± 0.008
Number of values	6	6	6
Average recovery (%)	93	94	96

2.4.2 SPM intercalibration

To validate the concentrations of SPM obtained throughout the LOIS cruises reported in this study, an inter-comparison was carried out between SPM data obtained from trace metal studies and gravimetric filtration. The latter procedure involved aliquots of seawater (typically 2 l) collected in Niskin bottles (General Oceanics) being filtered through GF/C filters (Whatman), 0.7 μm pore size, 47 mm diameter mounted on a 47 mm filtration apparatus (data obtained from the LOIS database, British Oceanographic data Centre). The following inter-comparison (see Figure 2.8) represents data of the two independently determined concentrations of SPM from the same water sample i.e. CTD cast from all cruise stations. It is evident from Figure 2.8a that considerable scatter ($r=0.83$) exists in the data at concentrations greater than 200 mg l^{-1} . Concentrations of SPM obtained from trace metal sampling consistently showed lower concentrations than the BODC data set. This phenomenon is thought to be an artefact of water sampling by the Go-Flo bottles i.e. larger particles with greater settling velocities falling below the tap/filtration line resulting in preferential recovery of small low density particles. Indeed

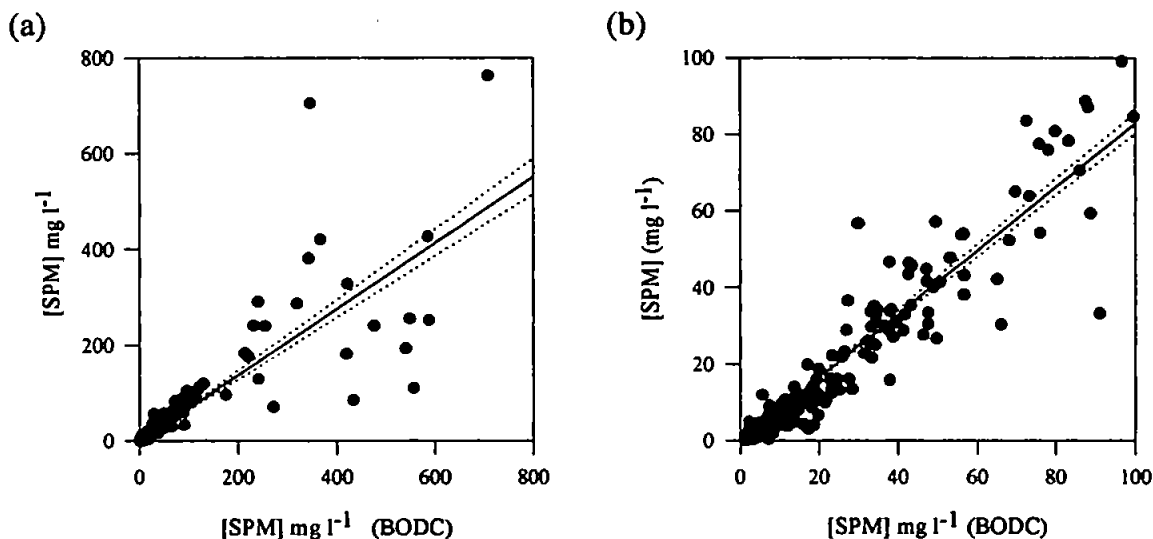


Figure 2.8 An inter-comparison of SPM concentrations for the LOIS RACS surveys. Independent SPM data obtained from British Oceanographic Data Centre (BODC) (a) for the entire concentration range where $r=0.83$ and (b) concentrations $<100\text{ mg l}^{-1}$ where $r=0.95$. The dotted lines represent the 95% confidence levels.

Turner (1990) showed that after approximately 20 minutes the concentration of particulate material held in suspension in the Go-Flo bottles had decreased by 50% due to settling below the level of the tap. Measurements of SPM provided by BODC were obtained by taking a sub sample of water from Niskin bottles (opened from the bottom) immediately following recovery of the CTD/rosette. It is therefore suggested that the systematic lower concentrations of SPM obtained from the current trace metal studies were a result of the water sampling technique.

The inter-correlation of SPM concentration increased i.e. $r=0.95$ (Figure 2.8b) when total particulates were less than 100 mg l^{-1} but still showed differences in total concentration of approximately 20%. This suggests that the determination of SPM concentration from trace metal work leads to an underestimation of the 'true' SPM concentration. More importantly, collection of particulate material from Go-Flo bottles via in line filtration (see section 2.1.2) collects a different size fraction population than is actually in the water column i.e. SPM collected has a bias towards smaller less dense particles that do not settle below the tap of the Go-Flo bottles.

2.5 Partition Experiments

2.5.1 Introduction

Trace metal partitioning experiments using a gamma emitting radioactive cocktail containing the isotopes ^{109}Cd , ^{137}Cs and ^{54}Mn in 0.1 M HCl solution were performed onboard RRS *Challenger* in the clean container during cruises CH117A/95, CH118A/95, CH118B/95 and CH119C/95. All the radiochemical experiments were performed within strict NERC guidelines for safe use at sea and regular checks of the radioactivity levels were made with a Geiger counter to ensure that the protocols were being upheld. A number of different experiments were performed throughout the cruises (for summary see Table 2.11) including;

- I. Incubation experiments, where water samples were incubated with the cocktail for a five day period prior to filtration in order to assess both spatial and seasonal changes in trace metal partitioning between the solid and solution phases,
- II. Settling velocity experiments with QUISSET tubes, where 5 settling fractions of SPM were distinguished by their settling velocity times. Each particle population was then incubated as detailed above in order to assess changes in particle reactivity as a function of particle settling velocity. These experiments were performed on each cruise (see Table 2.11) to also investigate any seasonal changes,
- III. Mixing experiments, where 2 'end member' waters were defined and collected before being mixed together in varying proportions. Each mixture was then incubated as above to assess changes in trace metal uptake as a function of water origin,
- IV. Biological Incubation experiments, in order to investigate the biological mediation of trace metal uptake as a function of season.

2.5.2 Experimental procedure

The gamma emitting 'cocktail' was freshly prepared from stock solutions (Amersham International) so that a 30 μl spike resulted in final radio-isotope concentrations of 0.23,

Table 2.11 Summary of radiochemical incubation experiments performed.

Cruise	Spatial Incubations	Settling Velocity Incubations	Mixing Experiments	Biological Incubations
CH117A/95	✓	HW5, flood tide HW5, ebb tide	✓	-
CH118A/95	-	-	-	✓
CH118B/95	✓	HW5, flood tide HW5, ebb tide	-	-
CH119C/95	✓	HW5, flood tide HW5, ebb tide	✓	✓

HW5 - Humber Estuary anchor station (for location refer to Figure 2.3)

0.11 and 0.017 ng l⁻¹ for ¹⁰⁹Cd, ¹³⁷Cs and ⁵⁴Mn respectively *cf.* typical background seawater concentrations of stable metals of the order 25 (Althaus, 1992), 400 (Martin & Whitfield, 1983) and 300 (Kremling & Hydes, 1988) ng l⁻¹ for Cd, Cs and Mn respectively. Prior to each cruise the activity of each metal checked to ensure sufficient counts. The isotopes ¹⁰⁹Cd, ¹³⁷Cs and ⁵⁴Mn were selected on the basis of a) sufficiently long half-lives, b) high γ -emissions, c) instrument detection limits and d) the contrasting geochemistries of the trace metals in marine environments (Turner *et al.*, 1981; Turner *et al.*, 1992a; Turner & Millward, 1994). Sample aliquots of 50 ml were taken from seawater, collected in the Go-Flo bottles, and decanted into pre acid cleaned Teflon beakers. Each sample was spiked with 30 μ l of the cocktail. The pH of each solution was checked, recorded and adjusted to between pH 7.5-8 if necessary with typically 10-20 μ l of 0.1 M sodium hydroxide solution (BDH, made up in Milli-Q water). The suspensions were then placed in a flow through cell and incubated for 5 days (see section 4.1) at ambient seawater temperature from the ships non-toxic supply. The beakers were regularly stirred and agitated to impede the settling of particulate matter. The dissolved oxygen content of the samples were also measured periodically throughout the incubations using a dissolved oxygen meter (YSI 58, Clandon/YSI Ltd), to check that anoxic conditions had not developed. Samples were then filtered through pre-weighed, 25 mm diameter, 0.4 μ m pore size, cellulose acetate filters placed in a glass vacuum micro filtration apparatus. The filters were then placed in Petri dishes and the filtrate transferred to 100 ml polyethylene containers after being acidified to approximately pH 1 (typically 1 ml of acid for every 100 ml of sample) with concentrated

HCl (AristaR). Both phases were stored at room temperature until transported back to the laboratory for analysis (see section 2.5.7).

2.5.3 Spatial and seasonal five day partition coefficients

These experiments were performed seasonally (Table 2.11) off the mouths of the major estuaries that discharge into the western North Sea namely, the Humber, Tees, Tyne and, for comparison purposes, the relatively pristine Tweed (refer to Figure 2.1 for the estuary locations). The experimental procedure followed was as detailed above in section 2.5.2.

2.5.4 Settling velocity fractions, partition coefficients

These experiments were performed exclusively at the Humber anchor station during flood and ebb tides. Sampling with the QUISSET tubes was timed to coincide, when logistically feasible, with maximum tidal streaming on both the flood and ebb tides. From each particle fraction collected (section 2.1.5) a sub sample of 50 ml was measured into Teflon containers and taken through the experimental procedure detailed in section 2.5.2. This work considered the differences in trace metal uptake between different particle populations as defined by their settling velocities, and the respective changes according to tidal state. The particle population on the ebbing tide was dominated by estuarine derived particles in comparison to the returning flood waters which were assumed to be more marine in character (refer to Chapter 5). These incubations were performed in the winter, spring and summer cruises (Table 2.11) to also ascertain any seasonal changes in trace metal behaviour.

2.5.5 Mixing experiments

The aim of the mixing experiments was to simulate the mixing of eroded Holderness cliff material with particles derived from the Humber Estuary, a process that occurs in the

Humber Plume. These experiments involved the collection of 2 end member water bodies and their subsequent mixing to produce seawater samples containing varying proportions of the initial end members. This experiment was simulated in winter and summer both using end member waters collected from the mouth of the Humber Estuary (HW5, refer to Figure 2.3) and from along the Holderness Coast (from station C2 and HW1 during winter and summer respectively, see Figure 2.2). The water samples were collected from Go-Flo bottles deployed from RRS *Challenger*. Holderness waters were collected from near shore as logistically possible but did not contain particulate material derived exclusively from the erosion of the Holderness boulder clay material. Humber Estuary seawater was collected at the anchor station during low tide in an attempt to collect waters originating predominantly from upstream of the estuary itself. The rationale behind this type of experiments is that waters of the Humber Plume are predominantly composed of two chemically distinct particle sources, the anthropogenically modified riverine particles and the fine boulder clay material eroded from the Holderness Cliffs. If each source has distinctly different metal reactivities it is postulated that by the mixing of different proportions of each you can simulate trace metal uptake in the Humber Plume as a function of particle origin. The proportions of end members were mixed together to produce 6 samples composed of 100, 80, 60, 40, 20 and 0% Humber Estuary material. Each fraction was then spiked with cocktail and incubated as in section 2.5.2..

2.5.6 Productivity experiments

The biological similarity in deep ocean profiles between dissolved trace metals such as Cd and Zn and the major nutrients e.g. phosphate and silicate respectively has been well documented (Boyle *et al.*, 1976; Bruland *et al.*, 1978; Broecker & Peng, 1982; Bruland & Franks, 1983; Chester, 1990). However, the extent of biological perturbations of trace metal distributions in dynamic coastal regimes remain largely unquantified. In an attempt to investigate the role of phytoplankton production on the cycling of trace metals in the coastal waters of the western North Sea a series of 'biological uptake' experiments were performed in the spring and summer cruises (CH118A/95 and CH119C/95 respectively, refer to Table 2.1).

2.5.6.1 Experimental procedure

Productivity experiments were undertaken in collaboration with Southampton University Department of Oceanography (SUDO) who performed simultaneous experiments using ^{14}C to ascertain primary production (for experimental protocol the reader is referred to Joint & Pomroy, 1993) and ^{33}P and ^{15}N (nitrate and ammonia) to investigate nutrient uptake. Thus the adopted experimental protocol was designed to compliment existing SUDO methodology to enable direct data comparison. Core LOIS measurements also provided dissolved nutrient (nitrate, nitrite, phosphate and silicate) concentrations in the surface waters of the Humber coastal zone throughout the cruises. Two water samples were also taken in glass bottles at every CTD station and preserved with lugols iodine and formalin respectively for shore based microscopic analysis of major phytoplankton species. A SPM sample (as described in section 2.1.2) was also collected for each productivity experiment in order to ascertain the 'readily available' (refer to section 2.2.1) concentration of particulate trace metals.

Sampling sites were selected by locations of high fluorescence as determined by the ships fluorometer. Table 2.12 summarises the date and location of all productivity experiments undertaken while Figure 2.9 illustrates sampling locations. The experimental procedure followed is summarised in Figure 2.10. Water samples were collected with Go-Flo bottles and decanted into plastic carboys before filling 60 ml Nalgene polycarbonate bottles (these bottles were chosen because of their light transmission properties and permeability to gases). Samples were then spiked with 30 μl of the γ -emitting cocktail as described in section 2.5.2. The radioactive isotope ^{137}Cs was also analysed as previous work by Williams *et al.* (1994) indicated that in contrast to ^{109}Cd and ^{54}Mn the extent of ^{137}Cs uptake was greater for Holderness derived particles than Humber particles i.e. contrasting geochemistry with different particle types. The pH of the samples was checked and adjusted to 7.5 with 0.1M NaOH if necessary. A control sample was poisoned by adding an aliquot of HgCl_2 (300 μl of 3.5% solution per 100 ml sample). The poisoned sample stopped active assimilation processes thereby providing a measure of passive surface uptake onto particle surfaces only.

Table 2.12 Summary of location and date of productivity experiments.

Cruise	Date	Position		Ref. No Fig 2.9
		Lat	Long	
CH118B/95	02/04/95	53.075 N	0.987 E	1
	03/04/95	53.255 N	0.657 E	2
	04/04/95	53.655 N	0.962 E	3
CH119C/95	02/07/95	53.420 N	0.772 E	4
	10/07/95	53.728 N	0.657 E	5
	11/07/95	53.000 N	0.393 E	6

Samples were incubated on-deck at ambient seawater temperatures from dawn to dusk prior to separation of the dissolved and particulate phases by filtration. The incubator consisted of 6 Perspex tubes, with different neutral density filters to give a range of light transmission of 97, 75, 36, 21, 6 and 1% of ambient irradiance (Joint & Pomroy, 1993). Due to limited resources bottles for trace metal uptake studies were only incubated in the 97 and 1% light levels, referred to herein as light and dark samples respectively. To prevent any effect of the ship's light at night, the samples in the neutral density tubes were transferred at dusk to a black tube, which was also supplied with surface seawater to control temperature. After a 24 hour incubation period each sample was filtered through a 0.2 μm pore-size, 0.25 mm diameter, Nuclepore polycarbonate filter. The filters were rinsed with a few ml of filtered seawater, dried and stored in Petri dishes at room temperature. The volume of filtrate was noted, transferred to a polyethylene pot, acidified to pH 1-2 with HCl (AristaR) and stored at room temperature until shore based counting of γ -emissions.

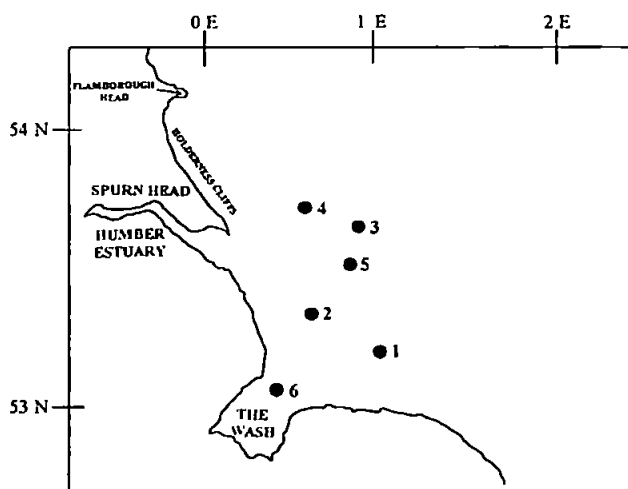


Figure 2.9 Sampling locations for productivity experiments.

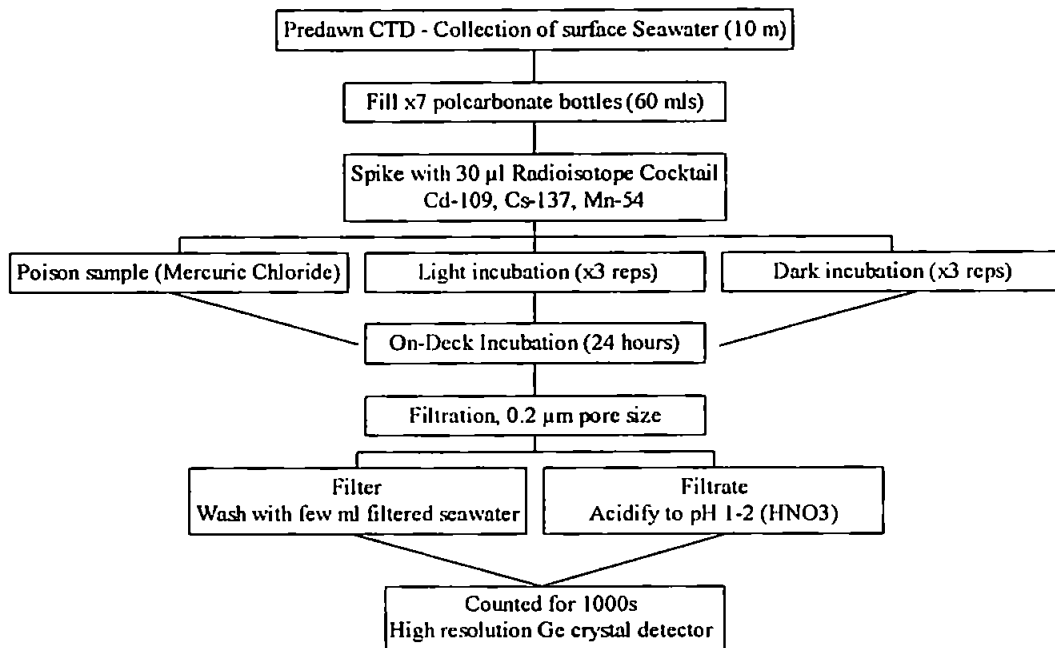


Figure 2.10 Schematic of experimental procedure followed for biological incubation experiments (for a fuller explanation of the γ -detector please refer to section 2.5.7).

2.5.7 Analysis of radiochemical samples

The filters and filtrate from the radiochemical incubation experiments were analysed by counting the gamma emissions from both phases for 1000 seconds on a high performance Ge crystal coaxial detector connected to a Canberra Series 80 multi-channel analyser (Turner *et al.*, 1992a;1993, Turner & Millward, 1994). Analysis of 5 replicate filter and solution samples yielded the following relative standard deviations (%): for solutions - Cd, 4.5; Cs, 5.5; Mn, 6.1; and for filters - Cd, 9.9; Cs, 9.6; Mn, 9.9. In order to account and correct for geometry differences between phases a 30 μ l spike of the cocktail was added to both a blank filter and 50 ml of Milli-Q water and both phases counted. The geometry correction factor (f), is then simply a ratio of the filter counts over the Milli-Q water counts. The counts from both phases together with the dry weights of SPM on the filters, were used to estimate the partition coefficient K_D as follows:

$$K_D = \frac{A_p V \cdot 10^3}{A_s m f} \quad 2.2$$

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 laden on the filter in mg; and f is the geometric correction factor (Turner & Millward, 1994). The units of K_D from dimension analysis are ml g^{-1} . However if you assume that a volume of 1 ml of water is equivalent to a mass of 1 g then K_D becomes *effectively* a dimensionless quantity.

3 Trace Metals in the western North Sea: Field Observations

3.1 Introduction

Coastal waters are complex systems in which a range of processes change the concentration of dissolved and particulate metals on relatively short temporal and spatial scales (Hydes & Kremling, 1993). The objective of the LOIS RACS cruises were to provide (a) an extensive coverage of the concurrent seasonal distributions of particulate trace metals in the western North Sea, including the major estuarine plumes in the study area, and (b) more intensive observations in the Humber coastal zone to quantify the fluxes into this area and trace metal reactivity in order to understand the processes leading to the observed distributions. This chapter therefore initially considers the seasonal distributions of Fe_p , Mn_p , Cu_p , Cd_p and Pb_p in SPM and surface sediments of the LOIS coastal zone (see section 1.2, Figure 1.1) incorporating the estuarine plumes of the Humber, Tees, Tyne and Tweed. The following section examines in more detail the Humber coastal zone (see Section 1.2.2, Figure 1.9) and includes (a) a discussion of the seasonal distributions of the aforementioned particulate metals associated with the SPM, (b) particulate and dissolved trace metal (Cu, Cd & Pb) fluxes from the Humber Estuary into the receiving coastal zone and (c) the seasonal partitioning of Cu, Cd and Pb as a function of SPM concentration. Trace metal data from the NSP cruises CH42/88, 15-29 December 1988; CH65/90, 6-17 May 1990 and CH69/90, 26 July-27 August 1990, herein referred to as winter'88, spring'90 and summer'90 are incorporated into the current LOIS data set in order to assess the inter-annual variability of the behaviour of Cu, Cd and Pb.

3.2 The LOIS Coastal Zone - Particulate Trace Metal Distributions

The distribution of SPM in the LOIS coastal zone is shown in Figure 3.1 and displayed a distinct seasonal trend with concentrations increasing from autumn'94 to a maximum average of $21 \pm 19 \text{ mg l}^{-1}$ obtained during winter'95 (see Table 3.1). The concentration of SPM subsequently decreased through the year to a minimum of $2.4 \pm 3.6 \text{ mg l}^{-1}$ obtained during summer'95. This SPM trend is similarly reflected in the mean concentration of particulate matter reported for the Humber coastal zone but the concentrations at least double in magnitude reflecting the importance of this area as a source of SPM to the southern North Sea (refer to section 1.2.2.3). The correlation between SPM and salinity ($P < 0.05$) for the Humber coastal zone during all seasons (see Table 3.1) suggests further that the Humber Estuary, in particular, is a significant SPM source.

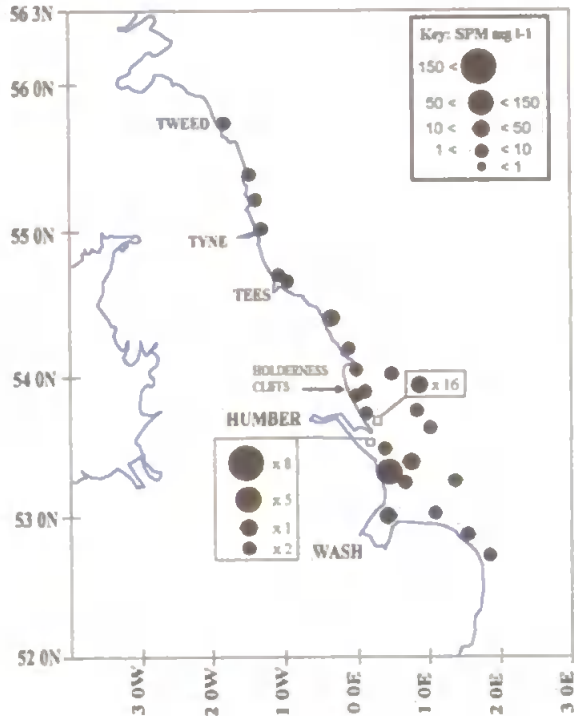
Table 3.1 Summary of the mean SPM concentrations in the LOIS and Humber coastal zones with corresponding SPM-salinity relationships and Humber Estuary outflow and tidal range data.

Cruise	Mean [SPM] (mg l^{-1})		r	Humber mouth	
	LOIS Coastal Zone	Humber Coastal Zone		SPM-Salinity Humber Coastal Zone ^a	Residual Outflow ($\text{m}^3 \text{ s}^{-1}$)
Autumn'94	7.7 ± 11 (28)	25 ± 68 (18)	-0.97	165	6.6
Winter'95	21 ± 19 (36)	41 ± 50 (21)	-0.87	425	5.0
Spring'95	5.7 ± 12 (55)	23 ± 61 (22)	-0.74	345	6.6
Summer'95	2.4 ± 3.6 (44)	7.1 ± 13 (23)	-0.86	70	4.9

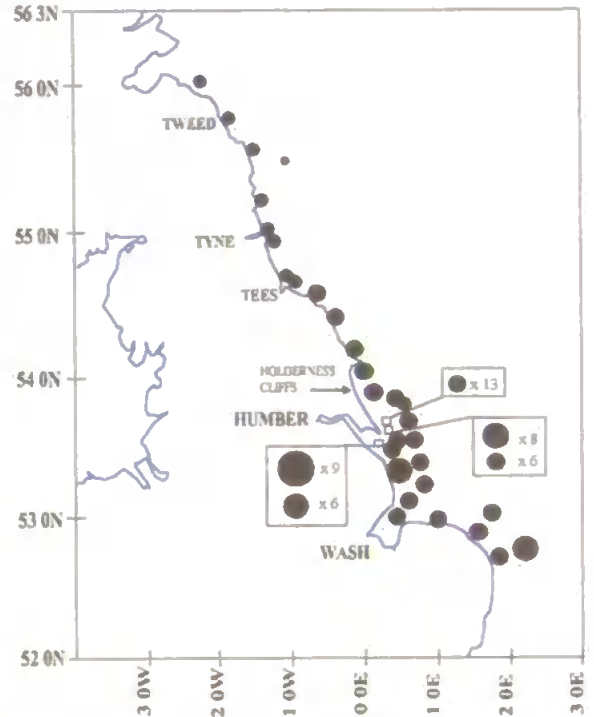
^aFor the Humber coastal zone only, all values significant for $P < 0.05$; ^bTidal range at Spurn Head; springs 5.7 m; neaps 2.8 m; numbers in brackets represent number of samples.

The maximum SPM concentrations reported are constrained to the mouth of the Humber Estuary throughout the year and do not show any pronounced seasonal variations. The propagation of the resulting plume of SPM is dependant on estuarine outflow, tidal regime and prevailing weather conditions. For example, during winter'95 a high estuarine outflow of $425 \text{ m}^3 \text{ s}^{-1}$ in combination with a relatively large tidal range and prevailing easterly to north easterly winds gusting up to 15 knots (see Figure 3.3c & d) resulted in an elevated plume of SPM ($>20 \text{ mg l}^{-1}$) extending south easterly with the residual currents off the Norfolk coast. The prevailing winds restrict the spatial

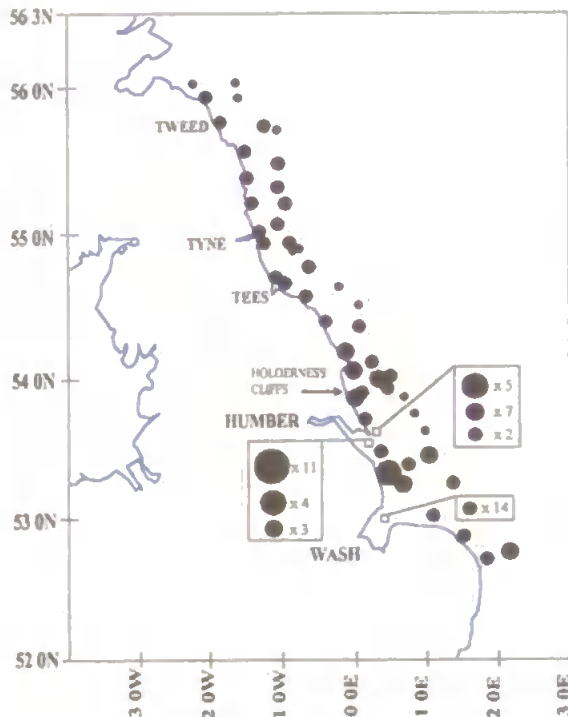
(a) Autumn



(b) Winter



(c) Spring



(d) Summer

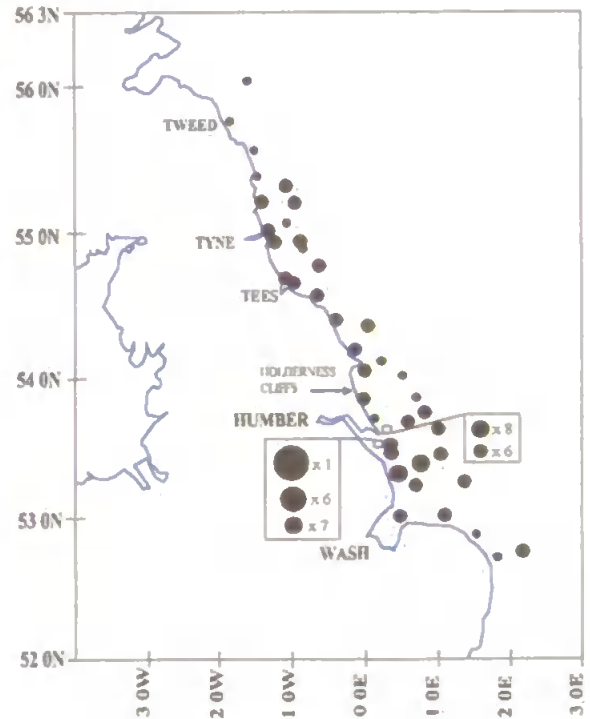


Figure 3.1 Distribution of SPM (mg l^{-1}) in the water column of the western North Sea coastal zone during (a) autumn'94, (b) winter'95, (c) spring'95 and (d) summer'95. The boxed concentration key in (a) applies to all distributions. The boxed insets are from tidal cycles where samples were taken every hour i.e. (● x 2) means that during the tidal cycle 2 samples exhibited SPM concentrations greater than 10 but less than 50 mg l^{-1} .

spreading of the SPM to inshore waters. This is illustrated by the light transmission of a continuously logging transmissometer mounted onboard RRS *Challenger* throughout the winter survey (see Figure 3.2). This is in sharp contrast to the following summer when a much reduced estuarine outflow of $70 \text{ m}^3 \text{ s}^{-1}$ and calm winds (5-10 knots) mixed in direction (see Figure 3.3g & h) resulted in lower SPM concentrations at the mouth of the Humber Estuary that were confined to the immediate vicinity and did not extend away from the estuary mouth.

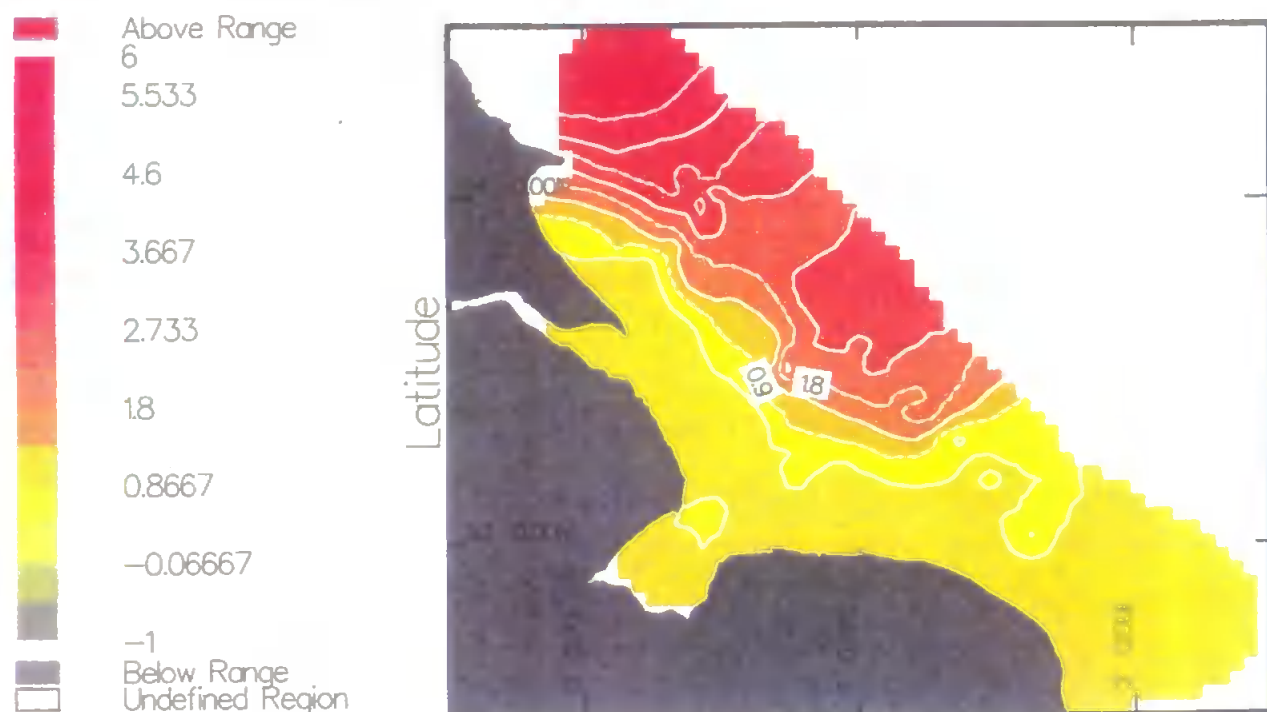


Figure 3.2 Distribution of transmission (raw ship time data in volts) in the Humber coastal zone during winter'95.

In organising the discussion of the large particulate trace metal database it is convenient to discuss Fe and Mn together owing to their (a) similar redox mediated reactions and (b) mass dominance in the Humber coastal zone. The trace metals Cu, Cd and Pb are subsequently considered separately due to their reported contrasting geochemical behaviours (Balls, 1985:1988 ; Statham *et al.*, 1993; Laslett, 1995; Tappin *et al.*, 1995).

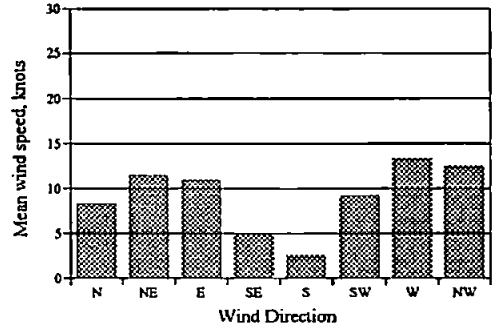
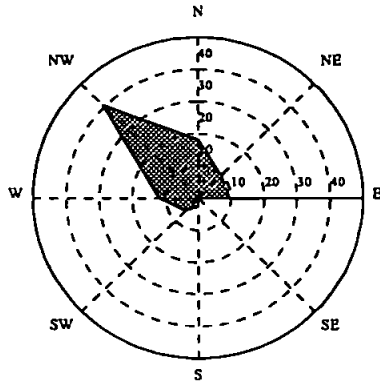
3.2.1 Particulate iron and manganese

The concentration of Fe_p varied by a factor of *c.* 300 (range $0.1\text{-}29 \text{ mg g}^{-1}$) over the period of the LOIS surveys; a seasonal trend was also evident (see Figure 3.4). During

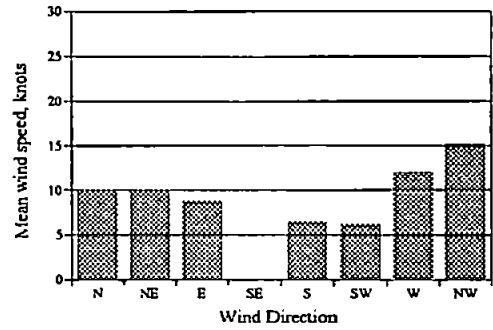
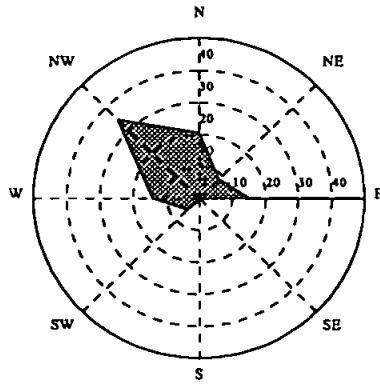
winter'95 Fe_p concentrations averaged 16 mg g^{-1} throughout the survey area with particularly high concentrations ($>20 \text{ mg g}^{-1}$) evident at the mouth of the Humber Estuary. Concentrations further north around the Tweed Estuary were noticeably lower (between $5\text{-}10 \text{ mg g}^{-1}$) compared to other locations. However the catchment area of the Tweed is sparsely populated and has been also reported to have low Mn_p and Pb_p concentrations compared to other north east estuaries (Laslett, 1995). Average Fe_p concentrations decreased from winter through spring (13 mg g^{-1}) to summer (8.4 mg g^{-1}). The concentrations north of the Tyne Estuary encompassing the Tweed Estuary remain consistently lower than the average concentrations for each respective season except autumn'94, when sampling was spatially limited by weather conditions. Elevated Fe_p concentrations (approximately 20 mg g^{-1}) compared to average figures were consistently displayed at the mouth of the Humber Estuary *cf.* SPM and are attributed to anthropogenic inputs as previously mentioned in section 1.2.2.4. This anthropogenic input has been reported by Tappin *et al.* (1995) to account for the persistently high Fe_p concentrations ($>6.6 \text{ mg g}^{-1}$) in the English coastal zone when compared to the rest of the southern North Sea, a view corroborated by Turner *et al.* (1991) from evidence of sediment analysis. Subsequent examination of Fe_p distributions in the Humber coastal zone during the LOIS surveys also revealed the persistence of relatively high concentrations ($>5.0 \text{ mg g}^{-1}$) throughout the year, except for a station north of the Humber, adjacent to the Holderness cliffs during autumn'94 and at stations further offshore during summer'95 when the corresponding estuarine output was very low ($70 \text{ m}^3 \text{ s}^{-1}$).

However, the extent of the estuarine plume is highly dependent on the prevailing hydrodynamic regime and weather. This is reflected in the distribution of Fe_p as concentrations in excess of 15 mg g^{-1} are shown emanating from the Humber Estuary and in the plume as it moves south easterly during winter'95, in comparison to summer'95, when similar concentrations were only found in the vicinity of the estuary mouth.

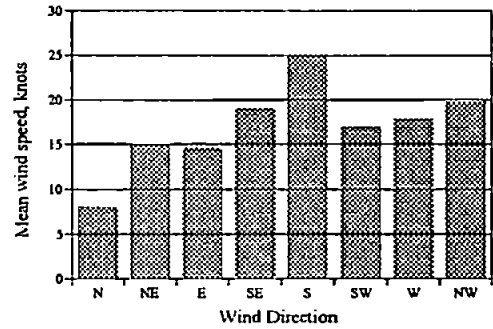
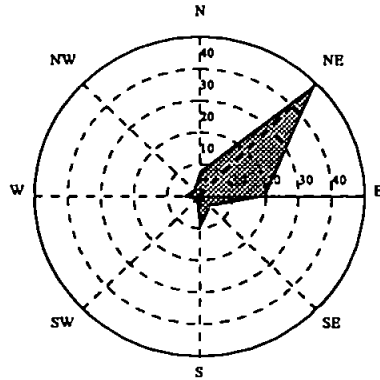
(a) Autumn'94 Donna Nook



(b) Autumn'94 Bridlington



(c) Winter'95 Donna Nook



(d) Winter'95 Bridlington

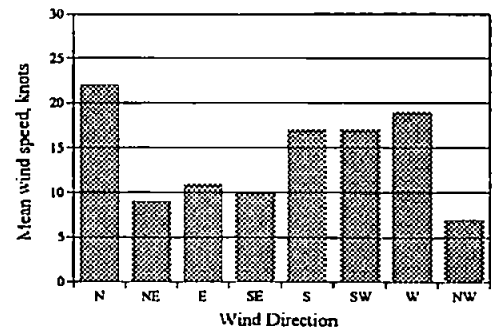
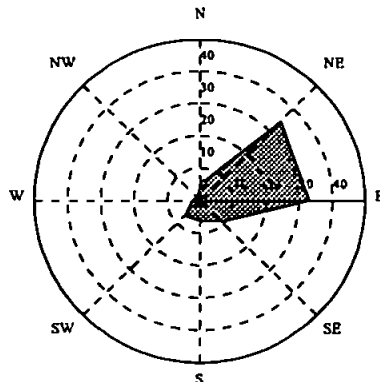
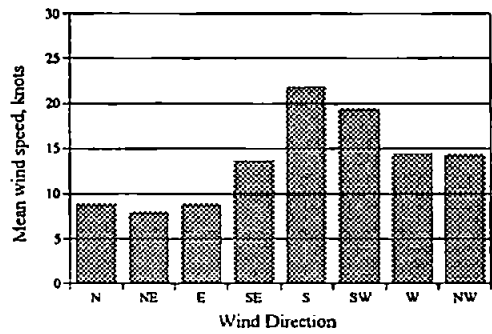
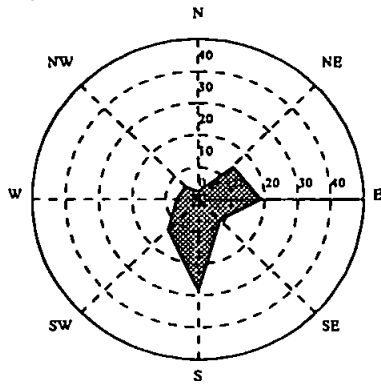
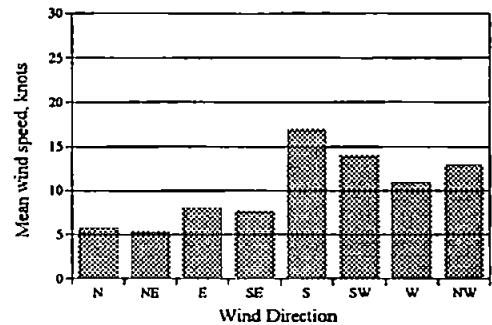
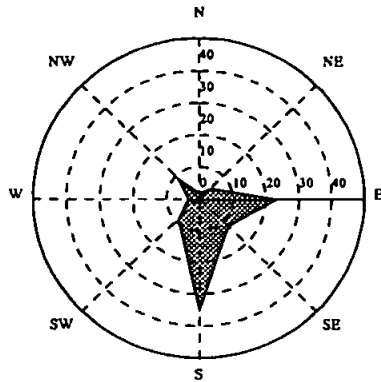


Figure 3.3 Spider plots showing wind direction (Degrees true) for the duration of each survey. Bar plots showing average wind speed (knots) for each respective direction. The data from the land based Bridlington MRSC meteorological station and the Donna Nook synoptic automatic meteorological office station were analysed for each survey in (a) and (b) Autumn'94, (c) and (d) Winter'95. For locations of the meteorological stations refer to Figure 2.1.

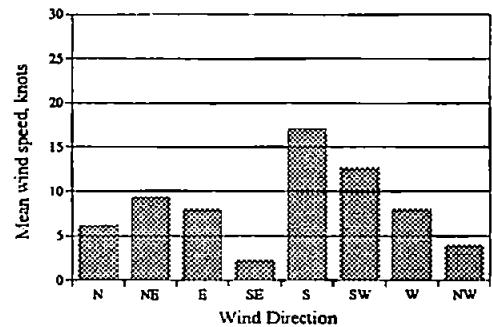
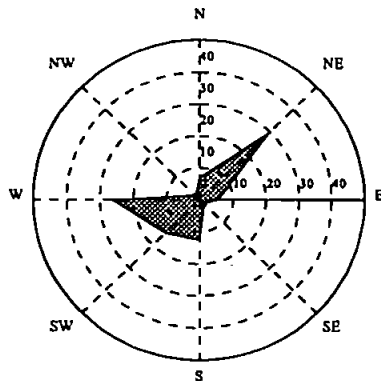
(e) Spring'95 Donna Nook



(f) Spring'95 Bridlington



(g) Summer'95 Donna Nook



(h) Summer'95 Bridlington

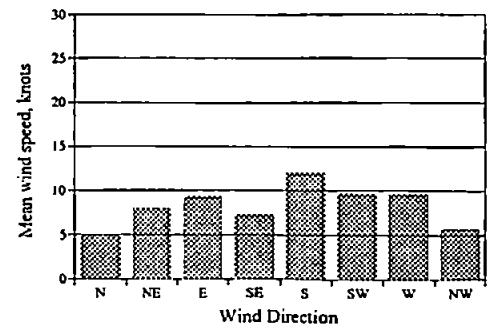
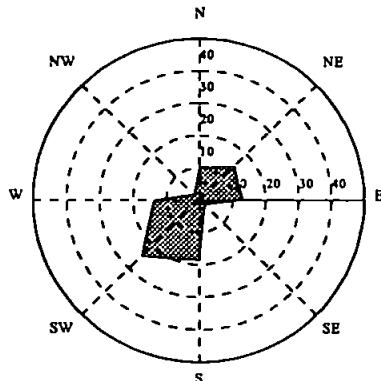
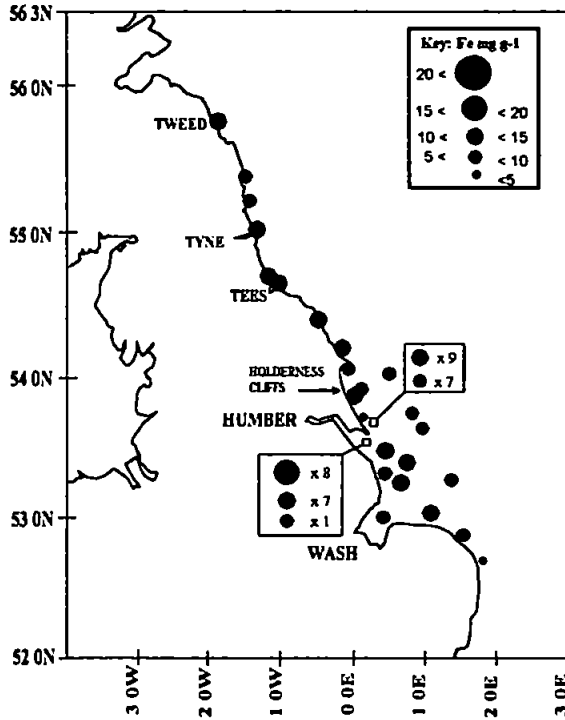
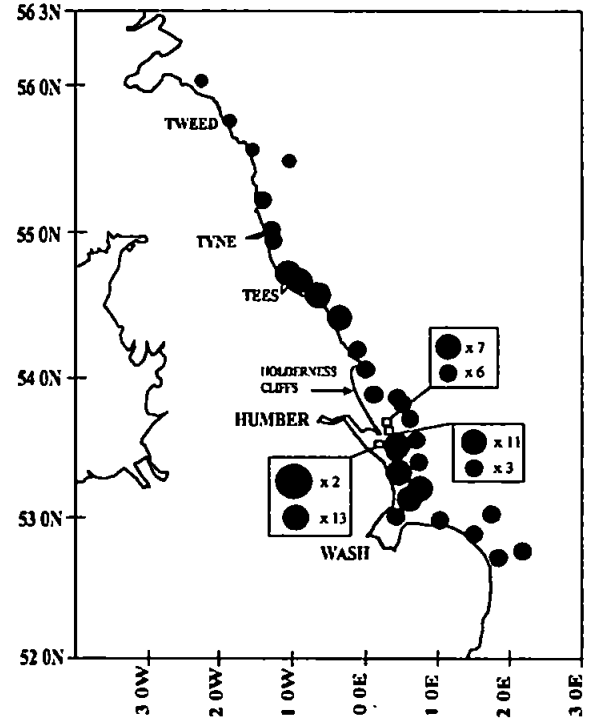


Figure 3.3 continued. Spider plots showing wind direction (Degrees true) for the duration of each survey. Bar plots showing average wind speed (knots) for each respective direction. The data from the land based Bridlington MRSC meteorological station and the Donna Nook synoptic automatic meteorological office station were analysed for each survey in (c) and (f) Spring'95, (g) and (h) Summer'95. For locations of the meteorological stations refer to Figure 2.1.

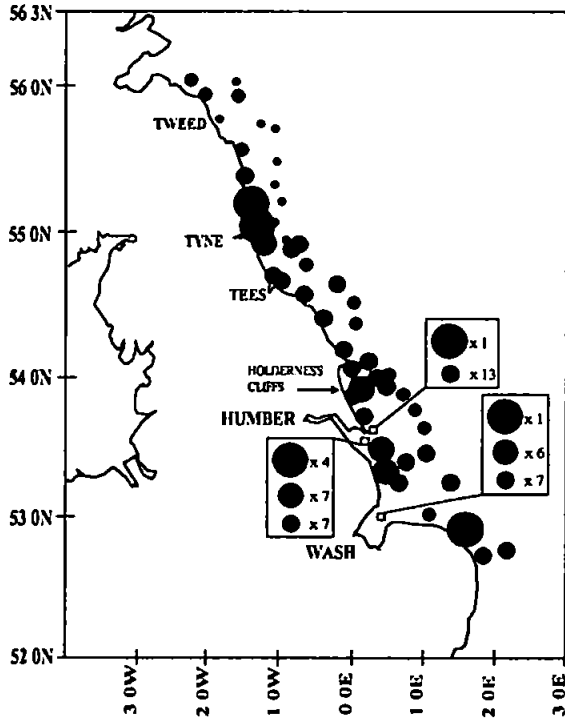
(a) Autumn



(b) Winter



(c) Spring



(d) Summer

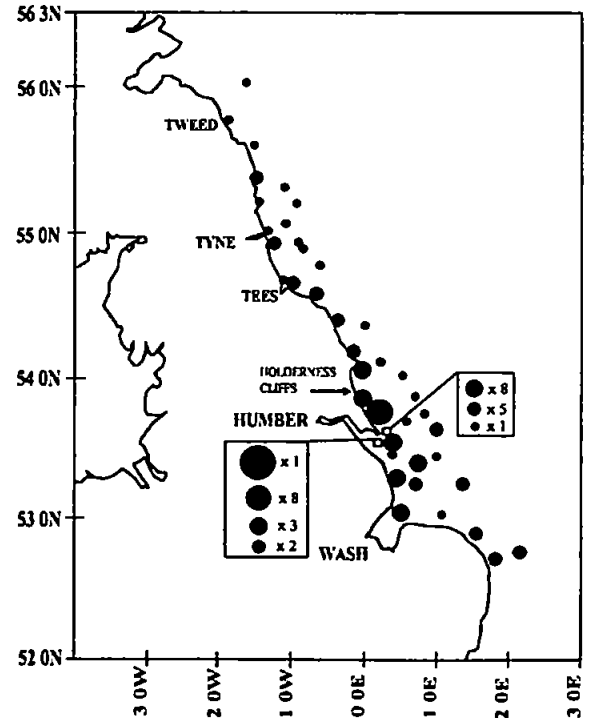


Figure 3.4 Distribution of Fe_p ($mg\ g^{-1}$) in the water column of the western North Sea coastal zone during (a) autumn'94, (b) winter'95, (c) spring'95 and (d) summer'95. The boxed concentration key in a) applies to all distributions. The boxed insets are from tidal cycles where samples were taken every hour i.e. (● x 2) means that during the tidal cycle 2 samples exhibited Fe_p concentrations greater than 10 but less than 15 $mg\ g^{-1}$.

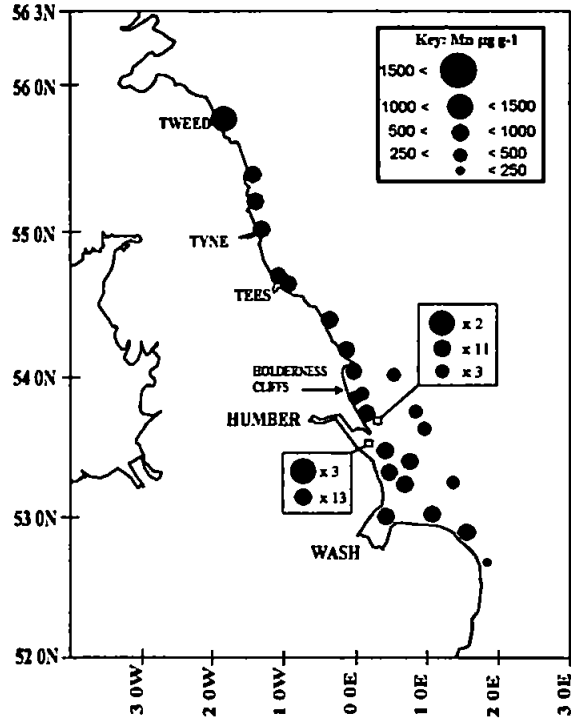
Levels of Mn_p (Figure 3.5) varied between 15-1483 $\mu\text{g g}^{-1}$ and exhibited a seasonal cycle similar to that of Fe_p . During winter'95 average Mn_p concentrations of 700 $\mu\text{g g}^{-1}$ for the LOIS coastal zone compared well with the average of 780 $\mu\text{g g}^{-1}$ reported by Tappin *et al.* (1995) for the southern North Sea. Average concentrations decreased throughout the year to 641 and 514 $\mu\text{g g}^{-1}$ in spring'95 and summer'95 respectively. The concentration of Mn_p and Fe_p are closely coupled as evident by the significant linear relationships ($P < 0.05$; see Table 3.2) between the two metals throughout the LOIS surveys.

Table 3.2 Values of r for linear relationships between salinity and the concentration of SPM, Fe_p and Mn_p in the Humber coastal zone during the LOIS surveys. Statistically significant ($P < 0.05$) correlation's are indicated in bold type.

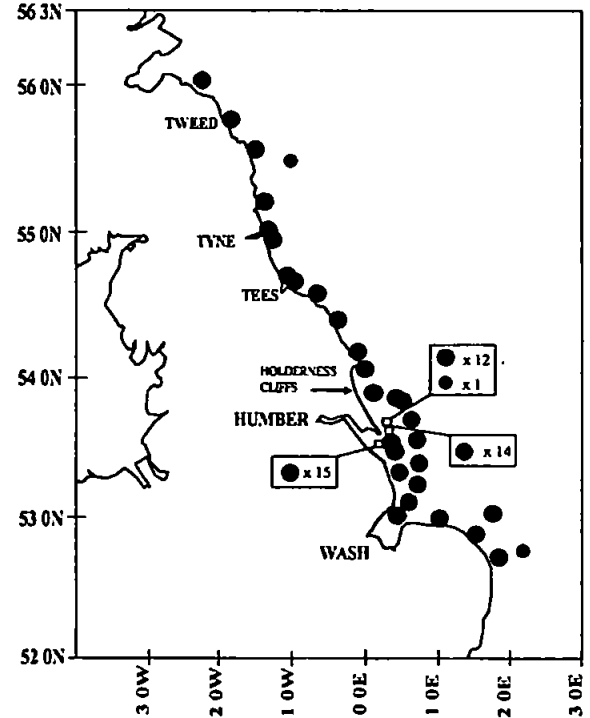
Season	n	Fe_p		Mn_p		
		Salinity	SPM	Salinity	SPM	Fe_p
Autumn'94	18	-0.41	0.48	-0.56	0.48	0.59
Winter'95	21	-0.20	0.39	-0.35	0.06	0.44
Spring'95	22	-0.53	0.34	-0.05	-0.10	0.83
Summer'95	23	-0.39	0.45	-0.28	0.28	0.68

Particularly high concentrations of Mn_p ($>1000 \mu\text{g g}^{-1}$) and Fe_p ($>20 \text{ mg g}^{-1}$) were observed off the Tyne Estuary during spring'95; the former observation consistent with the findings of Tappin *et al.* (1995), albeit during winter'89. Elevated Mn_p and Fe_p concentrations in the English coastal zone and southern North Sea have previously been attributed to resuspension of lithogenous material (Nolting & Eisma, 1988; Tappin *et al.*, 1995). However recent surface sediment analysis in the LOIS coastal zone during spring'95 off the Tyne Estuary (Figure 3.6) does not support the above argument where sediment concentrations are less than the overlying SPM concentrations. This would suggest elevated estuarine sources or preferential association of Fe_p with permanently suspended particles (see Chapter 5). The distribution of Fe and Mn in the surface sediments (Figure 3.6) does however confirm the presence of noticeably high concentrations of Fe and to some extent Mn ($>20 \text{ mg g}^{-1}$ & $1000 \mu\text{g g}^{-1}$ respectively) in the Humber Estuary, although more recent samples obtained during autumn'94 and spring'95 have indicated some reduction in the concentration of both metals. Samples adjacent to the Tweed Estuary, in agreement with SPM results, show substantially

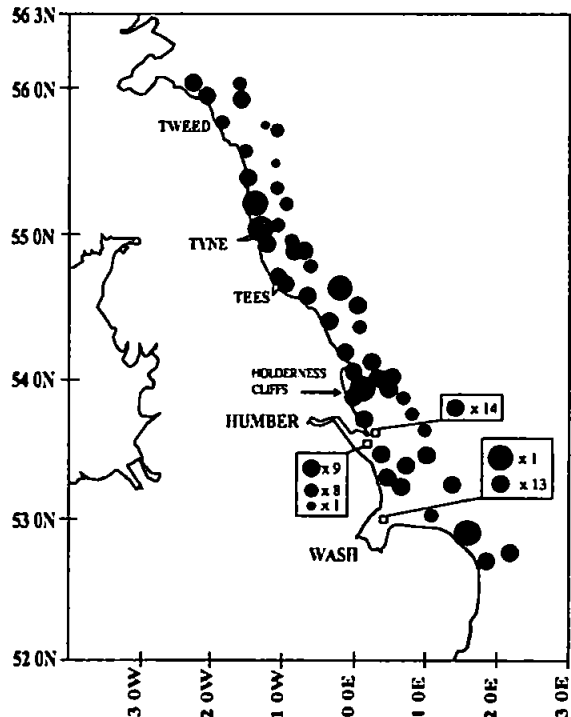
(a) Autumn



(b) Winter



(c) Spring



(d) Summer

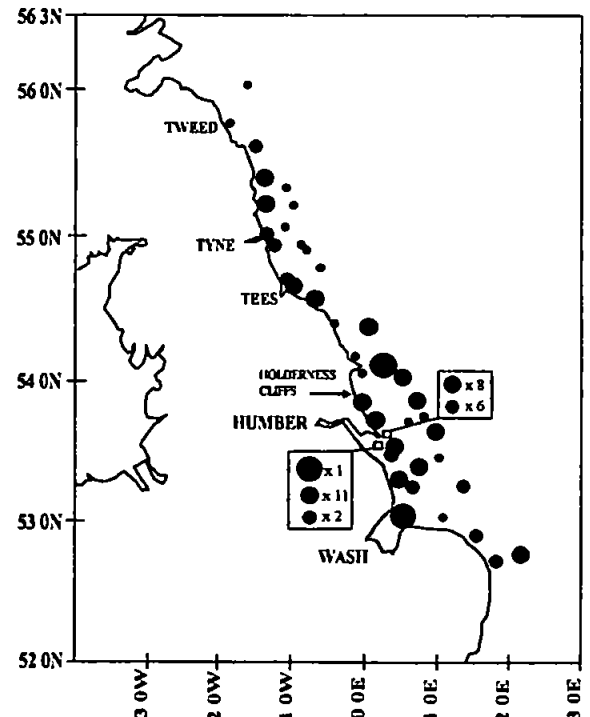


Figure 3.5 Distribution of Mn_p ($\mu g g^{-1}$) in the water column of the western North Sea coastal zone during (a) autumn '94, (b) winter '95, (c) spring '95 and (d) summer '95. The boxed concentration key in a) applies to all distributions. The boxed insets are from tidal cycles where samples were taken every hour i.e. (● x 2) means that during the tidal cycle 2 samples exhibited Mn_p concentrations greater than 500 but less than 1000 $\mu g g^{-1}$.

smaller sediment concentrations ($<10 \text{ mg g}^{-1}$ & $<500 \mu\text{g g}^{-1}$ for Fe and Mn respectively) compared to the Tees, Tyne and Humber regions of the survey area.

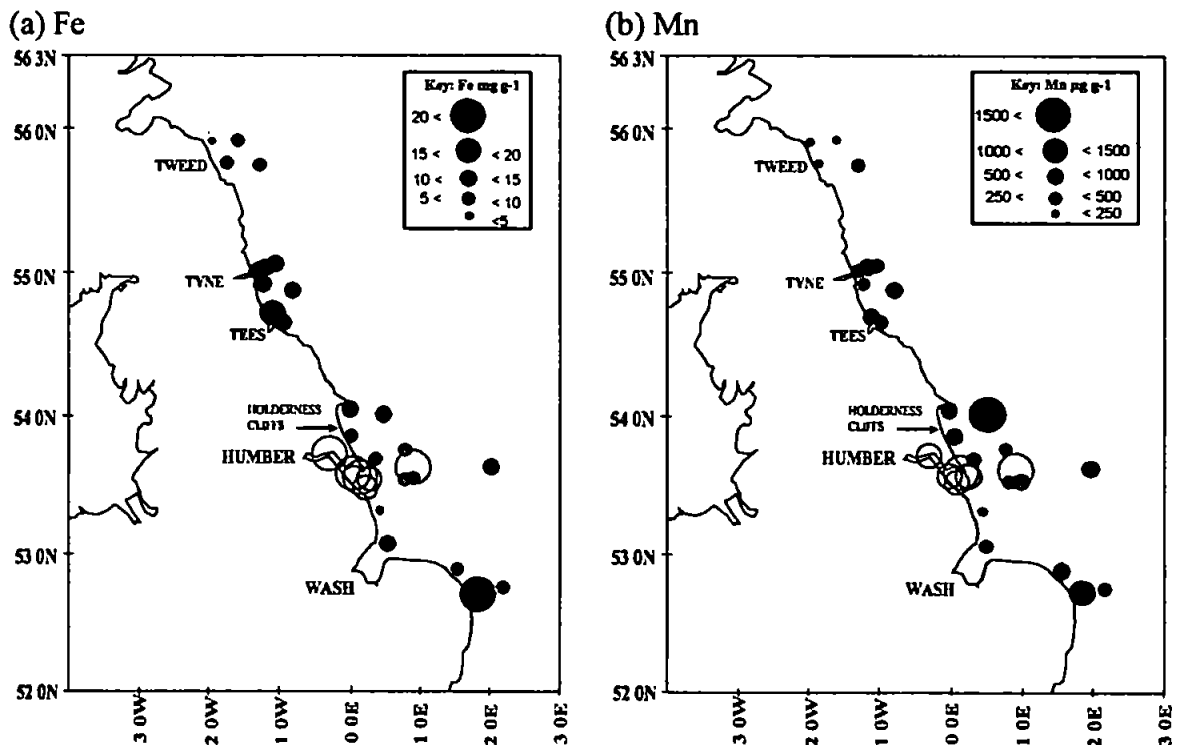


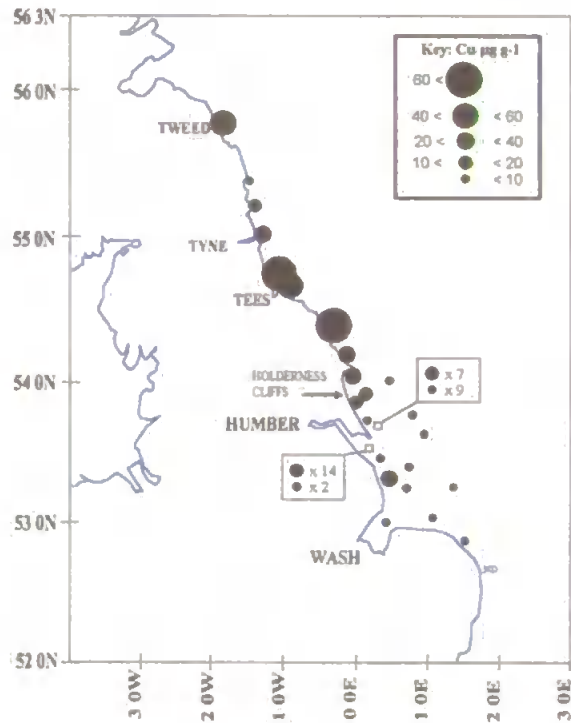
Figure 3.6 The distribution of (a) Fe and (b) Mn in the surface sediments of the LOIS coastal zone where (●) represents samples from winter'92 (CH99/92, refer to section 2.1.4, Table 2.3), (●) autumn'94 and (●) spring'95. Open circles are used to avoid obscuring smaller concentrations.

3.2.2. Particulate copper

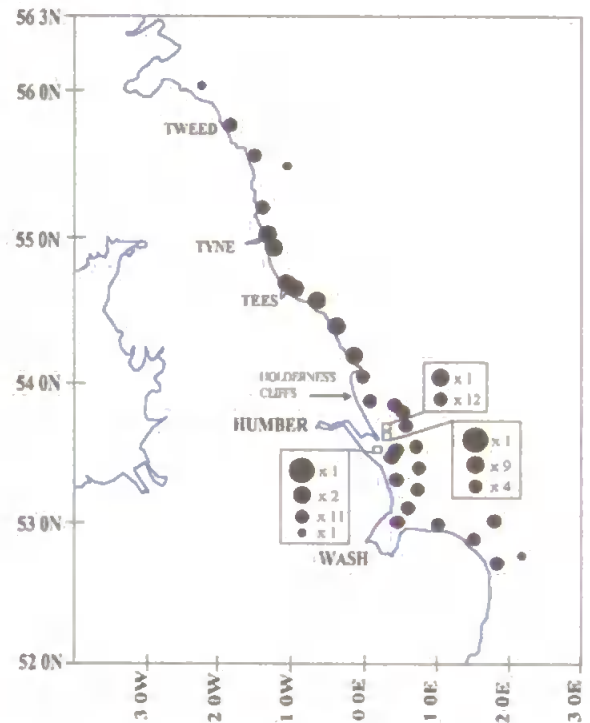
Concentrations of Cu_p ranged from below the limit of detection ($0.03 \mu\text{g g}^{-1}$, see Table 2.8) to $175 \mu\text{g g}^{-1}$ in the LOIS coastal area¹ and are shown in Figure 3.7. High values ($79\text{-}120 \mu\text{g g}^{-1}$) were found off the industrialised Tees Estuary and further to the south during autumn'94 (Laslett, 1995; Tappin *et al.*, 1995; Williams, 1995) and at 'hot spots' in the Humber coastal area during summer'95. The seasonal distributions of Cu_p did not reveal elevated concentrations near the mouth of the Humber Estuary when compared to the coastal zone during any survey in contrast to the case for Fe_p and Mn_p . These results

¹ Refer to Tables 1.4 & 1.6 for a comparison with other concentrations quoted in the literature.

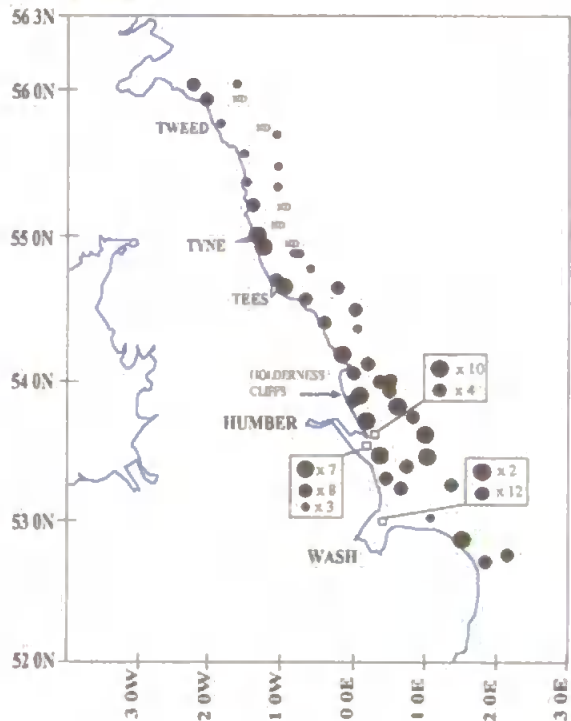
(a) Autumn



(b) Winter



(c) Spring



(d) Summer

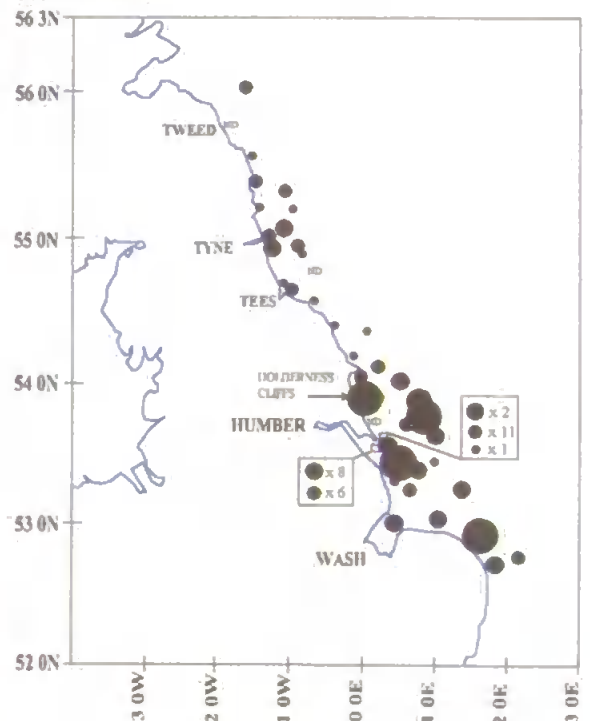


Figure 3.7 Distribution of Cu_p ($\mu\text{g g}^{-1}$) in the water column of the western North Sea coastal zone during (a) autumn '94, (b) winter '95, (c) spring '95 and (d) summer '95. The boxed concentration key in a) applies to all distributions. The boxed insets are from tidal cycles where samples were taken every hour i.e. (● x 2) means that during the tidal cycle 2 samples exhibited Cu_p concentrations greater than 20 but less than $40 \mu\text{g g}^{-1}$.

agree with those of Millward *et al.* (1996) for the Humber Plume region for particulate samples taken during the NSP surveys in winter'88, spring'90 and summer'90.

The distributions of Cu_p were reasonably uniform during winter'95 *cf.* Fe_p & Mn_p with concentrations ranging between 20–40 $\mu\text{g g}^{-1}$ north of the Holderness cliffs and slightly lower ranging between 10–20 $\mu\text{g g}^{-1}$ in the Humber coastal zone. During the following spring and summer concentrations north of the Holderness coast decreased noticeably offshore, a gradient that was probably allowed to establish during the calmer weather conditions compared to the autumn and winter (refer to Figure 3.3). The distribution of Cu_p in the Humber coastal zone during summer'95 showed no coherent pattern which may be because Cu was associated with phytoplankton and organic matter/detritus (Cabanis & Shuman, 1988; Paulson *et al.*, 1994a & b; Millward *et al.*, 1996) which are likely to be unevenly distributed.

The distribution of Cu in surface sediments of the LOIS coastal zone (Figure 3.8) showed similar concentrations off the Tees, Tyne and Humber estuaries (range 20–40 $\mu\text{g g}^{-1}$) when compared to their SPM counterparts, except for the Tees Estuary during autumn'94. This suggests anthropogenic contamination of surface sediments from the respective industrialised catchment areas implying that Cu may preferentially be associated with heavier particles that settle to the bed. However, Williams (1995) found that Cu preferentially associated with temporary suspended matter for the LOIS coastal zone during surveys in winter'92 and autumn'93. This was attributed to preferential association of Cu_p with mineral ores rather than organic matter. Laslett (1995) similarly reported elevated Cu_p concentrations in SPM off the Tees and Tyne estuaries (approximately 100 $\mu\text{g g}^{-1}$ & 200 $\mu\text{g g}^{-1}$ respectively) which was attributed to general contamination from anthropogenic sources as well as the mineralization of the respective catchment areas.

3.2.3 Particulate cadmium

The concentrations of Cd_p (Figure 3.9) associated with SPM varied from the detection limit (0.01 $\mu\text{g g}^{-1}$, see Table 2.8) to 2.25 $\mu\text{g g}^{-1}$, the highest concentrations evident

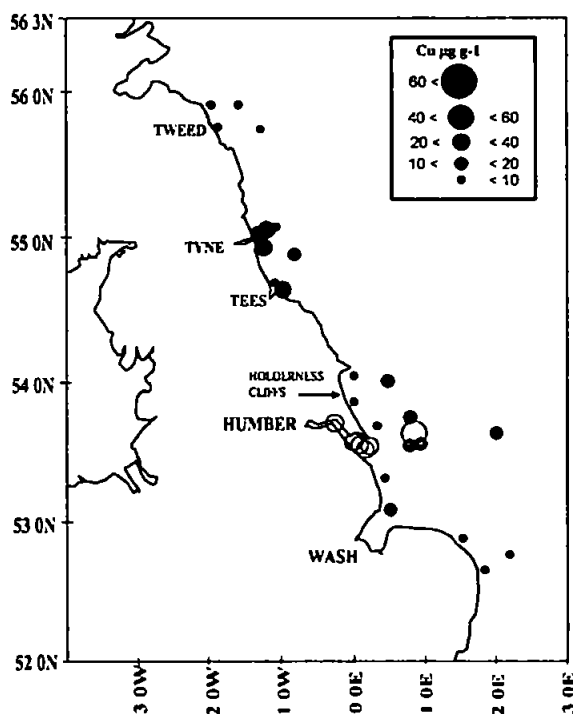


Figure 3.8 The distribution of Cu in the surface sediments of the LOIS coastal zone where (●) represents samples from winter'92 (CH99/92, refer to section 2.1.4, Table 2.3), (●) autumn'94 and (●) spring'95. Open circles are used to avoid obscuring smaller concentrations.

offshore in the northern part of the LOIS survey area during spring'95 and summer'95. Average Cd_p levels showed a strong seasonal trend in contrast to Fe_p and Mn_p , with concentrations increasing from winter'95 through spring'95 to summer'95 (0.28 , 0.45 & $0.53 \mu\text{g g}^{-1}$ respectively¹). This is consistent with the results from the English coastal zone reported by Tappin *et al.* (1995) and indicates the relative affinity of Cd for biogenous particles, relative to lithogenous material (Collier & Edmond, 1984; Noriki *et al.*, 1985; Valenta *et al.*, 1986; Golimowski *et al.*, 1990; Turner *et al.*, 1992a; Hall, 1993; James *et al.*, 1993; Laslett, 1995). The concentrations of Cd_p in the northern part of the coastal track were very low and often non detectable during autumn'94 and winter'95 compared to spring'95 and summer'95, coincident with low chlorophyll a concentrations. Indeed linear regression analysis of Cd_p vs. chlorophyll a concentrations yielded a significant positive relationship ($r=0.72$ for $n=40$, $P<0.05$) during spring'95.

¹ Refer to Tables 1.4 & 1.6 for a comparison with other concentrations quoted in the literature.

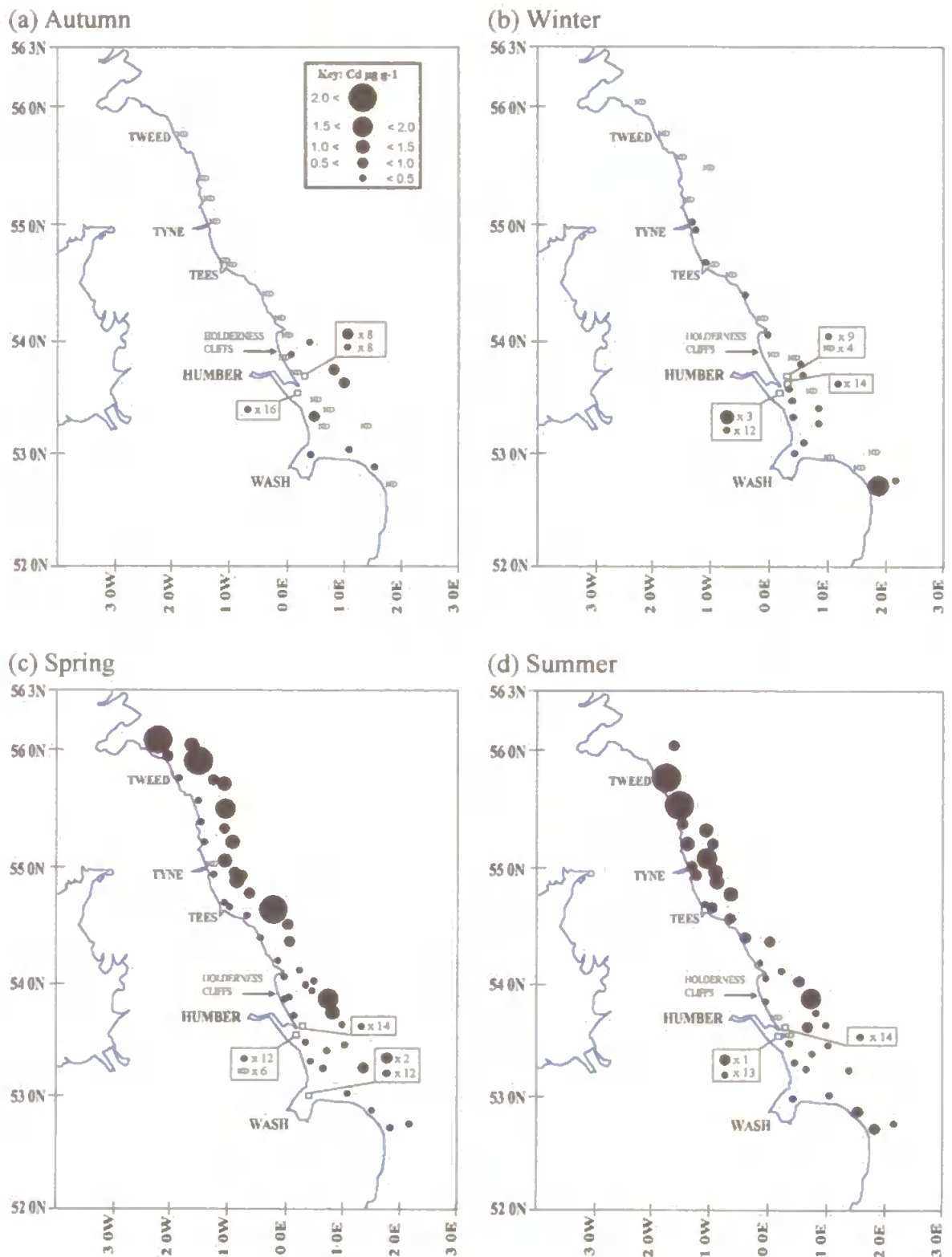


Figure 3.9 Distribution of Cd_p ($\mu g g^{-1}$) in the water column of the western North Sea coastal zone during (a) autumn '94, (b) winter '95, (c) spring '95 and (d) summer '95. The boxed concentration key in a) applies to all distributions. The boxed insets are from tidal cycles where samples were taken every hour i.e. ($\bullet \times 2$) means that during the tidal cycle 2 samples exhibited Cd_p concentrations greater than 1.0 but less than 1.5 $\mu g g^{-1}$.

However a significant correlation was not apparent during the summer period when the highest Cd_p concentrations ($>2.0 \mu\text{g g}^{-1}$) were detected adjacent to the Tweed Estuary. This may have been due to the preferential association of Cd with organic material and detritus, as the river Tweed contains high concentrations of humic substances in addition to sewage from the town of Berwick at the mouth of the estuary (Gardner & Ravenscroft, 1991a & b). The recent results of a study carried out in the Tweed Estuary by Martino (pers comm) have shown diminished concentrations of dissolved Ni during summer periods coincident with an increase in particulate Ni similarly suggesting strong biogenic particle-metal interactions.

The seasonal distributions of Cd_p did not show elevated concentrations in the mouth of the Humber Estuary for any survey period. The distributions of Cd in surface sediments (see Figure 3.10) of the LOIS coastal zone did show some elevated concentrations ($>2.0 \mu\text{g g}^{-1}$) south east of the Humber Estuary during autumn'94, which during periods of maximum bottom shear could provide a periodic source of Cd to the overlying waters. However a lack of supporting evidence e.g. chlorophyll a concentrations, POC etc. makes any rationalisation of elevated concentrations difficult. The surface sediment concentrations of Cd north of the Humber Estuary were otherwise below the limit of detection (see Table 2.8).

3.2.4 Particulate lead

The concentration of Pb_p in SPM varied by a factor of *c.*200 (range $1.5\text{-}340 \mu\text{g g}^{-1}$) over the period of the surveys³ (see Figure 3.11) in agreement with data from Tappin *et al.* (1995) for the southern North Sea during summer'88 to autumn'89. Nolting & Eisma (1988) similarly reported a range between $50\text{-}300 \mu\text{g g}^{-1}$ for the southern North Sea during winter'80. A seasonal trend was also evident. Average Pb_p concentrations for the LOIS coastal zone increased from autumn'94 to winter'95 and were greatest in spring'95 ($63, 85 \text{ \& } 97 \mu\text{g g}^{-1}$ respectively). During winter'95 Pb_p concentrations in the

³ Refer to Tables 1.4 & 1.6 for a comparison with other concentrations quoted in the literature.

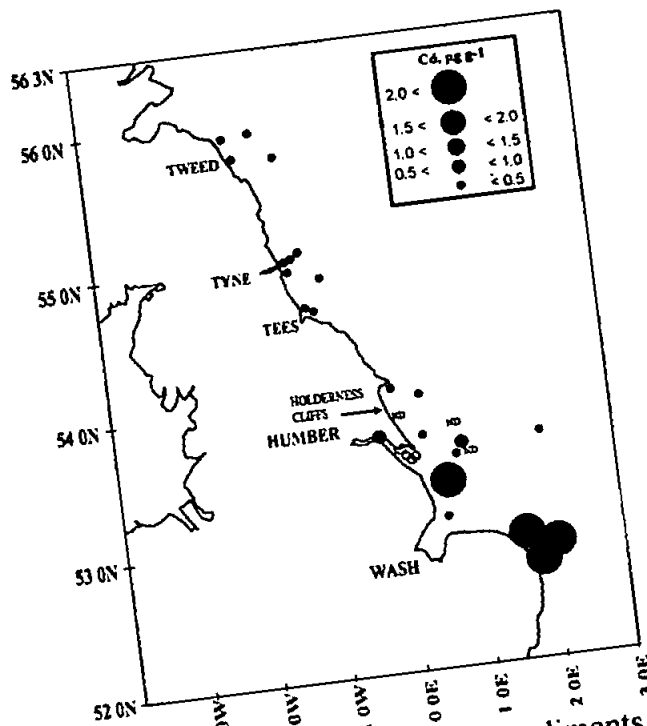


Figure 3.10 The distribution of Cd in the surface sediments of the LOIS coastal zone where (●) represents samples from winter'92 (CH99/92, refer to section 2.1.4, Table 2.3), (●) autumn'94 and (●) spring'95. Open circles are used to avoid obscuring smaller concentrations.

Humber coastal zone were reasonably uniform (between 50-100 $\mu\text{g g}^{-1}$) in distribution as were Fe_p , Mn_p , and Cu_p . Maximum Pb_p concentrations were noticeable adjacent to the Tyne Estuary during winter and spring (176 $\mu\text{g g}^{-1}$ & 202 $\mu\text{g g}^{-1}$ respectively) in agreement with results from Williams (1995) who attributed this to anthropogenic sources from the Pb refining industries in this region (e.g. Cooksons Industrial Materials Ltd, refer to Table 6.1). Indeed this is somewhat substantiated by the lower $^{206/207}\text{Pb}$ isotopic ratios found in sediments and SPM close to the Tyne Estuary indicative of anthropogenic contamination (refer to section 6.5.2).

Elevated Pb_p concentrations (<200 $\mu\text{g g}^{-1}$) were also shown at the mouth of the Humber Estuary during spring'95. The strong southerly winds (15-20 knots, see Figure 3.2e & f) dominate during this survey could have helped transport estuarine derived elevated Pb_p concentrations north, as seen off the Holderness coast *cf.* Fe_p & Mn_p distributions. Resuspension of Pb rich sediment (see Figure 3.12) could also have contributed to the elevated concentrations observed. During summer'95 Pb_p concentrations declined noticeably throughout the LOIS coastal zone to generally <50 $\mu\text{g g}^{-1}$. Although a plume

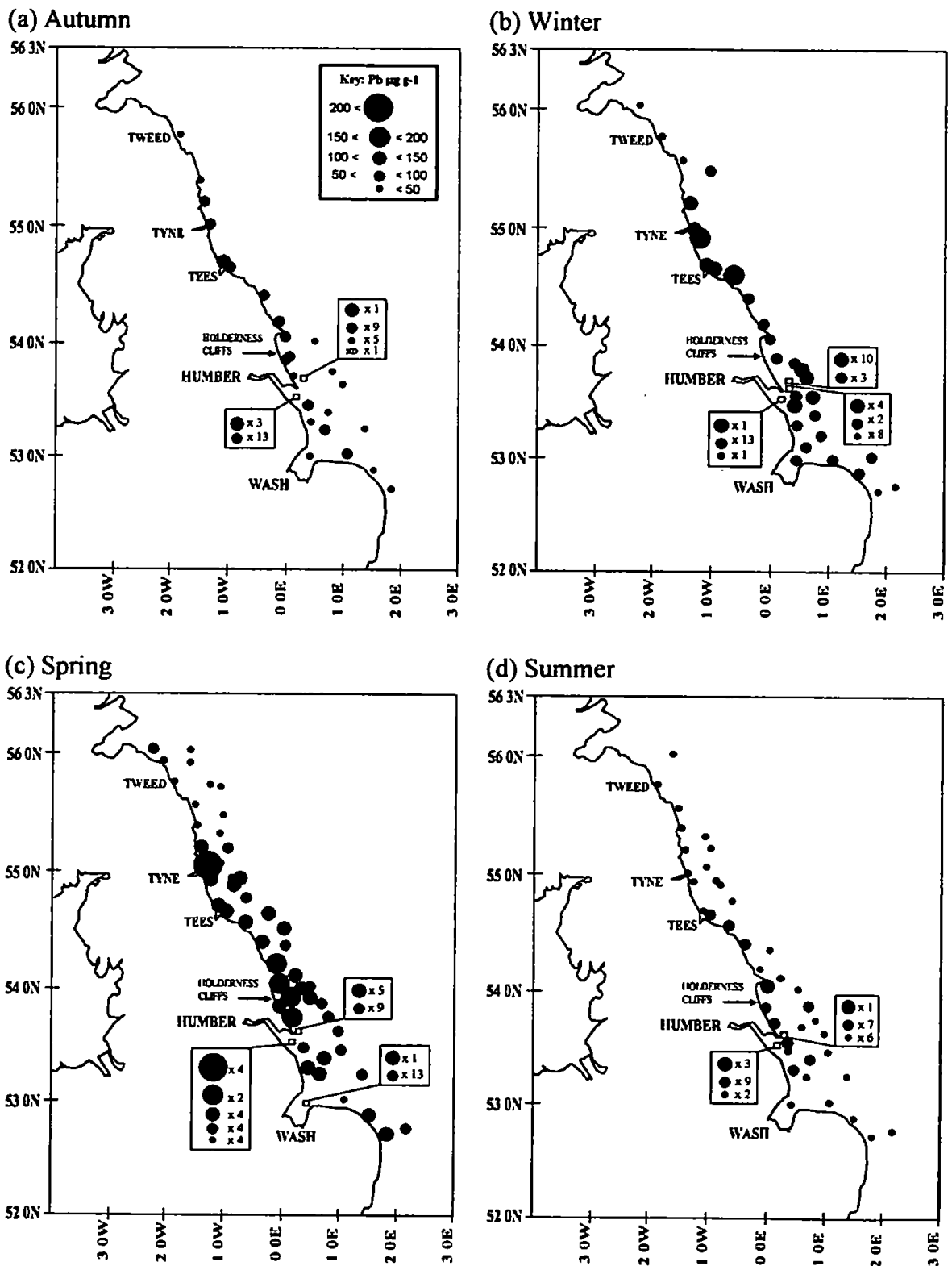


Figure 3.11 Distribution of Pb_p ($\mu g g^{-1}$) in the water column of the western North Sea coastal zone during (a) autumn'94, (b) winter'95, (c) spring'95 and (d) summer'95. The boxed concentration key in a) applies to all distributions. The boxed insets are from tidal cycles were samples were taken every hour i.e. (● x 2) means that during the tidal cycle 2 samples exhibited Pb_p concentrations greater than 100 but less than 150 $\mu g g^{-1}$.

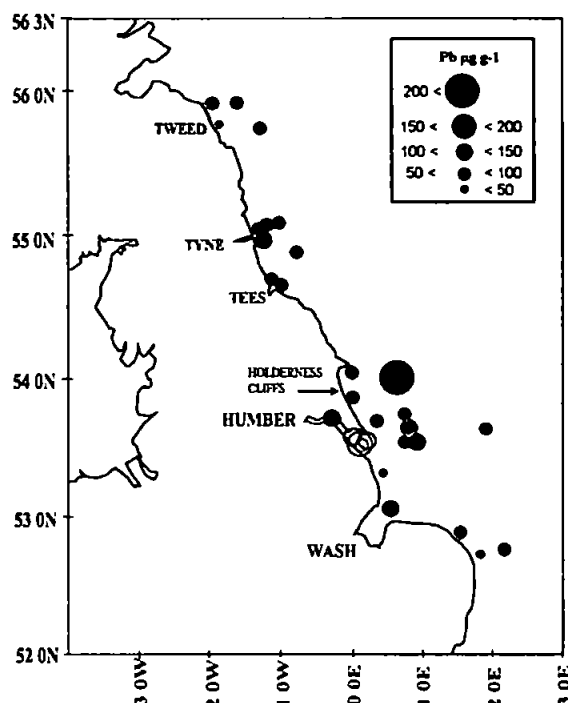


Figure 3.12 The distribution of Pb in the surface sediments of the LOIS coastal zone where (●) represents samples from winter'92 (CH99/92, refer to section 2.1.4, Table 2.3), (●) autumn'94 and (●) spring'95. Open circles are used to avoid obscuring smaller concentrations.

of slightly elevated Pb_p concentrations was still evident close to the mouth of the Humber Estuary cf. SPM, Fe_p & Mn_p . Concentrations of $Pb_p < 50 \mu g g^{-1}$ were persistent off the Tweed coastline throughout the survey period reflecting its sparsely populated catchment area with little industry (Laslett, 1995).

3.2.5 Summary

Highest concentrations of SPM and the particle reactive trace metals Fe, Pb and to some extent Mn (Tappin *et al.*, 1995) were found in the mouth of the Humber Estuary. The industrialised Tyne and Tees estuaries also showed elevated concentrations of Fe_p , Mn_p , Pb_p and Cu_p (Tees only during autumn'94). Measurements of particulate trace metal distributions offshore were restricted in extent during autumn and winter surveys due to adverse weather conditions, subsequently limiting interpretations away from estuarine sources. However spring and summer distributions in general revealed lower concentrations of SPM, Fe_p , Mn_p and Pb_p offshore, a pattern probably accentuated by

calmer prevailing weather conditions. The concentrations of Fe_p and Pb_p were particularly low ($<5 \text{ mg g}^{-1}$ and $<50 \text{ } \mu\text{g l}^{-1}$ respectively) during spring and summer at locations adjacent to the relatively pristine Tweed Estuary (Laslett, 1995).

During the winter almost uniform distributions of all SPM associated particulate metals studied, except Cd, were observed in the Humber coastal zone. This is consistent with a plume of anthropogenically enriched SPM emanating from the Humber Estuary and extending south east with the prevailing residual currents off the Norfolk coast (see Figure 3.2). The moderate (10-15 knots) north easterly winds during this survey (see Figure 3.3c & d) helped to confine the plume to inshore waters and reduce subsequent dilution with relatively uncontaminated marine particulate matter of the coastal North Sea (Turner *et al.*, 1991; Turner *et al.*, 1992b; Millward *et al.*, 1996). Elevated concentrations of SPM, Fe_p and Pb_p were also observed in the mouth of the Humber Estuary during the following spring. However the strong (15-20 knots) southerly winds present during this period could have aided in pushing contaminated estuarine SPM north, reflected in some elevated concentrations of Fe_p and Pb_p found adjacent to the Holderness cliffs. However SPM enriched in Mn was also found that cannot likewise be explained by an estuarine source. Significant ($P<0.05$) positive linear regressions of Mn_p vs. Fe_p (see Table 3.2) and Pb_p ($r=0.47, 0.62, 0.71$ & 0.45 for autumn, winter, spring and summer) suggest similar geochemical controls possibly indicating additional sources augmenting the estuarine signal i.e. resuspension of bed sediments, atmospheric deposition etc. Indeed the moderate (approximately 10 knots) easterly component of the wind (Figure 3.3e & f) originating from continental Europe has been previously reported to have elevated concentrations of trace metals relative to those from the west and north (Chester & Bradshaw, 1991; Rendell, 1992; Chester *et al.*, 1993).

During the summer survey average concentrations of SPM, Fe_p and Pb_p in the LOIS coastal zone reduced substantially (2.4 mg l^{-1} , 8.4 mg g^{-1} and $50 \text{ } \mu\text{g g}^{-1}$ respectively) relative to previous seasons and maximum concentrations for this period were confined to the mouth of the Humber Estuary coincident with a reduced river outflow of $70 \text{ m}^3 \text{ s}^{-1}$ (see Table 3.1) and light winds (5-10 knots) variable in direction. However this is in marked contrast to Cu_p whose incoherent distributions exaggerated in the Humber coastal zone showed elevated concentrations ($>60 \text{ } \mu\text{g g}^{-1}$) which are difficult to

rationalise due to lack of supporting data i.e. particulate organic carbon, dissolved organic carbon concentrations etc. Similar concentrations found adjacent to the estuary outputs are attributed to industrial inputs and the mineralogy of respective catchment areas. In contrast Cu_p concentrations around the Tweed Estuary were below the limit of detection (0.66-5.74 $\mu\text{g g}^{-1}$, refer to Table 2.8) reflecting its sparsely populated catchment area with little industry.

The distribution of Cd_p in SPM stands alone as indicated by the lack of any significant relationships with the other particulate trace metals studied. However a significant linear relationship during spring for the LOIS coastal zone between Cd_p and chlorophyll a concentrations together with past literature evidence, as cited in section 3.2.3, suggests a close geochemical coupling between Cd_p and biogenic/organic particulate matter.

3.3 The Humber Coastal Zone - Copper

3.3.1 Particulate Cu distributions

The Cu_p concentrations in the Humber coastal zone have been contoured and are shown in Figures 3.13 a-g representing distributions observed during winter'88, spring'90 and summer'90 NSP surveys (this data has previously been represented in Millward *et al.*, 1996) and autumn'94, winter'95, spring'95 and summer'95 LOIS surveys. During winter'88 a plume of particulate Cu ($>20 \mu\text{g g}^{-1}$) was evident from the mouth of the Humber Estuary extending to the north Norfolk coast. During spring'90 high concentrations of Cu_p were still observed in the Humber mouth but the plume became less well defined with Cu_p concentrations $<18 \mu\text{g g}^{-1}$ evident south east of the estuary mouth. Distributions during summer'90 revealed particularly high concentrations of Cu_p ($62 \mu\text{g g}^{-1}$) directly in the Humber mouth with a steep gradient of concentrations decreasing offshore. This data suggests that the Humber Estuary was a significant source of Cu_p to the nearshore coastal zone. Linear regressions analysis of Cu_p vs. salinity for the NSP surveys (see Table 3.3) showed a significant inverse ($P<0.05$) relationship for all surveys, likewise suggesting that the estuary is an important source of

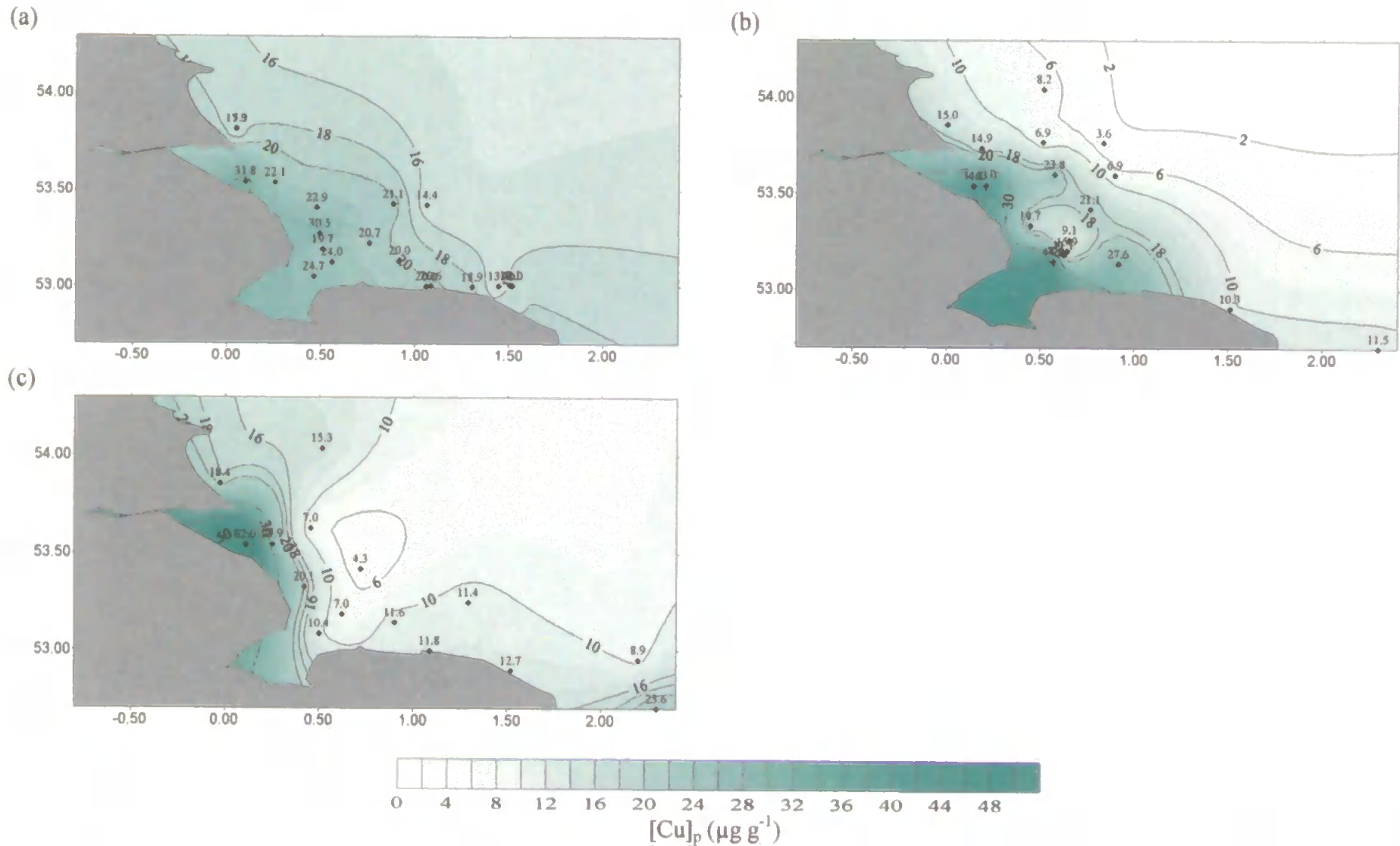


Figure 3.13 The contoured distributions of Cu_p in the Humber coastal zone during (a) winter '88, (b) spring '90 and (c) summer '90 NSP surveys. Data taken from the NERC North Sea project data set that is currently available on CD-ROM (Lowry *et al.*, 1992).

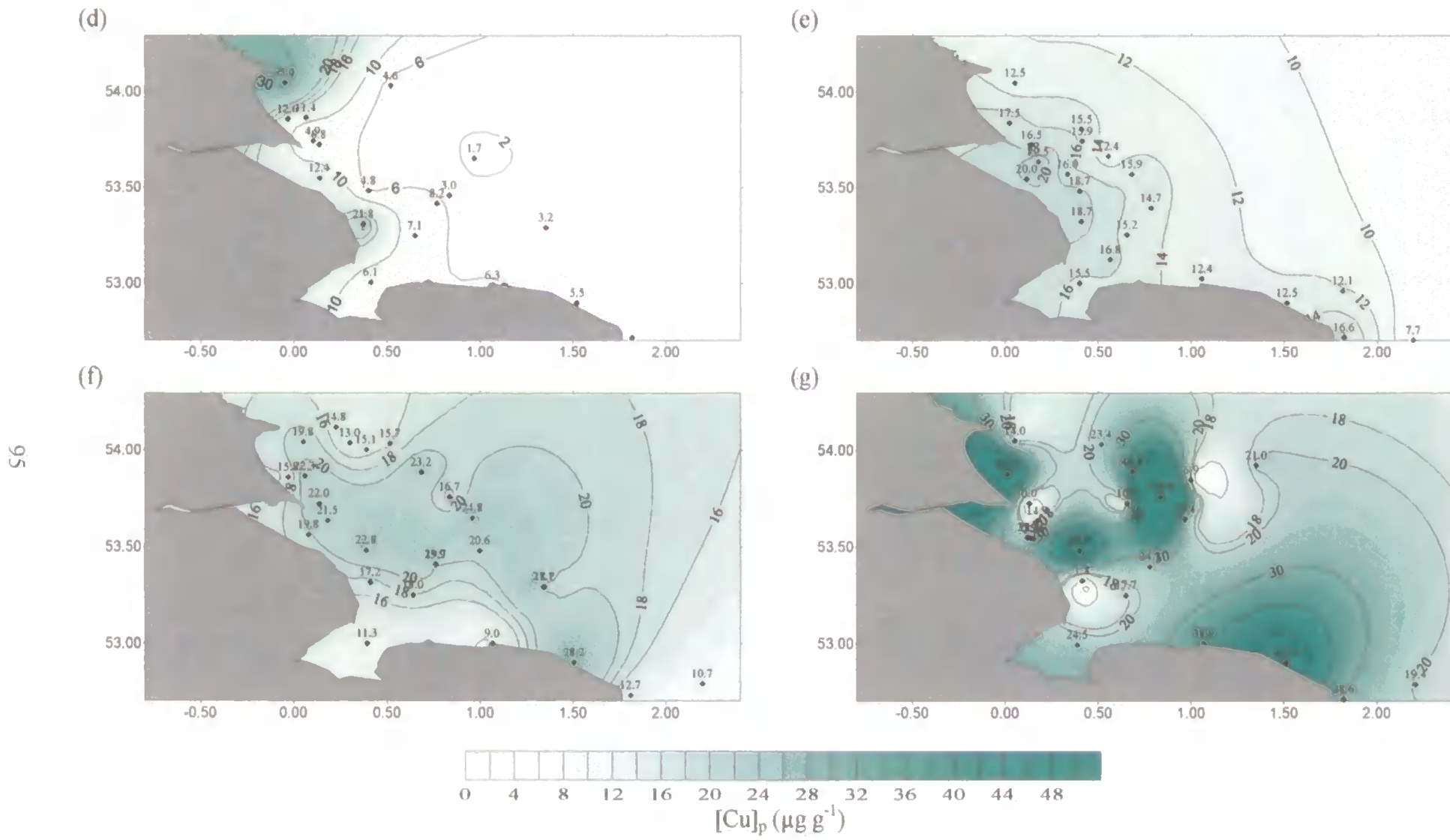


Figure 3.13 continued. The contoured distributions of Cu_p in the Humber coastal zone during (d) autumn'94, (e) winter'95, (f) spring'95 and (g) summer'95 present LOIS surveys.

Cu_p to the plume (Millward *et al.*, 1996). A significant ($P<0.05$) linear positive relationship was also shown for the NSP surveys between Cu_p and Fe_p indicating similar geochemical controls.

Table 3.3 Values of r for significant relationships between the concentration of Cu_p vs. salinity and the concentrations of SPM, Fe_p and Mn_p in the Humber coastal zone. Statistically significant ($P<0.05$) correlation's are indicated in bold type.

Cruise	n	Salinity	SPM	Fe _p	Mn _p
Winter'88 ^a	18	-0.77	0.68	0.87	0.37
Spring'90 ^a	19	-0.84	0.65	0.74	0.70
Summer'90 ^a	14	-0.54	0.16	0.56	0.24
Autumn'94	17	-0.29	0.40	0.09	0.34
Winter'95	20	-0.35	0.08	0.43	0.66
Spring'95	25	0.18	-0.16	0.29	0.35
Summer'95	21	0.21	-0.21	-0.29	-0.17

^aData taken from the NSP CD-ROM (Lowry *et al.*, 1992)

The winter'95 Cu_p distributions similarly showed an elevated plume emanating from the Humber Estuary. However comparison of the 18 µg g⁻¹ contour line to winter'88 distributions showed that it was limited to just offshore of the estuary mouth and did not extend to the Norfolk coastline. The moderate (10-15 knots) easterly component of the wind (see Figure 3.3c & d) could have assisted in keeping the elevated Cu_p plume closer inshore. The following spring and summer'95 surveys, contrary to all former data, did not reveal an elevated Cu_p plume coming from the Humber Estuary but rather showed concentrations often >20 µg g⁻¹ incoherently distributed in the Humber coastal zone, as previously commented in section 3.2.2 (Millward *et al.*, 1996). This was subsequently reflected by the lack of any statistical relationships for the spring and summer surveys between Cu_p and salinity, concentration of SPM, Fe_p and Mn_p (see Table 3.3).

The average concentrations of Cu_p in the Humber coastal zone for all the survey periods are shown in Table 3.4. For the NSP data a clear seasonal trend was evident where maximum concentrations were displayed in winter'88 (20 µg g⁻¹) with minimum variance and decreased through spring (17 µg g⁻¹) to summer (14 µg g⁻¹). This trend is consistent with the work of Tappin *et al.* (1995) for the English coastal zone who reported maximum Cu_p concentrations of 30 µg g⁻¹ in autumn and winter decreasing to 20 µg g⁻¹ and 10 µg g⁻¹ in spring and summer respectively. However data from the Humber

coastal zone incorporated within the English coastal zone presented by Tappin *et al.* (1995) is scarce and even absent from autumn surveys.

Table 3.4 Mean and standard deviation (SD) of the concentration of Cu_p in the Humber coastal zone, Holderness Cliff material and in Humber Estuary sediments.

Cruise	N ^e samples	[Cu] _p ± SD ($\mu\text{g g}^{-1}$) ^f	Coefficient of Variation (%)
SPM			
Winter'88 ^c	18	20 ± 4.0	20
Spring'90 ^c	19	17 ± 12	71
Summer'90 ^e	14	14 ± 6.4	46
Autumn'94	17	8.4 ± 8.1	96
Winter'95	20	15 ± 3.1	21
Spring'95	25	19 ± 5.1	27
Summer'95	21	36 ± 39	108
Holderness Cliff material ^b	10	7.0 ± 1.3	19
Humber sediments			
Humber mouth ^d	4	31 ± 4.5	15
Humber Estuary ^a	1	34	
Pre-industrial ^c	1	17	

^aSample number 6 taken from up the Humber Estuary, refer to Figure 2.5; ^b10 samples of Holderness Cliff clay material, <63 μm particle size fraction; ^cMiddleton & Grant (1990); ^dAverage of all surface sediments collected from the mouth of the Humber Estuary (refer to Figure 3.8); ^eData taken from the NSP CD-ROM (Lowry *et al.*, 1992); ^fCompare with literature in Tables 1.4 & 1.6.

In contrast to the above, the intensive observations made in the Humber coastal zone during the LOIS surveys showed that concentrations were lowest in autumn'94 ($8.4 \pm 8.1 \mu\text{g g}^{-1}$) and increased throughout the year to summer'95 ($36 \pm 39 \mu\text{g g}^{-1}$). The variability in Cu_p concentrations was highest in autumn'94 and summer'95 whilst winter'88, winter'95 and spring'95 distributions were more uniform possibly a consequence of large Humber Estuary outflows ($350, 425$ & $345 \text{ m}^3 \text{ s}^{-1}$ respectively) dominating the Cu_p source to the coastal zone during these times. Despite differing seasonal trends in Cu_p distributions between the NSP and LOIS databases, the average concentration during spring'90 and spring'95 were of similar magnitude (17 & $19 \mu\text{g g}^{-1}$ respectively). The large difference between Cu_p concentrations in summer'90 and

summer'95 surveys may have arisen owing to the collection of a smaller number of samples, mostly taken adjacent to the coast during the 1990 survey.

The results indicate that for winter'88, spring'90 and summer'90 the Humber Estuary was acting as a significant source of Cu_p to the coastal zone that is reflected in the observed distributions i.e. persistently high concentrations ($>30 \mu\text{g g}^{-1}$) at the mouth of the Humber Estuary. The seasonal extent of the plume was subsequently related to the residual Cu_p flux from the estuary. Table 3.6 lists output fluxes⁴ from the Humber Estuary to the North Sea for the NSP and LOIS surveys and indicates a decrease in Cu_p flux from 52-85 kg day^{-1} during winter'88 to 12 kg day^{-1} and 1.2 kg day^{-1} in spring'90 and summer'90 respectively, consistent with the apparent 'retreat' of the elevated Cu_p plume emanating from the estuary mouth i.e. compare the position of the $18 \mu\text{g g}^{-1}$ contour line in Figure 3.13 a, b and c.

In contrast to the above findings, the LOIS surveys did not indicate that the Humber Estuary was the predominant Cu_p source influencing the observed distributions in the coastal zone, except perhaps during winter'95 when, despite the lack of a significant ($P < 0.05$) relationship with salinity, the Cu_p contours (see Figure 3.13e) do seemingly suggest otherwise. However, the deviation from conservative behaviour apparent for the LOIS surveys does not mitigate the estuary as a Cu_p source, as evident by the flux data (Table 3.6), but suggests the significance of other sources and geochemical processes in the Humber coastal zone. Indeed the dominant local source of material is from erosion of the Holderness Cliffs, estimated to be $140 \times 10^4 \text{ t a}^{-1}$ (McCave, 1987) *cf.* the fluvial supply from the rivers of the Wash and Humber of $20 \times 10^4 \text{ t a}^{-1}$ (Wilmot & Collins, 1981). The mean Cu_p concentration of Holderness material collected in February'95 (see section 2.1.7) was $7.0 \pm 1.3 \mu\text{g g}^{-1}$ which amounts to a flux of 27 kg day^{-1} (see Table 3.6). The residual circulation transports Holderness material southwards, where it is mixed with anthropogenically modified SPM from the Humber Estuary (Grant & Middleton, 1990; Turner *et al.*, 1991) highlighting the potential for dilution of the estuarine signal and hence deviation from conservative behaviour. Indeed examination of the Cu_p distributions in the Humber coastal zone during autumn'94 (see Figures 3.7a &

⁴ For flux calculations refer to section 3.3.2

3.13d) revealed the dominance of low concentrations ($8.4 \pm 8.1 \mu\text{g g}^{-1}$, Table 3.4) in the region perhaps indicating the relative importance of eroded Holderness material to the coastal zone at this time. The subsequent southwards transport being aided by the prevailing moderate (10-15 knots) north westerly winds (refer to Figure 3.3a & b).

Resuspension of coastal sediments (refer to Figure 3.8) during periods of increased bed stress i.e. increasing current speed during a spring tide (Jago *et al.*, 1993) could also provide a transient Cu_p source to the region. The Cu_p contours shown for spring'95 (Figure 3.13f) show a central core of Cu_p concentrations $>20 \mu\text{g g}^{-1}$. Closer examination of the temporal Cu_p concentrations (see Figure 3.14d) in the mouth of the Humber Estuary (despite an overall average of $20 \mu\text{g g}^{-1}$ as shown in Figure 3.13f) shows concentrations between $20\text{-}40 \mu\text{g g}^{-1}$ during the ebb tide. This coupled with possible resuspension of contaminated bed sediments in the region ($10\text{-}56 \mu\text{g g}^{-1}$, refer to Figure 3.8) could have helped sustain the observed distributions, the predominate strong (15-20 knots) southerly winds possibly helping to spread the plume north. It is also interesting to note Cu_p concentrations $>20 \mu\text{g g}^{-1}$ at sampling stations just north of the Norfolk Coast during spring and summer'95. The Norfolk Cliffs are, similarly to the Holderness Cliffs, unconsolidated quaternary sediments that have been estimated to be eroding at $66.5 \times 10^4 \text{ t a}^{-1}$ (Cambers, 1975). Assuming a Cu_p concentration, equivalent to Holderness material of $7.0 \mu\text{g g}^{-1}$ yields a flux of approximately 13 kg day^{-1} which, although unlikely to influence the most part of the Humber coastal zone due to the southerly coastal circulation, will nevertheless provide another source of Cu_p to the immediate vicinity. The atmosphere is also a potential, although diffuse, Cu source (dissolved and particulate) and results reported in Chester *et al.* (1993) suggest that wet and dry atmospheric deposition fluxes to the North Sea amount to between 16-27% of the total flux (including fluvial discharges and direct dumping/discharges). In summary it is therefore likely that the deviation from conservative behaviour observed for Cu_p in SPM of the Humber coastal zone is due to the complex mixing of different particle sources or 'end members' characterised by different Cu_p concentrations e.g. fluvial SPM, eroded Cliff material and resuspended sediments.

3.3.2 Dissolved and particulate Cu at anchor stations

Typical particulate and dissolved Cu concentrations determined at the anchor stations in the Humber coastal zone for the LOIS surveys are shown in Figures 3.14a-f. Figures 3.14b & f show Cu_p distributions only. A summary of the master variables for each anchor station survey including those from the NSP are given in Table 3.5. The tidally-averaged salinity at the mouth of the Humber Estuary varied with seasonal changes in the input of freshwater (Millward *et al.*, 1996) as evident by a significant ($P < 0.05$) linear regression of the mean salinity obtained at the anchor station vs. residual water outflow ($r = -0.83$); whereas the variance in salinity was related to tidal range ($r = 0.85$, $P < 0.05$). For example maximum residual flows of 350, 425 and 345 m^3s^{-1} recorded during winter'88, winter'95 and spring'95 respectively, account for lower mean salinities of 30.89, 28.53 and 30.79. Similarly minimum Humber Estuary outflows of 90 and 70 m^3s^{-1} recorded during summer'90 and summer'95 correspond to higher mean salinities of 32.21 and 32.59 respectively. The maximum variations in salinity (as indicated by ± 1 SD in Table 3.5) were found during autumn'94, winter'95 and spring'95 when large tidal ranges (6.6, 5.0 & 6.6 m respectively) accounted for deviations of 2.09, 2.07 and 2.71 *cf.* spring'90 and summer'90 when tides approaching neaps (tidal range of 4.7 & 2.9 m) accounted for small variations in salinity of 0.88 and 0.49 respectively.

For the anchor stations located at Spurn Head (HW3a, see Figure 2.3) and further north off the Holderness coast (S2, see Figure 2.3) mean salinities increased with distance away from the Humber mouth or freshwater source. This is illustrated during the winter'95 surveys (Figures 3.14a, b & c) when the reduction in the propagation of the freshwater signal is clearly evident moving northwards up the coast as mean salinities increase from 28.53 at the Humber mouth, to 33.32 at Spurn Head and 34.23 off the Holderness coast, concurrent with decreasing variance in salinity. The mean concentration of SPM obtained in the Humber mouth varied with residual water flow and tidal regime. Regression of SPM concentration vs. tidal range produced a significant positive correlation of $r = 0.83$ ($P < 0.05$) and can help to explain the differences in mean SPM concentrations recorded between the NSP and LOIS surveys.

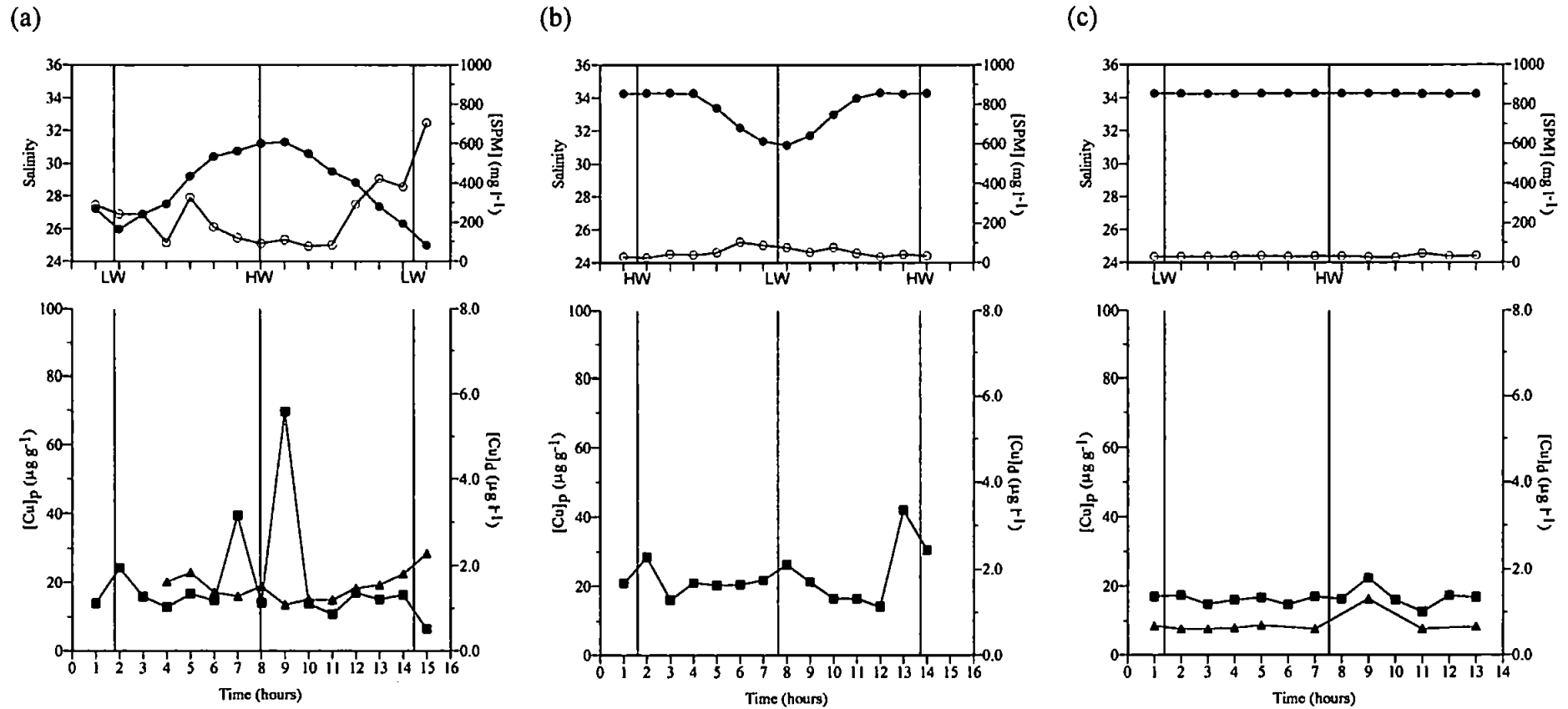


Figure 3.14 Salinity (●), concentration of SPM (○), Cu_p (■) and Cu_d (▲) as a function of time obtained during an anchor station (a) in the mouth of the Humber Estuary (HW5 - see Figure 2.3), (b) north of Spurn Head (HW3a - see Figure 2.3) and (c) adjacent to the Holderness Cliffs (S2 - see Figure 2.3) during winter'95.

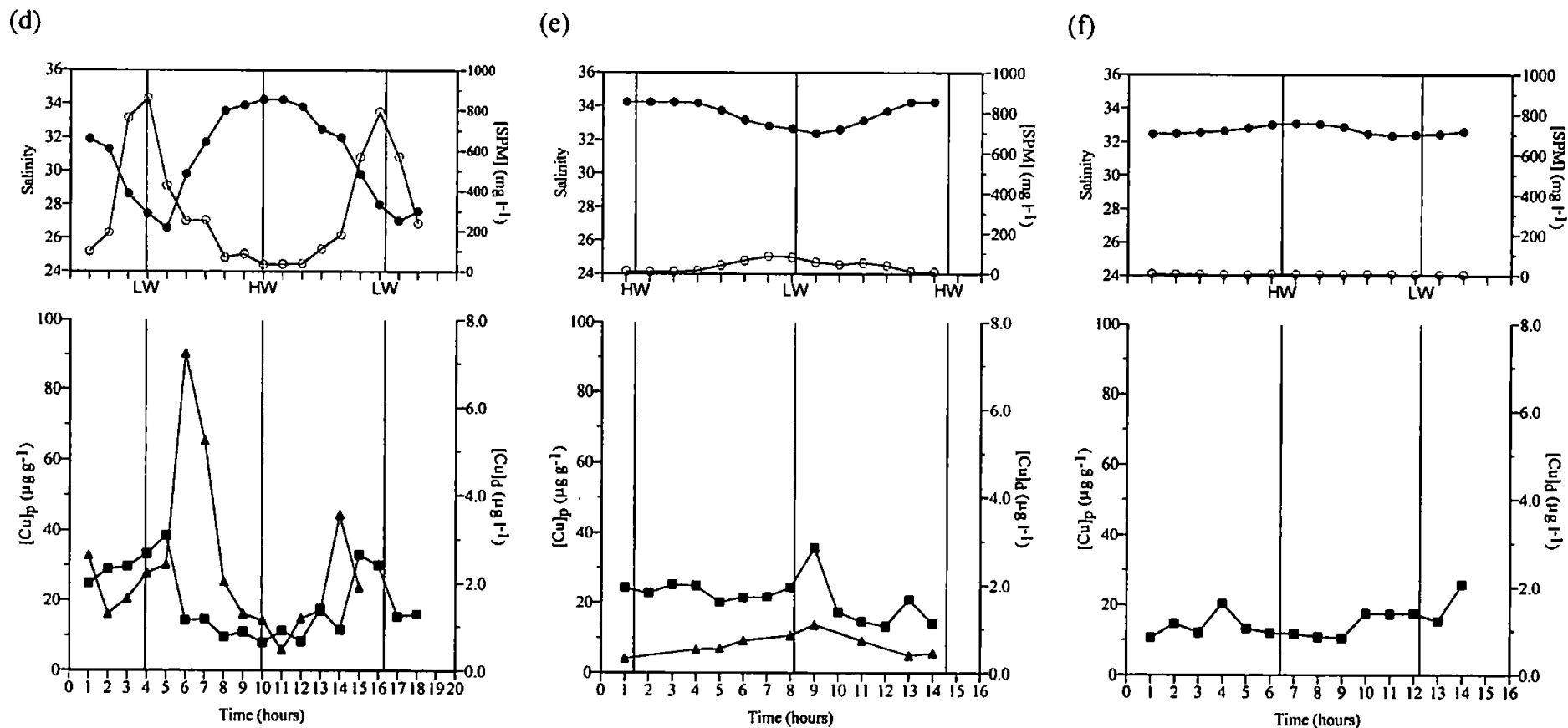


Figure 3.14 continued. Salinity (●), concentration of SPM (○), Cu_p (■) and Cu_d (▲) as a function of time obtained during an anchor station (d) in the mouth of the Humber Estuary (HW5 - see Figure 2.3), (e) north of Spurn Head (HW3a - see Figure 2.3) and (f) in the Wash embayment (HW13 - see Figure 2.3) during spring '95.

Table 3.5 Master variables at the anchor stations during the NSP and LOIS surveys (where applicable ± 1 SD).

Survey	Date	N ^a samples	Location [*]	Tidal range [†] (m)	Salinity	Temperature (°C)	[SPM] (mg l ⁻¹)	POC [Ⓞ] (%)	Chlorophyll a [‡] (µg l ⁻¹)	Humber Estuary outflow [‡] (m ³ s ⁻¹)
Winter'88(1) ^a	21-22 Dec'88	11	HW5	4.9	30.89 ± 1.78	6.82 ± 0.24	55 ± 29	n/a	<0.1	350
Winter'88(2) ^a	27-28 Dec'88	13	HW5	4.9	31.19 ± 1.06	7.20 ± 0.08	81 ± 41	n/a	<0.1	350
Spring'90 ^a	6-7 May'90	13	HW5	4.7	32.46 ± 0.88	11.68 ± 0.58	21 ± 11	n/a	3.5 ± 1.3	175
Summer'90 ^a	2 Aug'90	15	HW5	2.9	32.21 ± 0.49	17.99 ± 0.33	2.4 ± 1.3	n/a	2.4 ± 0.6	90
Autumn'94	4 Nov'94	15	HW5	6.6	31.10 ± 2.09	10.17 ± 0.27	292 ± 304	n/a	0.2	165
	6 Nov'94	15	S2	6.2	34.30 ± 0.00	11.05 ± 0.03	5.9 ± 1.5	n/a	n/a	
Winter'95	22-23 Jan'95	15	HW5	5.0	28.53 ± 2.07	4.77 ± 0.19	243 ± 171	n/a	n/a	425
	29 Jan'95	14	HW3a	4.6	33.32 ± 1.22	5.20 ± 0.29	53 ± 24	n/a	0.3 ± 0.1	
	28 Jan'95	13	S2	4.2	34.23 ± 0.00	5.71 ± 0.13	33 ± 5.0	21 ± 5.0	0.4 ± 0.2	
Spring'95	17-18 Apr'95	18	HW5	6.6	30.79 ± 2.71	8.56 ± 0.38	310 ± 282	15 ± 3.0	1.4 ± 0.8	345
	23-24 Apr'95	14	HW3a	3.8	33.54 ± 0.72	7.91 ± 0.45	39 ± 28	20 ± 2.0	0.9 ± 0.2	
	24-25 Apr'95	14	HW13	3.4	32.67 ± 0.26	8.66 ± 0.14	5.9 ± 1.6	n/a	3.0 ± 0.5	
Summer'95	1 July'95	14	HW5	4.9	32.59 ± 1.16	14.66 ± 0.55	60 ± 47	14 ± 2.0	1.1 ± 0.5	70
	8-9 July'95	14	HW3a	3.9	33.85 ± 0.29	14.93 ± 0.58	9.3 ± 3.7	n/a	0.7 ± 0.1	

^aData taken from NERC North Sea Project CD-ROM Lowry *et al.* (1992); ^{*}For sample locations refer to Figure 2.3; [†]Tidal range at Spurn Head, spring range 5.7 m & neap range 2.8 m; ^{*}Wood (1993); n/a denotes data not available; [Ⓞ]Particulate organic carbon analysed by Loss On Ignition, refer to section 2.2.5 (Mook & Hoskin, 1982); [‡]LOIS RACS core data courtesy of BODC.

For example during spring'90 a relatively low residual flow of $175 \text{ m}^3 \text{ s}^{-1}$ combined with a tidal range of 4.7 m resulted in a mean SPM concentration of 21 mg l^{-1} in contrast to spring'95, when a much larger residual flow of $345 \text{ m}^3 \text{ s}^{-1}$ and a large spring tidal range of 6.6 m produced more than a 10 fold increase in SPM concentration to 310 mg l^{-1} . The large influence that tidal range alone has on SPM concentrations in the mouth of the Humber Estuary is exemplified when comparing summer concentrations of SPM. During both years similar low residual outflows of 90 and $70 \text{ m}^3 \text{ s}^{-1}$ were obtained but the neap tide (2.9 m range) during summer'90 resulted in an exceptionally low mean concentration of 2.4 mg l^{-1} compared to 60 mg l^{-1} during summer'95 when the tidal range was nearer to springs (5.0 m range). Lindsay *et al.* (1996) similarly reported that spring/neap tidal cycles were the dominant influence in controlling the concentration of SPM and hence transport within the Forth Estuary.

The mean particulate and dissolved Cu concentrations determined at the anchor stations in the Humber coastal zone are shown in Table 3.6. The mean concentration of Cu_p ranged between $12\text{-}62 \text{ } \mu\text{g g}^{-1}$ for the Humber anchor station. Maximum concentrations were obtained during the summer anchor stations when compared to their respective winter surveys e.g. $62 \text{ } \mu\text{g g}^{-1}$ during summer'90 compared to $29\text{-}34 \text{ } \mu\text{g g}^{-1}$ for winter'88. The mean Cu_p concentrations obtained in the mouth of the Humber Estuary were between 30-60% lower during the LOIS surveys compared to the NSP surveys. The Cu_p concentrations obtained at the anchor station located furthest north adjacent to the Holderness Cliffs (S2) exhibited concentrations 15-27% lower than those at the mouth of the estuary which is attributed to the mixing of estuarine SPM with eroded Holderness material characterised by substantially lower concentrations of Cu_p ($7.0 \text{ } \mu\text{g g}^{-1}$, see Table 3.4) i.e. dilution of contaminated, or otherwise enriched estuarine particles with trace metal deficient particles (Turner *et al.*, 1992b). During winter'95 and spring'95 the mean Cu_p concentrations at the anchor station located near Spurn Head (HW3a) showed slightly elevated concentrations compared to those at the mouth of the Humber Estuary but were, nevertheless, still well within the range of concentrations observed. Consideration of the Cu_p anchor station profiles during spring'95 (Figure 3.14d & e) showed generally higher concentrations at Spurn Head compared to the Humber Estuary with a peak around low water. It is hypothesised that the neap tide (3.8 m) occurring during the Spurn Head anchor station led to an increase in the relative proportion of

Table 3.6 Mean Cu_p and Cu_d concentrations over the anchor stations including input and output fluxes of Cu to and from the Humber Estuary.

Survey	Location*	Mean Cu concentrations		Cu Flux (kg day ⁻¹)		Humber estuary			
		Particulate (µg g ⁻¹)	Dissolved (µg l ⁻¹)	Particulate	Dissolved	Output IAA [†] (kg day ⁻¹)	Input [‡] (kg day ⁻¹)	Output IAA [†] (kg day ⁻¹)	Input [‡] (kg day ⁻¹)
Winter'88(1) [Ⓐ]	HW5	29 ± 5.5	1.17 ± 0.49	52	35 (40)				
Winter'88(2) [Ⓐ]	HW5	34 ± 2.5	1.11 ± 0.18	85	33 (28)	49	269-281	153	205
Spring'90 [Ⓐ]	HW5	34 ± 7.2	1.23 ± 0.27	12	19 (61)				
Summer'90 [Ⓐ]	HW5	62 ± 50	1.42 ± 0.25	1.2	11 (90)				
Autumn'94	HW5	12 ± 2.1	0.96 ± 0.46	57	14 (20)				
	S2	8.8 ± 5.7	0.38 ± 0.16						
Winter'95	HW5	20 ± 16	1.51 ± 0.34	148	55 (27)				
	HW3a	23 ± 7.4	n/a						
	S2	17 ± 2.2	0.72 ± 0.22						
Spring'95	HW5	20 ± 10	2.37 ± 1.7	240	71 (23)				
	HW3a	22 ± 5.8	0.63 ± 0.25						
	HW13	15 ± 4.4	n/a						
Summer'95	HW5	21 ± 6.7	2.73 ± 1.84	8.7	17 (66)				
	HW3a	15 ± 4.2	0.54 ± 0.28						
	Holderness Cliffs	7.0 ± 1.3 [Ⓛ]		27 [Ⓜ]					

[Ⓐ]Data previously shown in Millward & Glegg (1997) but fluxes have been recalculated due to revised residual outflows from the Humber Estuary, Wood, pers com; *For sample locations refer to Figure 2.3; [Ⓛ]Average of 10 sample taken from the Holderness Cliffs during February'95 (see section 2.1.7); [Ⓜ] Assuming a constant erosion rate of 140 x 10⁴ t a⁻¹ (McCave, 1987); [†]Integrated annual average (IAA) of total Cu fluxes from the Humber Estuary to the North Sea. Calculated by assuming that for 1988-90 NSP data that each survey represented typical fluxes for a 4 month duration (an average was used for winter'88) and for the 1994-95 LOIS data that each survey represented typical rates for a 3 month duration; [‡]Total inputs into the Humber Estuary from rivers, industry and sewage sources - 1990 data (PARCOM, 1991) low and high loads respectively; [‡] Total inputs into the Humber Estuary from rivers, industry and sewage sources - 1992 data (NRA, 1993a & b). This was the most recent input flux data currently available for comparison with 1994-95 output flux data from the present LOIS study; n/a denotes data not available. Values in brackets indicate the % dissolved metal flux.

estuarine SPM in the water column. Conversely the strong spring tide (6.6 m) during the Humber mouth anchor station diluted the estuarine signal with Holderness and background marine particles relatively deficient in Cu_p as suggested by the lower Cu_p concentrations around high water (see Figure 3.14d). The following summer surveys showed a decrease in the mean Cu_p concentrations observed near to Spurn Head (site HW3a, Table 3.6) compared to the Humber Estuary⁵. This is attributed to the permanently suspended estuarine SPM either (a) mixing with relatively uncontaminated Holderness material or (b) desorption of Cu from estuarine particles due to an increase in salinity (Windom *et al.*, 1983; Turner *et al.*, 1992a) i.e. 33.85 at Spurn Head compared to 32.59 in the mouth of the Humber Estuary, although this is not a large difference and is thus unlikely to show any effects. The depressed residual outflow from the Humber Estuary ($70 \text{ m}^3 \text{ s}^{-1}$) would have also reduced the relative proportion of estuarine derived SPM reaching Spurn Head i.e. reduction in the propagation of the estuarine signal.

The concentration of Cu_d ranged between $0.96\text{-}2.73 \mu\text{g l}^{-1}$ *cf.* literature values quoted in Table 1.6 for the Humber anchor stations (refer to Table 3.6) and consistently showed a seasonal trend of increasing concentrations from winter through spring to summer. Anchor stations away from the Humber mouth displayed much lower concentrations ranging between $0.54\text{-}0.63 \mu\text{g l}^{-1}$ for Spurn Head and $0.38\text{-}0.72 \mu\text{g l}^{-1}$ for the Holderness site possibly reflecting dilution of estuarine waters with seawater. This also infers that desorption of Cu from estuarine SPM as a consequence of increasing salinity is not a major process or it may not be a significant enough process to influence the Cu_d concentrations.

The inverse relationships between Cu_p and Cu_d against salinity (Table 3.7) for the Humber anchor station data indicate that the temporal particulate and dissolved Cu distributions can largely be explained on the basis of the freshwater input into the Humber Estuary. Gardiner (1982), Jones & Jefferies (1983) and Balls (1985), also reported conservative mixing for Cu samples taken in the mouth of the Humber Estuary.

⁵ Offshore in the Humber coastal zone the average concentration of Cu_p increased during the summer as stated and shown in section 3.3.1 & Figure 3.13g respectively. This was attributed to enhanced biogenic- Cu_p interactions that would presumably be swamped close to Spurn Head by lithogenic particles from the Humber Estuary and Holderness Cliffs.

Although it must be remembered that such conservative behaviour does not always persist throughout the plume and coastal zone (refer to Table 3.3) often due to additional inputs e.g. resuspension of bed sediments, atmospheric deposition and coastal erosion, as previously demonstrated for the recent LOIS surveys. The concentration of Cu_p does not however show conservative behaviour in the Humber estuary during summer'90 and winter'95 surveys for reasons that cannot be fully explained. Examination of the temporal series in winter'95 (see Figure 3.14a) revealed a twin peak either side of high water. The so called 'twin peaks' signature is often associated with the concentration of SPM and has previously been attributed to the combination of an advective and resuspended signal (Jago *et al.*, 1993). It is possible then that the twin peaks observed in Cu_p could be explained by an advective riverine source combined with local bed resuspension. The latter process a distinct possibility due to an enhanced river outflow ($425 \text{ m}^3 \text{ s}^{-1}$) likely to increase the bed shear stress. However, the lack of 'real time' tidal displacement and current speed data renders such explanations purely speculative in nature.

Table 3.7 Values of r for linear relationships between the concentration of Cu_p and Cu_d vs. salinity and the concentrations of SPM, Fe_p and Mn_p in the mouth of the Humber Estuary. Statistically significant ($P < 0.05$) correlations are indicated in bold type.

Cruise		n	Salinity	SPM	Fe_p	Mn_p
Winter'88(1) ^a	Cu_p	9	-0.93	0.75	-0.16	-0.83
	Cu_d	11	-0.95	0.77	-0.39	-0.72
Winter'88(2) ^a	Cu_p	13	-0.61	0.60	-0.38	-0.20
	Cu_d	13	-0.85	0.41	-0.32	-0.31
Spring'90 ^a	Cu_p	10	-0.74	0.92	-0.85	-0.63
	Cu_d	13	-0.97	0.78	-0.84	-0.25
Summer'90 ^a	Cu_p	9	0.22	0.60	-0.16	-0.41
	Cu_d	15	-0.90	0.41	0.68	0.77
Autumn'94	Cu_p	16	-0.81	0.68	0.27	0.05
	Cu_d	14	-0.57	0.56	0.45	0.13
Winter'95	Cu_p	15	0.45	-0.34	0.17	0.16
	Cu_d	12	-0.82	0.85	-0.69	-0.42
Spring'95	Cu_p	18	-0.70	0.72	0.63	0.95
	Cu_d	15	-0.52	0.10	0.59	-0.21
Summer'95	Cu_p	14	-0.71	0.54	0.78	0.80
	Cu_d	12	-0.79	0.58	0.80	0.78

^aData taken from the NERC NSP CD-ROM (Lowry *et al.*, 1992; Millward *et al.*, 1996)

The subsequent fluxes of Cu_p and Cu_d from the Humber Estuary to the coastal zone have been calculated using a mathematical approach based on work originally carried out by Prandle (1984) and modified by Wood (1993), who additionally incorporated concepts developed by Jouanneau & Latouche (1982). This approach used a two-dimensional depth averaged hydrodynamic model of the Humber Estuary (4.5 km grid) to estimate residual velocity across the boundary of the estuary mouth to the North Sea (location defined by the HW5 anchor station, see Figure 2.3). This was then combined with the cross sectional area of the Humber at this point to yield a volume outflow of water, V ($m^3 s^{-1}$). The trace metal flux was then computed by combining the volume outflow (V) with mean concentration of metal $[M]$ ($\mu g m^{-3}$) to calculate the flux of metal (dissolved or particulate) in $kg day^{-1}$ (see Equation 3.1) across the estuarine boundary.

$$\text{Flux} = 8.64 \times 10^{-5} \times [M] \times V \quad 3.1$$

Assumptions within this equation are that there are negligible lateral variations in residual velocity⁶ and that the average concentration of trace metal obtained at the anchor station is representative of that found with depth and distance across the mouth of the estuary. The mouth of the Humber and Plume have been reported to be vertically well mixed (Zwolsman, 1994 and all references therein) and the chemical analysis of samples taken from near-surface, mid and near-bottom have been found to be not significantly different in composition (Morris & Allen, 1993). This model was forced by M_2 tidal predictors together with seasonal variations in the river flow, but did not include wind forcing (Millward *et al.*, 1996). The calculated fluxes of Cu_p and Cu_d are summarised in Table 3.6 and show pronounced differences both with season and year. Total Cu fluxes have increased by a factor of *c.* 2 when comparing winter'88 to winter'95 and summer'90 to summer'95 data and by a factor of *c.* 10 when comparing respective spring seasons. The percentage of Cu transported in the dissolved phase compared to the total also varies with season from between 20-40% in winter to between 66-90% during summer surveys. The large discrepancy in flux estimates between the NSP and LOIS data sets is attributed to a combination of elevated residual water outflows (175 & $345 m^3 s^{-1}$ for spring'90 and

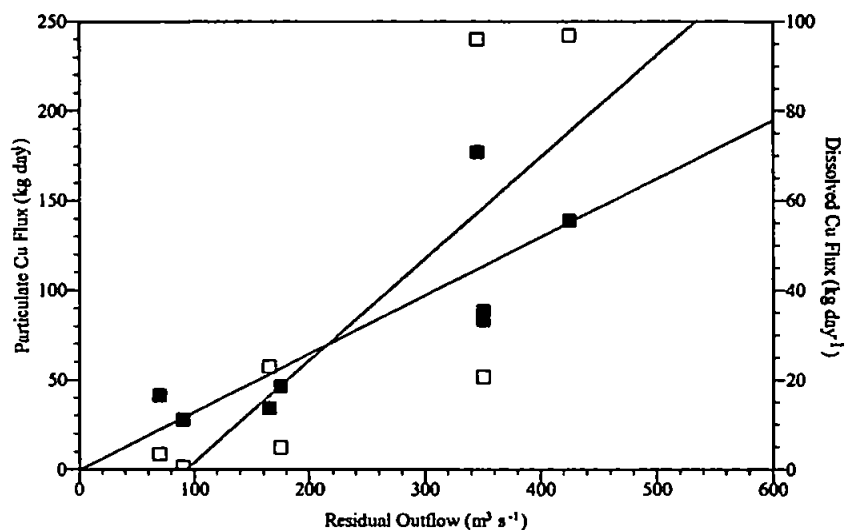
⁶ Preliminary Acoustic Doppler Current Profiler results from the spring'95 survey suggested that significant variations in the current velocity observed across a transect of the mouth of the estuary could lead to an underestimation of the water outflow by up to 40% (Millward, 1995).

spring'95 respectively) and tidal amplitudes (4.7 & 6.6 m for spring'90 and spring'95 respectively) resulting in higher fluxes dominating the LOIS budgets, particularly during spring'95.

On semi-diurnal time scales Lindsay *et al.* (1996) found that SPM concentrations were closely related to current velocities in the Forth Estuary. To investigate trends of this nature the fluxes of Cu_p , Cu_d and SPM were plotted against residual outflow of water (Figure 3.15) from the mouth of the Humber Estuary to the North Sea. A significant ($P < 0.05$) linear relationship was observed between the fluxes of Cu_p , Cu_d and residual water outflow ($r = 0.73$ & 0.82 respectively) suggesting that the variability in the flux of Cu can largely be accounted for by the changes in residual flow from the Humber Estuary. The Cu_p flux does however show more scatter in the data suggesting the influence of other factors. The relationship between the flux of SPM and residual flow as shown in Figure 3.15b indicates the relative influence of the tidal range. A significant ($P < 0.05$) positive relationship ($r = 0.93$) is shown when tidal conditions approach smaller neap ranges (≤ 5.0 m). It is therefore feasible that the increased variability in Cu_p fluxes could be partially explained by tidal state. Indeed if flux data from autumn'94 and spring'94 are excluded (as they both exhibit large spring tidal ranges of 6.6 m compared to the other surveys, refer to Table 3.5) then the correlation coefficients between the flux of Cd_p and Cd_d vs. outflow increase ($r = 0.90$ & 0.94 respectively $P < 0.05$). This serves to illustrate the importance of carrying out studies of a comparative nature over similar tidal cycles.

The relationship between Cu_p and residual water (dotted line in Figure 3.15a, includes all flux data) outflow implies no transport of Cu_p across the mouth of the Humber Estuary if residual flows drop below approximately $80 \text{ m}^3 \text{ s}^{-1}$ NB. The absence of spring tidal flux data i.e. autumn'94 and spring'95 does not significantly change the value of the x intercept. Typical summer outflows between $70\text{-}90 \text{ m}^3 \text{ s}^{-1}$ would therefore imply no transport of Cu_p from the Humber Estuary to the receiving waters of the coastal zone and hence little influence on the observed offshore coastal Cu_p distributions. This is subsequently reflected in the lack of correlation between the concentration of Cu_p and salinity during summer'95 for the Humber coastal zone but not during the former NSP summer'90 survey (refer to Table 3.3).

(a)



(b)

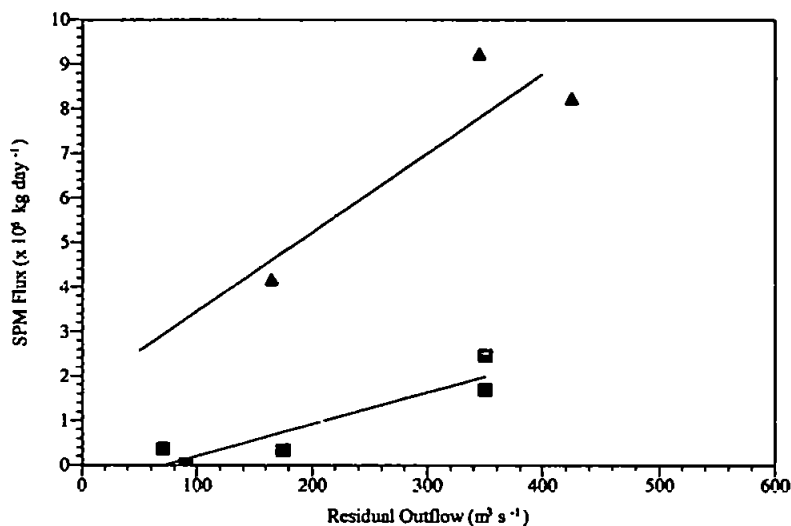


Figure 3.15 The flux of (a) Cu_p (□, red line) and Cu_d (■, black line) and (b) SPM where (▲) represents spring tides (tidal range $\geq 5.0\text{m}$) and (■) represents tides approaching neaps (tidal range $\leq 5.0\text{m}$) as a function of residual water outflow from the mouth of the Humber Estuary.

If it is assumed that the observed conditions for the four LOIS surveys (autumn'94 to summer'95) are each representative of a 3 month period then the total current Cu flux may be calculated yearly and an estimate of the integrated annual average (IAA) flux obtained. A similar calculation can be performed on the data from the NSP if you assume that inter-annual variability in the years 1988-90 is relatively small (Millward *et al.*, 1996). For such calculations, the total inputs of Cu to the Humber coastal zone from the estuary are 6.5×10^3 kg during autumn'94, 1.9×10^4 kg during winter'95, 2.8×10^4 kg during spring'95 and 2.3×10^3 kg during summer'95. This gives a daily integrated average mean of approximately 153 kg day^{-1} (see Table 3.6). Comparison of annual

average output fluxes from the Humber Estuary to the coastal zone with total inputs into the estuary from rivers, industry and sewage sources (PARCOM, 1991; NRA, 1993) indicates Cu estuarine retention of 82% in the year 1988-90 and 25% in 1994-95 (Zwolsman, 1994; Millward & Glegg, 1997). This feature is in agreement with observations made in the Scheldt macrotidal estuary by Zwolsman *et al.* (1993).

3.3.3 Predictive modelling of Cu concentrations in the coastal zone

The previous sections have highlighted the significance of the Humber Estuary and Holderness Cliffs as important sources of SPM and Cu_p to the Humber coastal zone. Duinker (1983) modelled the composition of SPM in seawater by assuming that it was principally composed of two fractions; (i) small/low density particles i.e. Holderness material (refer to Chapter 5) and (ii) larger/denser particles derived from bottom sediments i.e. similar to SPM and resuspended sediments from the Humber Estuary. Implicit in this assumption was that large particles present at high SPM loads were more dense than smaller particles typical of low SPM concentrations. Using this approach Duinker classified trace metals into three groups according to their profile when plotted against the concentration of SPM (Figure 3.16).

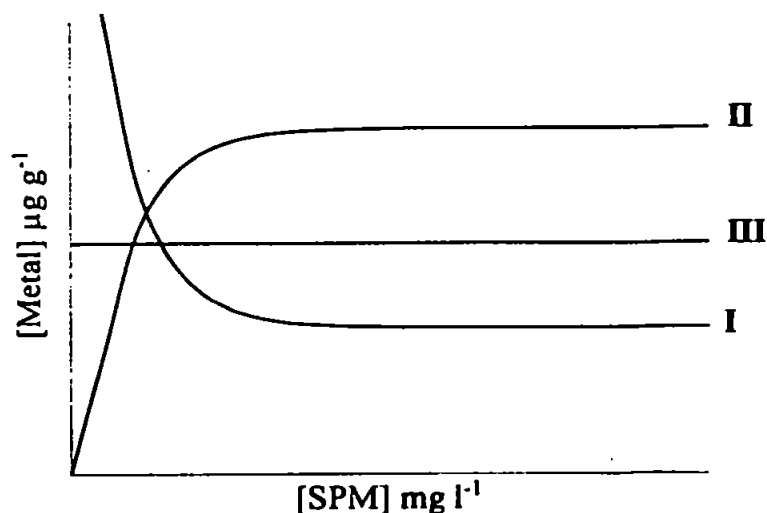


Figure 3.16 A schematic illustration of the Duinker model showing group I, II and III behaviour.

Group I : Preferential association of trace metals with low density particulate matter in permanent suspension,

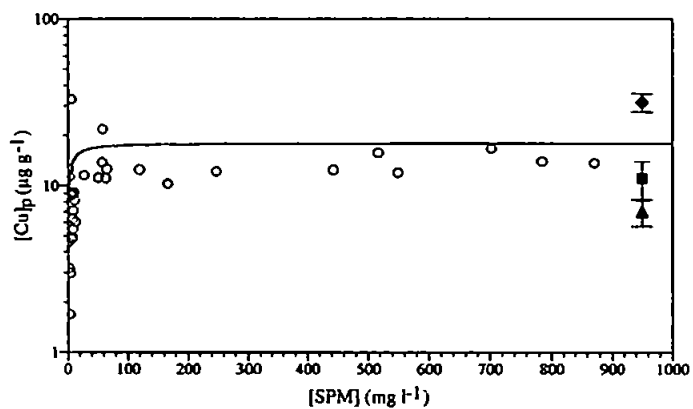
Group II : Preferential association of trace metals with high density particulate matter often in temporary suspension and

Group III : Trace metals which show no preferential association with either particle fraction.

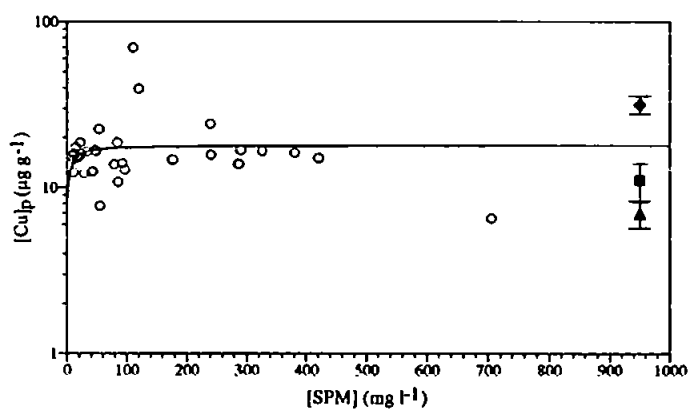
The concentrations of Cu_p for the Humber coastal zone obtained during the LOIS surveys were subsequently plotted against the concentrations of SPM and are displayed in Figure 3.17. It can be seen from this plot that there is a switch in behaviour during the year from Group II during autumn'94 to Group I during summer'95. Intermediate seasons showed no preferential association with particle population i.e. Group III. During autumn'94 the highest concentrations of Cu_p (between 10-20 $\mu g g^{-1}$) were dominant at SPM concentrations greater than 40 $mg l^{-1}$. These samples generally originated from the mouth of the Humber Estuary. The lowest concentrations of Cu_p ($<10 \mu g g^{-1}$) were generally associated with samples of low SPM concentration originating from locations adjacent to the Holderness Cliffs or from offshore sites. This infers the preferential association of Cu_p with high particulate loads, typically dense resuspended bed material as previously suggested in section 3.3.1. During the following winter and spring 1995 Cu_p concentrations do not show any convincing preferences for either high or low concentrations of SPM i.e. Group III behaviour. However, during spring'95 Cu_p concentrations $>30 \mu g g^{-1}$ found at SPM concentrations $>400 mg l^{-1}$ were taken during the ebb tide at the Humber mouth anchor station (refer to Figure 3.14d) *cf.* average concentration of Cu_p in Humber Estuary sediments in Figure 3.17.

The mechanism for the observed enhanced association of Cu with high density particles originating from the Humber Estuary during autumn'94 (and perhaps spring'95) is not fully understood. The Humber Estuary has previously been established as a primary source of Fe, and to some extent Mn (refer to sections 1.2.2.4 & 3.2.1). The surfaces of Fe and Mn oxyhydroxides have extremely high adsorption capacities for trace metals (Drever, 1988), possibly due to an associated increase in the specific surface area of particles coated with Fe and Mn (Martin *et al.*, 1986; Glegg *et al.*, 1987; Millward *et al.*, 1989). The above phenomena could therefore be attributed to the adsorption of Cu onto Fe and Mn oxyhydroxide coated particles originating from the Humber Estuary enhanced by anthropogenic Cu inputs (refer to Table 1.5).

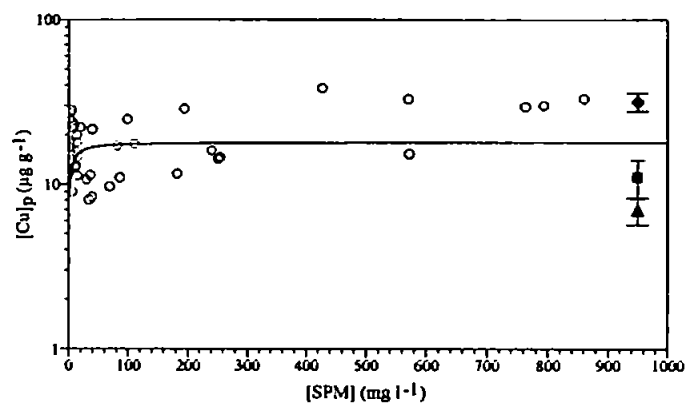
(a) Autumn



(b) Winter



(c) Spring



(d) Summer

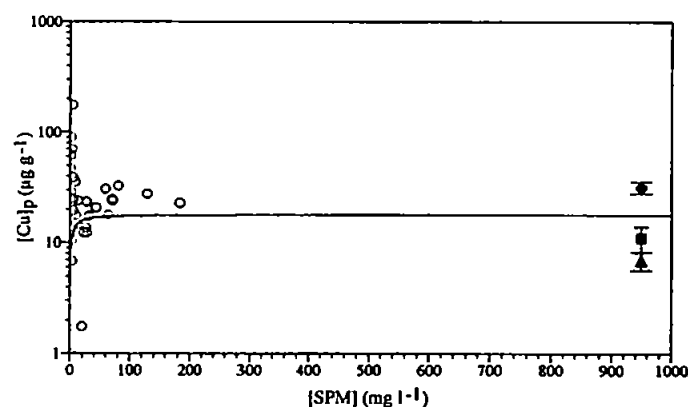


Figure 3.17 The concentration of Cu_p as a function of the concentration of SPM for samples collected in the Humber coastal zone (including Humber anchor station data) during (a) autumn'94, (b) winter'95, (c) spring'95 and (d) summer'95. Average Cu concentrations (± 1 SD) for the Humber Estuary (\blacklozenge), Plume (\blacksquare) and Holderness (\blacktriangle) sediments are also shown (see sediment data, Appendix D). The solid line represents modelled concentrations of Cu_p according to equation 3.2, see page 116 for the derivation of the 2 component end member model.

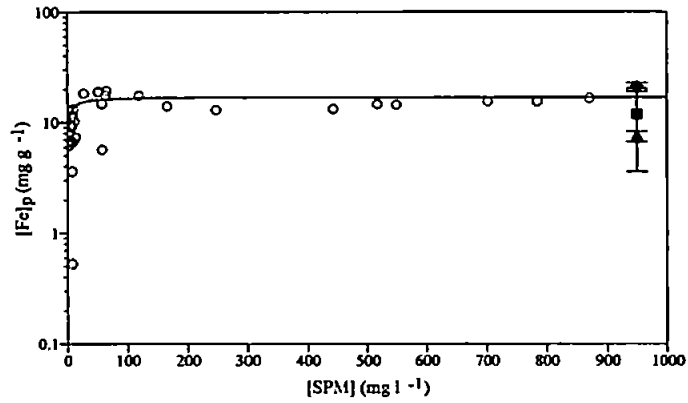
During the following summer Cu_p concentrations showed some particularly elevated concentrations (between 30-176 $\mu\text{g g}^{-1}$) corresponding to SPM loads <10-15 mg l^{-1} (Figure 3.17d) in the Humber coastal zone (refer to Figure 3.13g). Similar SPM relationships for Cu_p have been previously noted in the Dutch Wadden Sea by Duinker *et al.* (1974), in the Irish and southern North Sea by Jones & Jefferies (1983) and in the Dover Strait by James *et al.* (1993). They suggested that proportionally more Cu is associated with the finer fractions of the SPM (where surface area is generally greater), and in less turbulent waters (i.e. summer conditions when estuarine particulate fluxes were minimal) where there is a greater proportion of fine permanently suspended material (James *et al.*, 1993). It is interesting to note that James *et al.* (1993) reported a positive correlation in December'90 between Cu_p and Al_p in the Dover Strait suggesting a simple relationship between Cu_p and the terrigenous derived component of SPM. A clear positive deviation from this relationship was found in June'91 implying that Cu was no longer dominantly associated with the terrigenous fraction. It was therefore suggested that Cu showed an affinity for particulate organic material (Comber *et al.*, 1995) which being more ubiquitous during periods of intense biological activity lead to an enhancement of Cu_p levels in the summer. Such a distributional trend was also evident during summer'95 LOIS surveys⁷.

In an attempt to further investigate the geochemical role of Fe_p in the Humber coastal zone the observed concentrations were, similarly to Cu_p , plotted as a function of the concentration of SPM and are displayed in Figure 3.18. In all seasons Fe_p displayed Group II behaviour (with concentrations between 15-20 mg g^{-1} associated mainly with higher SPM concentrations and conversely, low Fe_p concentrations between 1-10 mg g^{-1} found at low SPM concentrations. The lower scatter in Figure 3.18 possibly reflects the dominance of the Humber Estuary as a Fe_p source (see section 1.2.2.4).

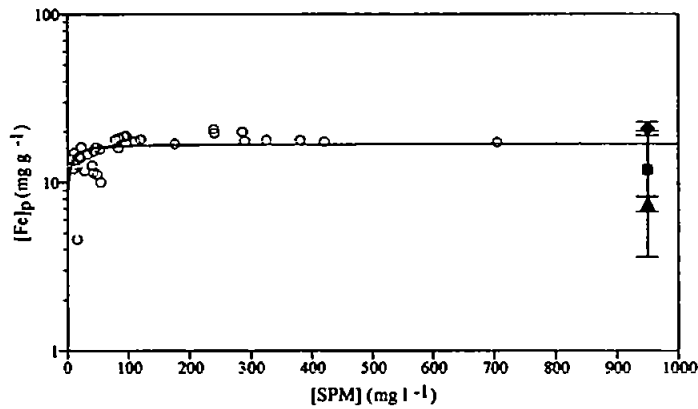
All the Cu_p data from the Humber coastal zone, including the anchor station profiles, for the LOIS surveys were subsequently plotted as a function of the concentration of Fe_p and are shown in Figure 3.19. A significant ($P < 0.05$) correlation ($r = 0.42$ for $n = 125$) was found between the two metals when all the data (except summer'95 coastal samples) was

⁷ Unfortunately there are not any supporting Al_p or POC data for the present study.

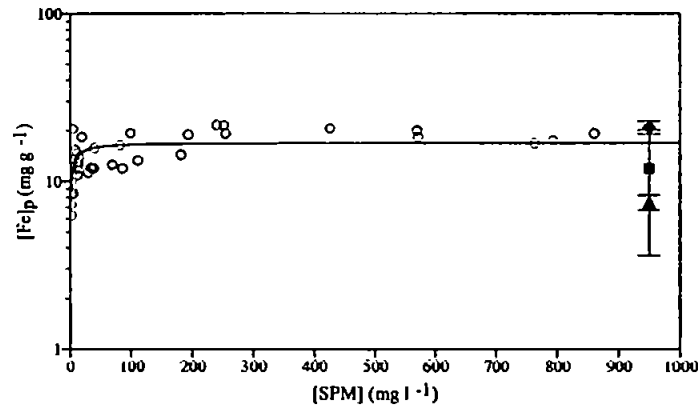
(a) Autumn



(b) Winter



(c) Spring



(d) Summer

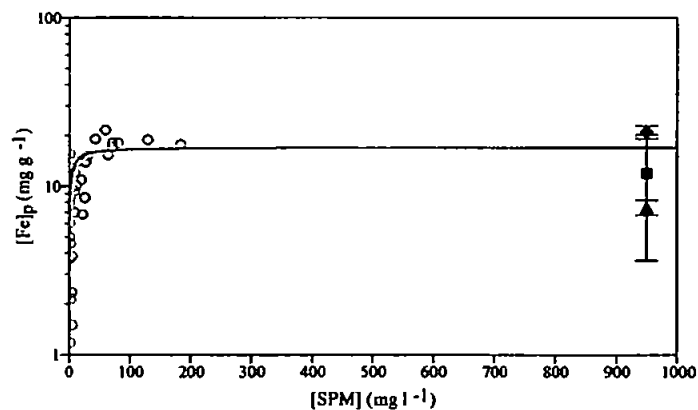


Figure 3.18 The concentration of Fe_p as a function of the concentration of SPM for samples collected in the Humber coastal zone (including Humber anchor station data) during (a) autumn'94, (b) winter'95, (c) spring'95 and (d) summer'95. Average Fe concentrations (± 1 SD) for the Humber Estuary (\blacklozenge), Plume (\blacksquare) and Holderness (\blacktriangle) sediments are also shown (see sediment data, Appendix D). The solid line represents modelled concentrations of Fe_p according to equation 3.2, see page 116 for the derivation of the 2 component end member model.

considered together suggesting that Cu adsorbs onto the Fe rich particles emanating from the Humber Estuary. However Cu_p samples taken from the Humber coastal zone (but not from the Humber mouth anchor station) during summer'95 clearly showed a positive deviation from the above relationship (as shown by ● in Figure 3.19) suggesting other geochemical controls i.e. association with particulate organic material, refer to section 3.2.2. Indeed calculations on trace metal-humic acid complexation in model seawater at pH 8.2 made by Turner *et al.* (1981) suggested that 47% of Cu^{2+} was complexed with humic acids (pH typically between 7.8-8.0 for the Humber coastal zone during summer'95). Experiments reported by Chester *et al.* (1988) on the solid state speciation of Cu in water particulates also concluded that around 50% of the total Cu in Atlantic ocean surface water particulates was held in organic associations. Similarly van den Berg *et al.* (1987) suggested that Cu_d in the Scheldt Estuary is up to 99.99% organically complexed which implies the greater potential for surface Cu associations with biogenic/organic particulate material by surface complexation. Furthermore complexed metal ions have also been shown to adsorb onto metal oxide surfaces (Elliot & Huang, 1979; Davies, 1984).

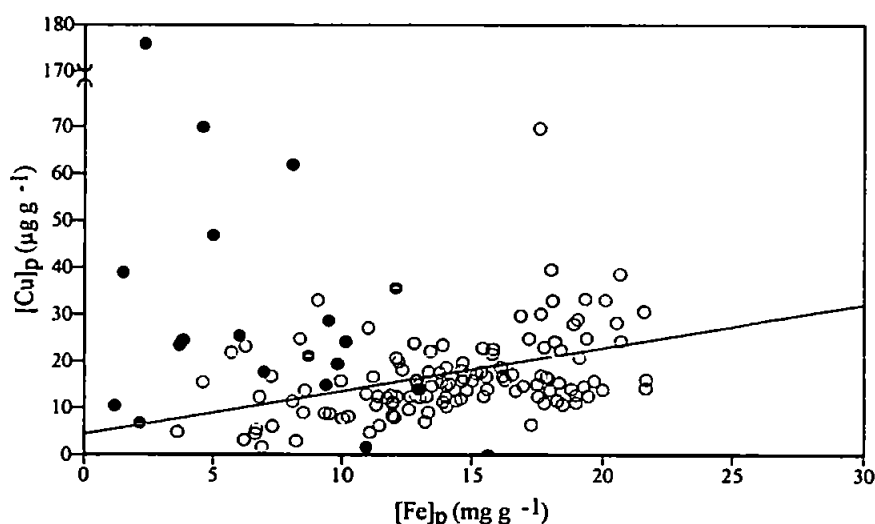


Figure 3.19 The concentration of Cu_p as a function of the concentration of Fe_p for all samples collected in the Humber coastal zone (all seasons) where $r=0.42$ for $n=125$ ($P<0.05$). (●) indicates data from the Humber Plume during summer'95.

In summary it would appear that there was a switch from Group II to Group I behaviour between autumn'94 and summer'95. The former season showed enhanced association of Cu_p with high density particles originating from the Humber Estuary. However, during

the following summer Cu_p showed enhanced affinity for low density particles perhaps particulate organic material (as previously suggested in section 3.2.2) which being more ubiquitous during periods of enhanced biological activity lead to an enhancement of Cu_p at low SPM concentrations. This effect was likely inhibited during the former spring due to a highly elevated estuarine SPM flux ($9.2 \times 10^6 \text{ kg day}^{-1}$) swamping the Humber coastal zone and lowering the impact of Cu associated with biogenic particulate matter.

3.3.3.1 A two component end member model

In the Humber coastal zone there is a complex mixing of SPM arising from sources such as the erosion of the Holderness Cliff clay material, transport of anthropogenically modified Humber estuarine material, advection of background Atlantic inflow waters and associated SPM, resuspension of bed material etc. (see section 1.2.2.3). In an attempt to model and predict particulate trace metal distributions in the Plume Millward *et al.* (1996) derived a 2 component SPM end member model to simulate SPM mixing. He assumed that the distribution of SPM in the Humber Plume was principally the result of the direct mixing of permanently suspended estuarine and Holderness end member particles (based on flux estimates by McCave, 1987 and Dyer & Moffat, 1992, refer to section 1.2.2.3) and predicted that the concentration of trace metals in plume particles, M^P , could be predicted from the following particle mixing equation;

$$[M^P] = \frac{[SPM^{HE}][M^{HE}] + [SPM^{HC}][M^{HC}]}{[SPM^P]} \quad 3.2$$

where M^{HE} and M^{HC} are, respectively, the concentration of trace metal in the Humber Estuary and Holderness Cliff material and SPM^P , SPM^{HE} and SPM^{HC} are the concentration of SPM in the Humber Plume, Estuary and nearshore Holderness region respectively. Assuming the following;

- (i) $[SPM^P] = [SPM^{HE}] + [SPM^{HC}]$,
- (ii) conservative mixing of particles in the plume and
- (ii) the following end member concentrations based on the trace metal analysis of Holderness Clay material and average Cu_p and Fe_p concentrations observed at the

Humber mouth anchor stations; $[SPM^{HC}] = 5 \text{ mg l}^{-1}$, $[Cu^{HC}] = 7.0 \text{ } \mu\text{g g}^{-1}$, $[Cu^{HE}] = 18 \text{ } \mu\text{g g}^{-1}$, $[Fe^{HC}] = 7.0 \text{ mg g}^{-1}$, $[Fe^{HE}] = 17 \text{ mg g}^{-1}$

modelled Cu_p and Fe_p concentrations in the Humber coastal zone can be evaluated according to equation 3.2 and are plotted in Figures 3.17 and 3.18 respectively. The modelled concentrations of both Cu_p and Fe_p represent the data reasonably well which suggests that within the Humber coastal zone both metals can be described by the same model or geochemical processes. However there are two main deviations from the modelled behaviour; (i) both Cu_p and Fe_p exhibited higher concentrations than those predicted by the model at high SPM loads during spring'95 possibly reflecting inputs due to bed resuspension or enhanced particulate organic metal complexes that are neglected by the model, and (ii) elevated Cu_p concentrations at low SPM concentrations during summer'95 previously attributed to enhanced association with organic material, marine in origin. This emphasises the need for caution when using simple models in attempting to predict seasonal trace metal estuarine behaviour.

3.3.4 The distribution of Cu between the dissolved and particulate phases

The distribution of a trace metal between the particulate and dissolved phase is governed by a range of different processes including (i) flocculation, adsorption, precipitation and biological uptake of dissolved trace metals resulting in their transfer to the particulate phase, (ii) desorption from particle surfaces and the breakdown of organics which result in the addition of trace metals to the dissolved phase and (iii) complexation and chelation reactions with inorganic and organic ligands which act to stabilise trace metals in the dissolved phase (Chester, 1990). The net result of the total processes is often summarised by the conditional partition coefficient, or K_D , defined as the ratio of the exchangeable concentration of metal per unit mass of particulate material to the concentration of the metal per unit mass (or volume) of seawater (Tappin *et al.*, 1995). The K_D concept is conditional on the operational distinction between the dissolved and particulate phase of the filter pore size and has an inherent number of assumptions. Firstly, the concept assumes a heterogeneous reaction which achieves instantaneous equilibrium. This assumption in practice is rarely achieved due to kinetic constraints of

the system (physically) preventing equilibrium being attained e.g. particularly apparent during short estuarine flushing time. Secondly, it assumes uniform properties of the solid phase which is very unlikely considering the different particle populations/sources i.e. clay material, Fe-rich estuarine material & biogenic particles alluded to in previous sections. Indeed recent work has shown K_D to be highly sensitive to particle type especially those biogenic in origin. There is evidence to suggest that some phytoplankton have a greater affinity for some trace metals (e.g. Cd & Zn) than lithogenic particles (Wartel *et al.*, 1991; Turner *et al.*, 1992a) as evident by higher K_D values. Additionally the magnitude of the K_D is also dependent on accurate estimates of the exchangeable particulate metal species and the concentration of dissolved metals truly available to participate in particle-water interactions. Both of which are conditional on the sample preparation and analytical methodology applied. However despite these limitations K_D calculations are used as simple empirical measures of describing metal partitioning between the dissolved and solid phases (Tappin *et al.*, 1995).

Figure 3.20a & b shows the partitioning of Cu as a function of SPM concentration (refer to the algorithm in Equation 3.3) for the LOIS and NSP surveys respectively (all data is from the anchor station based in the mouth of the Humber Estuary).

$$\% \text{ Particulate Metal} = 100 - \left[\frac{100}{1 + (K_D \times [\text{SPM}] \times 10^{-6})} \right] \quad 3.3$$

Irrespective of season, the behaviour of Cu for the LOIS samples can be described by a small range of $\log K_D$ values of approximately 4, irrespective of the number of available sorption sites. This is in good agreement with the published results of Tappin *et al.* (1995) for the southern North Sea and those of Comber *et al.* (1995) for the Humber Estuary ($\log K_D$ between 4-5 & ~3.9 respectively). Similarly, concentration data from the NSP surveys in the mouth of the Humber Estuary show consistent $\log K_D$ values of approximately 4.5. However a distinct seasonality is apparent in the percentage of particulate bound Cu ranging between 50-90% in winter'88 down to <20% in summer'90, a trend not seen in the LOIS data. The reason for this is not known but could reflect the changes in prevailing hydrodynamic regimes between the two survey periods i.e. approximately a 2 fold increase in residual water outflow from the Humber

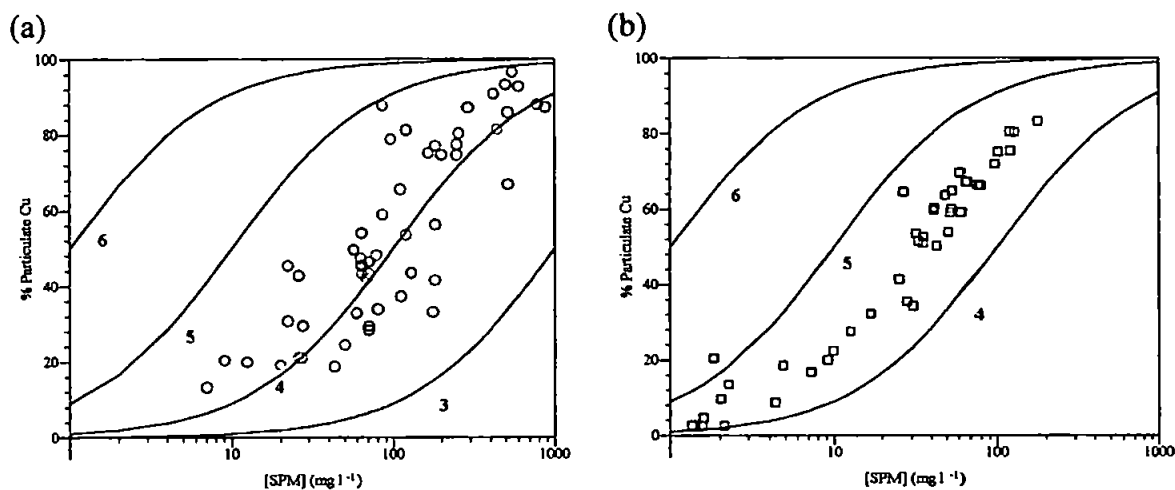


Figure 3.20 Percentage particle-bound Cu as a function of SPM concentration for samples collected at anchor stations in the mouth of the Humber Estuary during (a) the LOIS surveys autumn'94 (○), winter'95 (○), spring'95 (○) and summer'95 (○) and (b) the NSP surveys during winter'88 (□), spring'90 (□) and summer'90 (□). The lines represent log K_D values.

Estuary when comparing spring'90 to spring'95 combined with an elevated tidal range resulted in an anomalously high mean SPM concentration and hence increase in % particulate bound Cu (refer to Table 3.5).

3.4 The Humber Coastal Zone - Cadmium

3.4.1 Particulate Cd distributions

The Cd_p concentrations in the Humber coastal zone have been contoured and are shown in Figures 3.21 a-g representing distributions observed during winter'88, spring'90 and summer'90 NSP surveys and autumn'94, winter'95, spring'95 and summer'95 LOIS surveys. The concentrations of Cd_p in the Humber coastal zone did not show any clear discernible trends with season or year but rather remained remarkably low ($<2.0 \mu\text{g g}^{-1}$) throughout all surveys. Indeed Cd_p concentrations $>2.0 \mu\text{g g}^{-1}$ were only found in the northern part of the LOIS coastal track during spring and summer'95 as previously mentioned in section 3.2.3 (see Figure 3.9). This trend is in good agreement with the earlier findings of Nolting & Eisma (1988) and Kersten *et al.* (1988) who reported high Cd content ($>2.0 \mu\text{g g}^{-1}$) in SPM of the northern North Sea and generally low Cd content ($<2.0 \mu\text{g g}^{-1}$) of SPM in the southern North sea for surveys carried out in January'80.

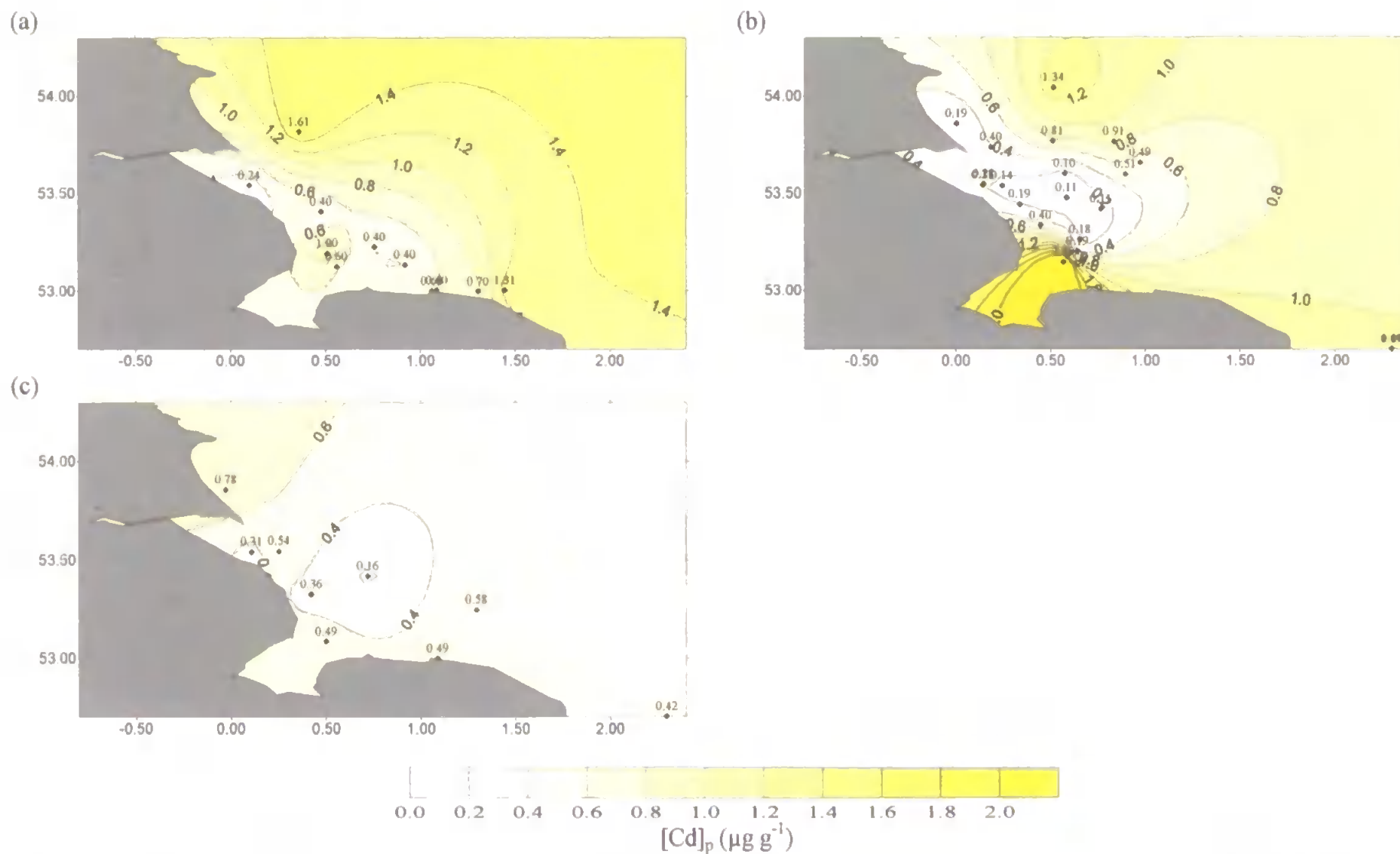


Figure 3.21 The contoured distributions of Cd_p in the Humber coastal zone during (a) winter'88, (b) spring'90 and (c) summer'90 NSP surveys. Data taken from the NERC North Sea project data set that is currently available on CD-ROM (Lowry *et al.*, 1992).

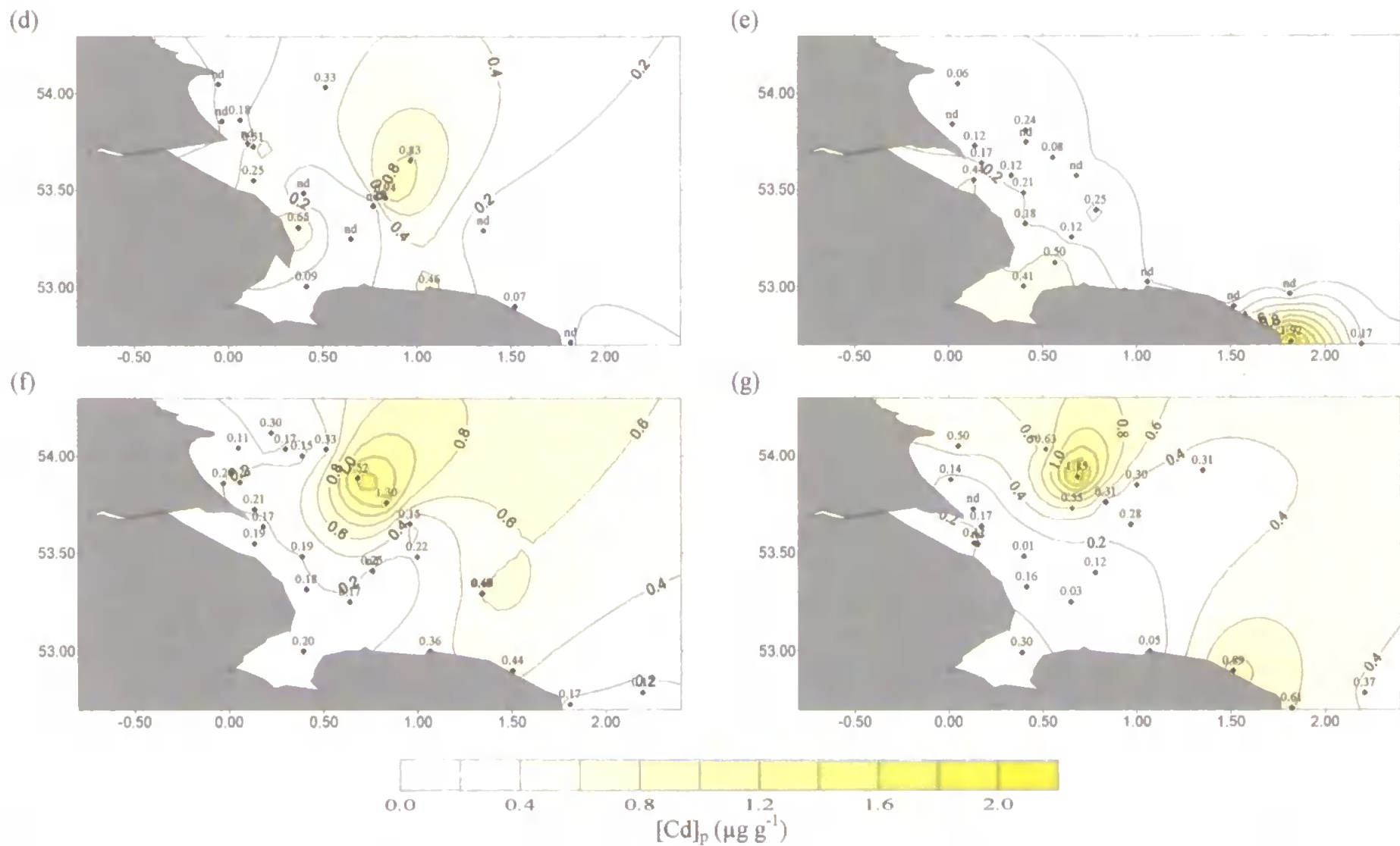


Figure 3.21 continued. The distribution of Cd_p in the Humber coastal zone during (d) autumn'94, (e) winter'95, (f) spring'95 and (g) summer'95 present LOIS surveys.

The general lack of any statistical relationships between Cd_p and salinity, concentration of SPM, Fe_p and Mn_p (see Table 3.8) suggests that (a) Cd_p was not behaving conservatively and (b) the Humber Estuary was not a significant source of Cd_p to the nearshore coastal zone. During winter'88 and spring'95 a positive correlation was however found between Cd_p vs. salinity for the Humber coastal zone in agreement with the findings of Tappin *et al.* (1995) for the English coastal zone during autumn'89. This was coincident with a negative relationship between Cd_p and Fe_p further suggesting a marine source of Cd_p . In agreement with Cu_p distributions for the LOIS data, the highest concentrations of Cd_p ($>1.0 \mu g g^{-1}$) were observed offshore during spring and summer surveys.

Table 3.8 Values of r for significant relationships between the concentration of Cd_p vs. salinity and the concentrations of SPM, Fe_p and Mn_p in the Humber coastal zone. Statistically significant ($P < 0.05$) correlation's are indicated in bold type.

Cruise	n	Salinity	SPM	Fe_p	Mn_p
Winter'88 ^a	10	0.67	-0.32	-0.68	-0.35
Spring'90 ^a	20	0.23	-0.22	-0.25	-0.27
Summer'90 ^a	9	0.03	-0.41	0.34	0.75
Autumn'94	17	0.09	0.14	0.06	-0.25
Winter'95	20	-0.09	0.18	-0.27	-0.20
Spring'95	25	0.41	-0.29	-0.50	-0.33
Summer'95	21	0.22	-0.40	-0.22	0.07

^aData taken from the NSP CD-ROM (Lowry *et al.*, 1992)

The average concentrations of Cd_p in the Humber coastal zone for all survey periods are shown in Table 3.9. Seasonal average concentrations of Cd_p obtained during the LOIS cruises were all considerably lower than those obtained during the NSP surveys. For example the concentration of Cd_p during winter'95 is approximately 70% lower than that obtained during winter'88. However this may in part reflect the larger number of samples taken, particularly adjacent to the Holderness Cliff region, during the winter'95 survey. The LOIS surveys showed that average Cd_p concentrations were of similar magnitude during autumn and winter (~ 0.23 - $0.24 \mu g g^{-1}$) and increased throughout the year to summer ($0.36 \mu g g^{-1}$) in agreement with the trend displayed for Cu_p in the Humber coastal zone (section 3.3.1). Tappin *et al.* (1995) also reported that the concentrations of Cd_p were higher during summer periods for the English coastal zone which was attributed to the relatively high affinity of Cd for biogenous particle relative to

lithogenous material (Noriki *et al.*, 1985; Valenta *et al.*, 1986; Golimowski *et al.*, 1990; Turner *et al.*, 1992a; Hall, 1993). The subsequent increase in concentration of Cd_p offshore during spring'95 and summer'95 (Figure 3.21f & g respectively) is therefore possibly due to dilution of lithogenic material with biogenic material or rather an increase in the relative proportion of biogenic particles in the water column. It is interesting to note that average Cd_p concentrations obtained during autumn'94 and winter'95 are also similar to the average concentration of Cd in surface sediments in the mouth of the Humber Estuary (see Table 3.9). This perhaps suggests that the estuarine flux of Cd_p, and subsequent dilution with seawater and Holderness material characterised by lower Cd_p concentrations ($0.13 \pm 0.02 \mu\text{g g}^{-1}$) could, in part, explain the observed concentrations in the Humber coastal zone during autumn'94 and winter'95.

Table 3.9 Mean and standard deviation (SD) of the concentration of Cd_p in the Humber coastal zone, Holderness Cliff material and in Humber Estuary sediments.

Cruise	N ^o samples	[Cd] _p ± SD ($\mu\text{g g}^{-1}$) ^f	Coefficient of Variation (%)
SPM			
Winter'88 ^c	10	0.76 ± 0.41	54
Spring'90 ^c	20	0.53 ± 0.66	123
Summer'90 ^c	9	0.48 ± 0.18	37
Autumn'94	17	0.24 ± 0.32	133
Winter'95	20	0.23 ± 0.42	183
Spring'95	25	0.34 ± 0.35	103
Summer'95	21	0.36 ± 0.42	117
Holderness Cliff material ^b	10	0.13 ± 0.02	15
Humber sediments			
Humber mouth ^d	4	0.22 ± 0.10	48
Humber Estuary ^a	1	0.80	
Pre-industrial ^e	1	n/a	

^aSample number 6 taken from up the Humber Estuary, refer to Figure 2.5; ^b10 samples of Holderness Cliff clay material, <63 μm particle size fraction; ^cMiddleton & Grant (1990); ^dAverage of all surface sediments collected from the mouth of the Humber Estuary (refer to Figure 3.10); n/a denotes data not available; ^eData taken from the NSP CD-ROM (Lowry *et al.*, 1992); ^fCompare with literature in Tables 1.4 & 1.6

Consideration of the fluxes of Cd from the Humber Estuary to the North Sea (Table 3.10) revealed that during winter'88, autumn'94 and winter'95 between 30-75% of the Cd was transported in the dissolved phase. This percentage increases to between 80-99% for spring and summer periods suggesting the significance of the Humber Estuary as a source of Cd_d (Balls, 1985; Williams, 1995) to the North Sea, particularly during spring and summer months. This is possibly an artefact of decreasing SPM concentrations combined with the preferred complexation of Cd with chloride anions (Comans & van Dijk, 1988) which has been shown to control the partitioning of Cd in the Humber Estuary (Comber *et al.*, 1995). The preference of Cd for the dissolved phase possibly explains why the estuary does not act as a significant source of Cd_p to the coastal environment.

However the likelihood of other sources of Cd_p to the coastal zone must not be entirely neglected. The severe erosion of the Holderness Cliffs results in an estimated Cd_p flux of 0.50 kg day⁻¹ (see Table 3.10) which is comparable, and during spring and summer months often greater than the estuarine flux. Whilst the similarity in Cd concentrations between average SPM in the Humber coastal zone and bed sediments in the mouth of the Humber Estuary during autumn'94 and winter'95 surveys suggests resuspension processes. Chester *et al.*, (1993) compared the magnitude of Cd fluxes to the North Sea and showed that the combination of atmospheric 'wet' and 'dry' fluxes were approximately equal in magnitude to fluvial fluxes suggesting that diffuse atmospheric inputs of Cd could also contribute to the budget. However the relatively small area of the Humber coastal zone in comparison to the whole of the North Sea, in combination with the proximity to the Humber Estuary and Holderness Cliffs intuitively suggests that lithogenic sources are likely to dominate under most circumstances. In summary the observed largely incoherent Cd_p distributions are the result of a number of interactions of different Cd_p sources and source strengths which are further complicated due to the reactivity of Cd in seawater and hence unconservative behaviour.

3.4.2 Dissolved and particulate Cd at anchor stations

Typical particulate and dissolved Cd concentrations determined at the anchor stations in the Humber coastal zone for the LOIS surveys are shown in Figures 3.22a-f. Figures 3.22b & f show Cd_p distributions only (a different scale has been used for the Cd_d trends in the winter'95 and spring'95 surveys shown). A summary and discussion of the master variables for each anchor station, including those of the NSP surveys, has previously been given in Table 3.5 and section 3.3.2. The mean particulate and dissolved Cd concentrations determined at the anchor stations in the Humber coastal zone are shown in Table 3.10. The mean concentration of Cd_p for the LOIS data ranged between 0.19-0.44 $\mu\text{g g}^{-1}$. The highest concentrations of Cd_p were obtained during winter'95 and summer'95 (0.44 and 0.42 $\mu\text{g g}^{-1}$ respectively) coincident with maximum variations in concentration. In general mean Cd_p concentrations obtained during the anchor stations decreased with distance away from the mouth of the Humber Estuary. This is illustrated by winter'95 profiles when average concentrations decreased from 0.44 $\mu\text{g g}^{-1}$ at the estuary mouth to 0.17 $\mu\text{g g}^{-1}$ at Spurn Head and 0.12 $\mu\text{g g}^{-1}$ further north adjacent to the Holderness Cliffs (Figure 3.22a, b & c, for sample locations refer to Figure 2.3). This presumably reflects the mixing and subsequent dilution of estuarine SPM with eroded Holderness Cliff material of lower Cd_p concentration (0.13 $\mu\text{g g}^{-1}$, refer to Table 3.9). There are however two exceptions to this trend; autumn'94 when the average Cd_p concentration adjacent to the Holderness Cliffs are approximately double that at the mouth of the Humber, and spring'95 when the average concentration obtained in the Wash embayment is approximately 60% greater than that in the Humber Estuary. The reasons for this are not understood but could reflect alternative Cd_p sources e.g. fluvial inputs into the Wash or dissolved to particulate interactions associated with the high affinity of Cd for biogenic particles. The high chlorophyll a concentration of $3.0 \pm 0.5 \mu\text{g l}^{-1}$ (Table 3.5) obtained during the spring'95 anchor station in the Wash provides circumstantial evidence to support the latter hypothesis a high proportion of biogenic particles in the water column at this time. However the lack of chlorophyll a concentration data available during autumn'94 adjacent to the Holderness Cliffs renders such an explanation inconclusive.

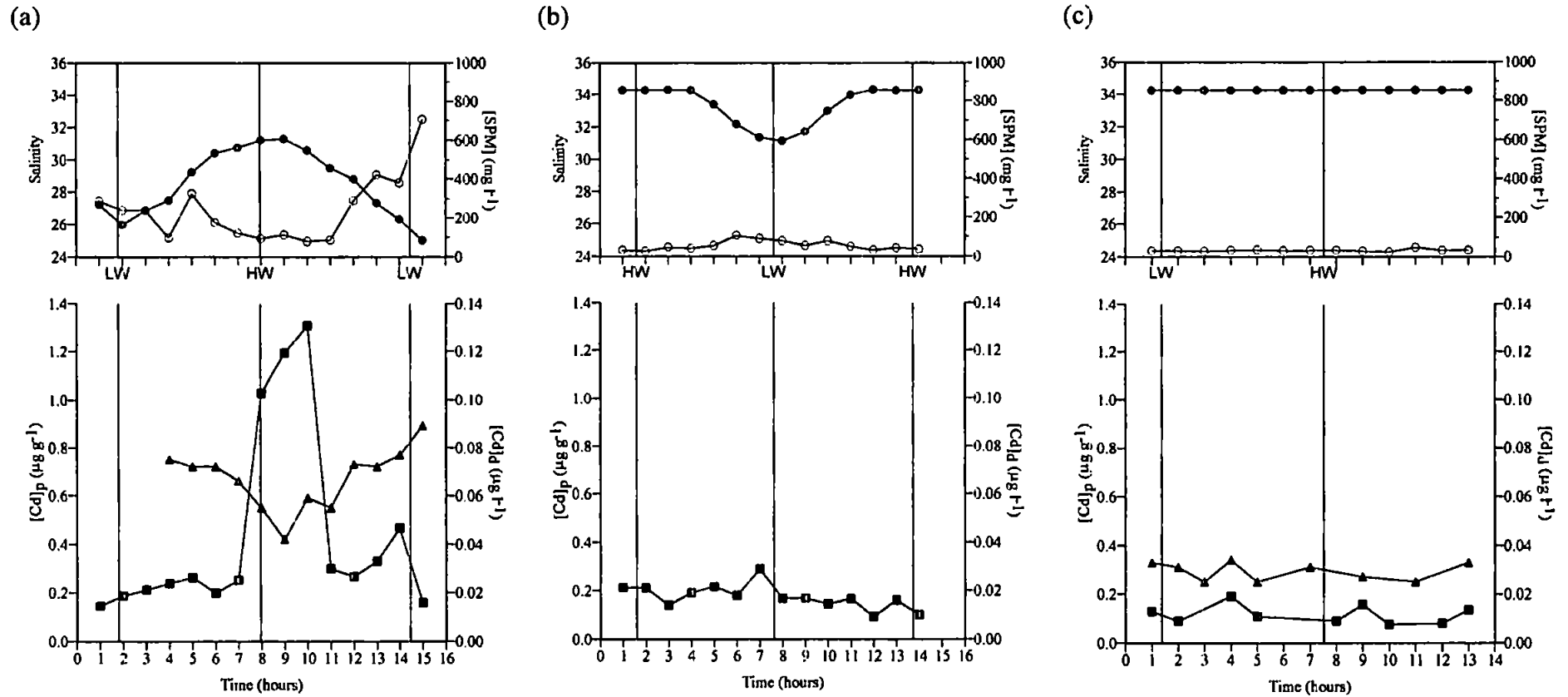


Figure 3.22 Salinity (●), concentration of SPM (○), Cd_p (■) and Cd_d (▲) as a function of time obtained during an anchor station (a) in the mouth of the Humber Estuary (HW5 - see Figure 2.3), (b) north of Spurn Head (HW3a - see Figure 2.3) and (c) adjacent to the Holderness Cliffs (S2 - see Figure 2.3) during winter'95.

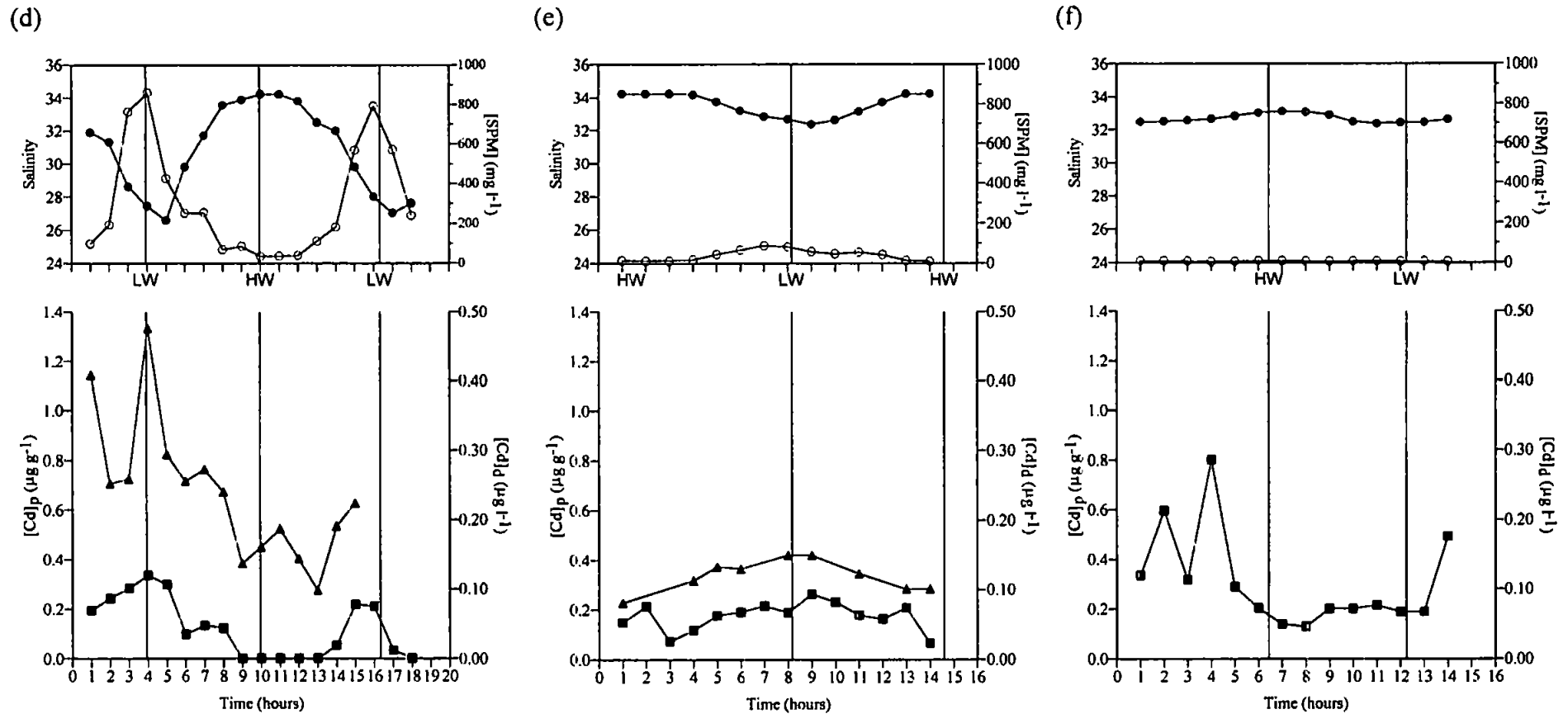


Figure 3.22 continued. Salinity (●), concentration of SPM (○), Cd_p (■) and Cd_d (▲) as a function of time obtained during an anchor station (d) in the mouth of the Humber Estuary (HW5 - see Figure 2.3), (e) north of Spurn Head (HW3a - see Figure 2.3) and (f) in the Wash embayment (HW13 - see Figure 2.3) during spring'95.

Table 3.10 Mean Cd_p and Cd_d concentrations over the anchor stations including input and output fluxes of Cd to and from the Humber Estuary.

Survey	Location ^a	Mean Cd concentrations		Cd Flux (kg day ⁻¹)		Humber Estuary			
		Particulate (µg g ⁻¹)	Dissolved (µg l ⁻¹)	Particulate	Dissolved	Output IAA [†] (kg day ⁻¹)	Input [*] (kg day ⁻¹)	Output IAA [†] (kg day ⁻¹)	Input [‡] (kg day ⁻¹)
Winter'88(1) ^a	HW5	0.33 ± 0.15	0.055 ± 0.018	0.79	1.68 (68)	1988-90		1994-95	
Winter'88(2) ^a	HW5	0.22 ± 0.12	0.067 ± 0.021	0.69	2.03 (75)	1.50	2.1-10.1	4.29	9.72
Spring'90 ^a	HW5	0.31 ± 0.23	0.075 ± 0.027	0.10	1.13 (92)				
Summer'90 ^a	HW5	0.32 ± 0.27	0.085 ± 0.020	0.01	0.66 (99)				
Autumn'94	HW5	0.25 ± 0.07	0.037 ± 0.024	1.21	0.52 (30)				
	S2	0.51 ± 0.21	nd						
Winter'95	HW5	0.44 ± 0.39	0.067 ± 0.013	2.87	2.47 (46)				
	HW3a	0.17 ± 0.05	n/a						
	S2	0.12 ± 0.04	0.029 ± 0.004						
Spring'95	HW5	0.19 ± 0.09	0.240 ± 0.100	1.80	7.16 (80)				
	HW3a	0.17 ± 0.06	0.120 ± 0.023						
	HW13	0.31 ± 0.19	n/a						
Summer'95	HW5	0.42 ± 0.56	0.161 ± 0.008	0.11	1.01 (90)				
	HW3a	0.17 ± 0.12	0.045 ± 0.020						
	Holderness Cliffs	0.13 ± 0.02 [‡]		0.50 [#]					

^aData previously shown in Millward & Glegg (1997) but fluxes have been recalculated due to revised residual outflows from the Humber Estuary, Wood, pers com; ^bFor sample locations refer to Figure 2.3; ^cAverage of 10 sample taken from the Holderness Cliffs during February'95 (see section 2.1.7); ^dAssuming a constant erosion rate of 140 x 10⁴ t a⁻¹ (McCave, 1987); ^eIntegrated annual average (IAA) of total Cd fluxes from the Humber Estuary to the North Sea. Calculated by assuming that for 1988-90 NSP data that each survey represented typical fluxes for a 4 month duration (an average was used for winter'88) and for the 1994-95 LOIS data that each survey represented typical rates for a 3 month duration; ^fTotal inputs into the Humber Estuary from rivers, industry and sewage sources - 1990 data (PARCOM, 1991) low and high loads respectively; ^gTotal inputs into the Humber Estuary from rivers, industry and sewage sources - 1992 data (NRA, 1993a & b). This was the most recent input flux data currently available for comparison with 1994-95 output flux data from the present LOIS study; nd denotes non detectable; n/a denotes data not available. Values in brackets indicate the % dissolved metal flux.

The concentration of Cd_d ranged between 0.037-0.240 $\mu\text{g l}^{-1}$ (Table 3.10) *cf.* literature values quoted in Table 1.6 for the Humber anchor stations. The NSP surveys showed average concentrations increasing from winter to summer *cf.* Cu_p section 3.3.2. Similarly LOIS surveys revealed pronounced increases in average Cd_d concentrations during spring and summer seasons (0.240 & 0.161 $\mu\text{g l}^{-1}$ respectively) compared to autumn and winter (0.037 & 0.067 $\mu\text{g l}^{-1}$ respectively). Indeed comparison of spring and summer surveys between the LOIS and NSP data shows a 2 and 3 fold increase in mean Cd_d concentrations respectively which cannot be attributed to subsequent increases in estuarine outflow (see Table 3.5). Examination of the temporal trends in Cd_d in the mouth of the Humber Estuary (Figure 3.22a & d) reveals a persistent increase in concentration around low water suggesting an estuarine source. Indeed significant inverse relationships are demonstrated for all surveys between Cd_d and salinity (Table 3.11). This result agrees with the seasonal relationships observed by Tappin *et al.* (1995) for the English coastal zone and Humber-Wash Plume between summer'88 and autumn'89, who further concluded that the concentrations of Cd_d were frequently higher in the Humber Plume compared to the rest of the southern North Sea and were largely influenced by salinity distributions. Balls (1985) and Althaus (1992) reported a similar control on Cd_d distributions in this area. Indeed Balls (1985) from the observed conservative behaviour of Cd_d in the Humber Estuary during spring'83 calculated a 'zero salinity end member' (ZSEM) concentration of 1.84 $\mu\text{g l}^{-1}$. Similar calculations with the NSP & LOIS data in spring'90 and spring'95 revealed comparable concentrations of 1.01 and 1.04 $\mu\text{g l}^{-1}$ respectively. Examination of the seasonal ZSEM concentrations shows up to a 4 fold increase in spring and summer seasons compared to autumn and winter. Balls (1985) subsequently reported that the calculated ZSEM for Cd was ca. 6-8 times higher than that reported for river waters entering the Humber Estuary (Gardiner, 1982) and thus attributed the elevated concentrations to industrial inputs.

In comparison the observed Cd_p concentrations at the anchor station in the Humber mouth can only be explained on the basis of their salinity distributions in autumn'94 and winter'95 LOIS surveys. Generally Cd_p concentrations did not exhibit any significant relationships with salinity, concentration of SPM, Fe_p or Mn_p (see Table 3.11). This suggested, contrary to Cu_p , that the geochemical cycling of Cd is not associated with Fe and Mn oxyhydroxide coatings on Humber estuarine SPM during any season. A

Table 3.11 Values of r for linear relationships between the concentration of Cd_p and Cd_d vs. salinity and the concentrations of SPM, Fe_p and Mn_p in the mouth of the Humber Estuary. Statistically significant ($P < 0.05$) correlation's are indicated in bold type.

Cruise		n	Salinity	SPM	Fe_p	Mn_p
Winter'88(1) ^a	Cd_p	9	0.68	0.41	-0.22	0.31
	Cd_d	11	-0.76	0.21	-0.37	-0.29
Winter'88(2) ^{a,b}	Cd_p					
	Cd_d	13	-0.85	0.56	-0.02	-0.67
Spring'90 ^a	Cd_p	10	-0.35	0.23	-0.11	-0.22
	Cd_d	13	-0.95	0.61	-0.74	0.03
Summer'90 ^a	Cd_p	9	0.08	0.37	-0.09	-0.20
	Cd_d	15	-0.92	0.74	0.82	0.89
Autumn'94	Cd_p	16	-0.75	0.68	0.45	0.48
	Cd_d	12	-0.77	0.76	-0.22	0.28
Winter'95	Cd_p	15	0.61	-0.45	0.10	0.01
	Cd_d	12	-0.82	0.75	-0.56	-0.35
Spring'95	Cd_p	12	-0.40	0.50	0.32	0.86
	Cd_d	15	-0.63	0.59	0.68	0.56
Summer'95	Cd_p	14	0.19	-0.31	-0.08	-0.09
	Cd_d	12	-0.58	-0.25	-0.44	-0.45

^aData taken from the NERC NSP CD-ROM (Lowry *et al.*, 1992; Millward *et al.*, 1996);

^bInsufficient data for correlation statistics.

significant positive correlation was obtained between Cd_p and chlorophyll a concentrations ($r=0.59$ for $n=12$, $P < 0.05$) during spring'95 for the Humber anchor station data *cf.* Cd_p concentrations from the whole of the western North Sea previously described in section 3.2.3. This further implies the preferred association of Cd with particulate matter of a biogenic nature as mentioned previously in section 3.4.1. This observation however may be somewhat fortuitous due to the lack of any supporting correlation between Cd_p and chlorophyll a concentrations in the following summer. Although it is possible that the Cd readsorbed onto decaying biogenic matter/detritus and hence the deviation from correlation with chlorophyll a concentrations.

The particulate and dissolved fluxes of Cd have been calculated according to the method outlined in section 3.3.2 and are given in Table 3.10. The flux of Cd_p exhibits a distinct seasonal trend of decreasing from winter through to summer periods for both the NSP and LOIS surveys. Similarly the flux of Cd_d also decreases throughout the year for the NSP data. The anomalously high Cd_d flux (7.16 kg day^{-1}) obtained during spring'95 obscures the aforementioned trend for the LOIS data and is attributed to a combination

of highly elevated Cd_d concentrations in the water column coupled with a relatively high residual water outflow and spring tidal range *cf.* Cu_p flux, Table 3.6. However total Cd fluxes have, similarly to total Cu fluxes, increased approximately by a factor of *c.* 2 when comparing respective winter and summer surveys and by a factor of *c.* 7 when comparing spring surveys. This indicates that the seasonal total Cd fluxes have increased in more recent LOIS sampling periods although this may be because recent surveys were conducted during larger tidal ranges i.e. 6.6 m during autumn'94 and spring'95 surveys compared to those of the NSP. The percentage of Cd transported in the dissolved phase also shows consistent seasonal variations increasing from winter (46-75%) through spring (80-92%) to summer (90-99%) in agreement with the trends observed for Cu (section 3.3.2). The fluxes of Cd_p and Cd_d have been plotted against the residual water outflow from the mouth of the Humber Estuary to the North Sea and are presented in Figure 3.23.

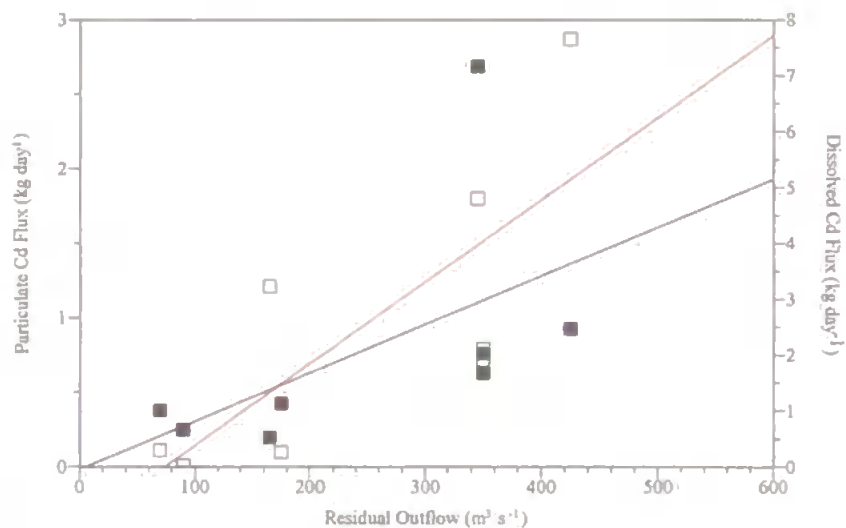


Figure 3.23 The flux of Cd_p (□, red line) and Cd_d (■, black line) as a function of residual water outflow from the mouth of the Humber Estuary.

A significant ($P < 0.05$) linear relationship was only observed between the flux of Cd_p (all data) and residual water outflow ($r = 0.76$), suggesting that the variability can largely be accounted for by the changes in residual water flow from the Humber Estuary. The Cd_d flux does however exhibit more scatter in the data possibly suggesting the influence of other factors such as tidal range as previously mentioned for the flux of Cu_p in section 3.3.2. Indeed if flux data from autumn'94 and spring'95 are excluded (as they both exhibit exceptionally large tidal ranges of 6.6 m compared to the other surveys, see Table

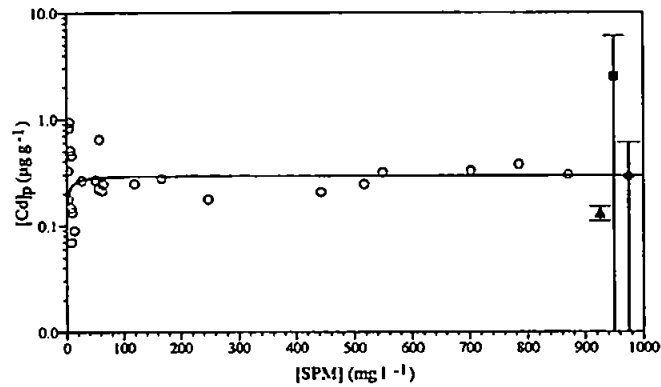
3.5) then (a) the correlation between the flux of Cd_d vs. outflow becomes significant ($r=0.95$, $P<0.05$) and (b) an increase in the significant correlation between Cd_p and outflow ($r=0.80$) is observed. This serves to illustrate the significance of tidal range, in addition to residual water outflow (at the mouth of the Humber Estuary) in explaining the variability in Cd fluxes. The observed relationship in Figure 3.23 in agreement with Cu fluxes (refer to Figure 3.15a) implies no transport of Cd_p across the mouth of the Humber Estuary if residual flows drop below approximately $80 \text{ m}^3 \text{ s}^{-1}$ i.e. typical summer conditions (Table 3.5). NB. The absence of spring tidal flux data i.e. autumn'94 and spring'95 does not significantly change the value of the x intercept. This is subsequently reflected by the lack of any correlation between the concentration of Cd_p and salinity during summer'90 and summer'95 for the Humber coastal zone (refer to Table 3.8).

A comparison of the IAA output (refer to section 3.3.2) of Cd from the Humber Estuary between the NSP and LOIS surveys periods reveals an almost 3 fold increase in the flux of total Cd emanating from the estuary during 1994/95. The total inputs (rivers, industry and sewage sources) into the Humber Estuary during 1992 (9.72 kg day^{-1} , NRA, 1993b) are within the range defined in 1990 ($2.1\text{-}10.1 \text{ kg day}^{-1}$, PARCOM, 1991) and when compared to respective output fluxes (see Table 3.10) indicates significant estuarine retention for Cd ranging between 29-85% in 1988-90 and 56% in 1994-95. *cf.* Cu section 3.3.2.

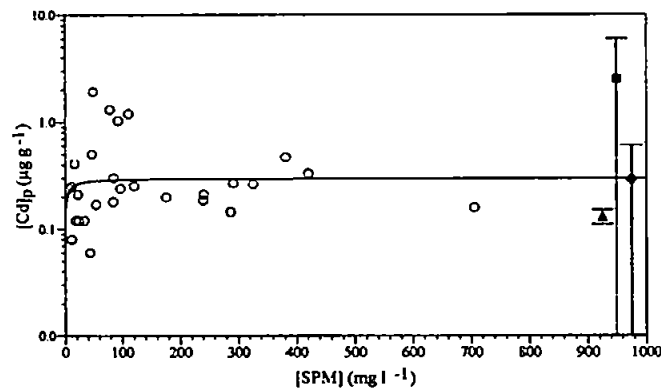
3.4.3 Predictive modelling of Cd concentrations in the coastal zone

In section 3.3.3 the Duinker model (Duinker, 1983) was described and the concentration of Cu_p subsequently plotted as a function of SPM concentration for samples from the Humber coastal zone. Similarly the concentrations of Cd_p found in the Humber coastal zone have been plotted against SPM concentration and are shown in Figure 3.24. The seasonal trends in Cd_p behaviour are not as well defined as those for Cu_p (refer to Figure 3.17). Two general patterns of behaviour are shown alternating between a distribution pattern that cannot easily be ascribed to a single group but rather shows traits of Group I and II type behaviour (autumn'94 & winter'95) and a Group I pattern (spring'95 & summer'95).

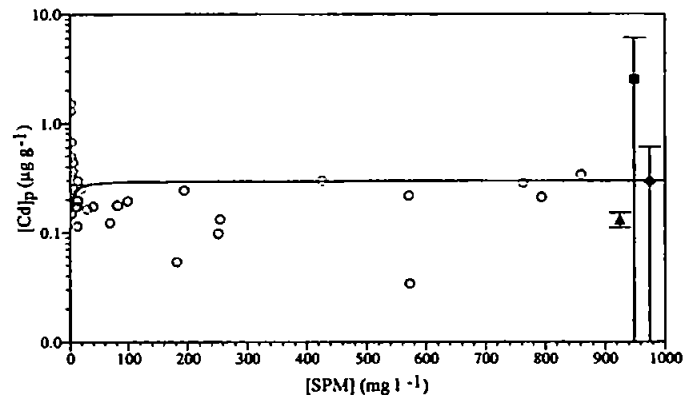
(a) Autumn



(b) Winter



(c) Spring



(d) Summer

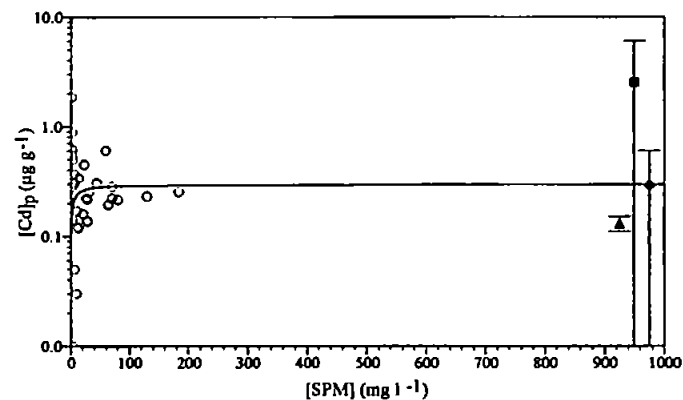


Figure 3.24 The concentration of Cd_p as a function of the concentration of SPM for samples collected in the Humber coastal zone (including Humber anchor station data) during (a) autumn'94, (b) winter'95, (c) spring'95 and (d) summer'95. Average Cd concentrations (± 1 SD) for the Humber Estuary (\blacklozenge), Plume (\blacksquare) and Holderness (\blacktriangle) sediments are also shown (see sediment data, Appendix D). The solid line represents modelled concentrations of Cd_p according to equation 3.2, see page 116 for the derivation of the 2 component end member model.

During autumn'94 and winter'95 SPM from the Humber Plume displayed varying Cd_p concentrations for any one particle concentration i.e. at SPM concentrations $<80 \text{ mg l}^{-1}$ corresponding high and low Cd_p levels were found. This behaviour perhaps reflects the mixing of different particle types including Humber Estuary particles, eroded Holderness Clay material and resuspension of Humber Plume sediments (see Figure 3.10) which are highly variable in Cd_p concentration as indicated in Figure 3.24. However on closer inspection during autumn'94 and winter'95 Cd_p samples originating from the Humber anchor station only (not the Plume) actually displayed Group III behaviour or rather constant Cd_p concentrations that largely reflect the same concentrations found in Humber Estuary sediments. Kersten *et al.* (1988) suggested that elements exhibiting Group III behaviour may have been associated with Fe and Mn oxide coatings, occurring in association with organic matter and clay minerals. This hypothesis was subsequently supported by the positive correlation between Mn and Group III Cd_p samples. In agreement a significant ($P<0.05$) positive relationship was found between Cd_p and Mn_p ($r=0.45$, $n=31$) for autumn'94 and winter'95 SPM samples originating from the mouth of the Humber Estuary.

During spring'95 Group I type behaviour (Figure 3.24c) was clearly exhibited by Cd_p in the coastal zone. This suggests that the more permanently suspended particle fraction contained higher concentrations of bound Cd. This phenomena has also been observed for Cd by Duinker *et al.* (1974) in the Dutch Wadden Sea, Kersten *et al.* (1988) in the North Sea and by James *et al.* (1993) in the Dover Strait. The former author also described particulate organic carbon and nitrogen as Group I elements perhaps suggesting that Cd_p during spring'95 is to a large extent associated with the organic fraction of the SPM (Duinker, 1983; Collier & Edmond, 1984; Kersten *et al.*, 1988; James *et al.*, 1993) as previously implied in sections 3.2.3 and 3.4.2. Indeed Dehairs *et al.* (1989) have shown accordingly that both living plankton and detrital organic matter are potentially a sorption site for Group I elements. In general Cd_p samples during summer'95 also demonstrated Group I behaviour except for three samples taken in the Humber Plume (refer to Figure 3.21g) that have Cd_p concentrations $<0.10 \mu\text{g g}^{-1}$ at SPM concentrations $<10 \text{ mg l}^{-1}$ indicating the heterogeneous nature of particles in the Plume region.

The different and somewhat complicated Cd_p signatures found in the Humber coastal zone are further reflected by the lack of any significant relationship with Fe_p and intense scatter in the data as displayed in Figure 3.25. This implies that Fe oxyhydroxides are generally not important carrier phases of Cd a view corroborated by James *et al.* (1993). It is therefore not surprising that the modelled Cd_p concentrations¹ in the Humber coastal zone (the model was previously described in section 3.3.3) as shown by the solid line in Figure 3.24 do not accurately represent the observed concentrations found with changing season. This presumably reflects the importance of particle populations other than those originating from the Humber Estuary and Holderness Cliffs (as assumed in the model described by Millward *et al.*, 1996) i.e. marine biogenic particles, resuspended coastal sediments etc. in controlling the distribution and concentration of Cd_p in the Humber coastal zone.

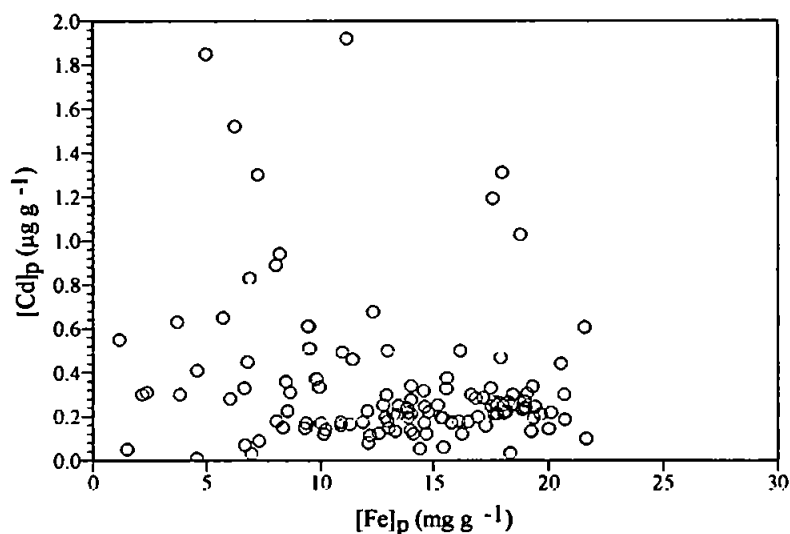


Figure 3.25 The concentration of Cd_p as a function of the concentration of Fe_p for samples collected in the Humber coastal zone (all seasons) where $r=-0.10$, for $n=125$ ($P<0.05$).

3.4.4 The distributions of Cd between the dissolved and particulate phases

The partitioning of Cd (expressed as $\log K_D$ - see section 3.3.4) at the mouth of the Humber Estuary as a function of SPM concentration is illustrated for the LOIS surveys in Figure 3.26a and the NSP surveys in Figure 3.26b. It is noticeable that unlike Cu

¹ the following end member concentrations were used based on the trace metal analysis of Holderness Clay material and average Cd_p and Fe_p concentrations observed at the Humber mouth anchor stations; $[SPM^{HC}] = 5 \text{ mg l}^{-1}$, $[Cd^{HC}] = 0.13 \text{ } \mu\text{g g}^{-1}$, $[Cd^{HE}] = 0.30 \text{ } \mu\text{g g}^{-1}$, $[Fe^{HC}] = 7.0 \text{ mg g}^{-1}$, $[Fe^{HE}] = 17 \text{ mg g}^{-1}$.

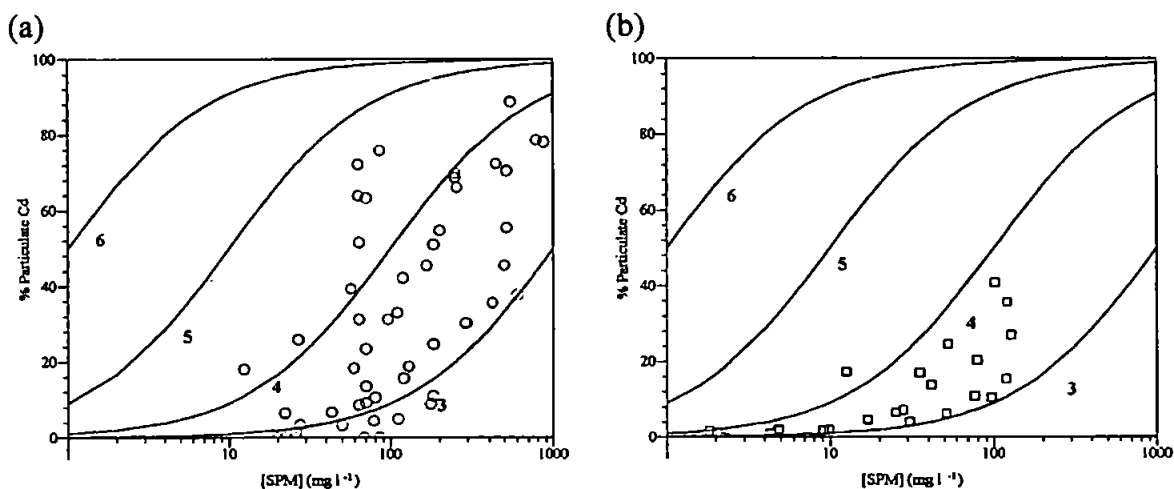


Figure 3.26 Percentage particle-bound Cd as a function of SPM concentration for samples collected at anchor stations in the mouth of the Humber Estuary during (a) the LOIS surveys autumn'94 (○), winter'95 (○), spring'95 (○) and summer'95 (○) and (b) the NSP surveys during winter'88 (□), spring'90 (□) and summer'90 (□). The lines represent log K_D values.

(section 3.3.4) the behaviour of Cd can not be described by a single value of log K_D but varies with season. During autumn'94 and winter'95 the % Cd in the particulate phase varies widely from 20-90% but all points can be described by a log K_D of approximately equal to 4 which compares with that found for Cu irrespective of season. This suggests that Cu and Cd (during autumn'94 and winter'95 only) appear to be held on easily exchangeable sites *cf.* log K_D for Fe and Mn between 7-8 & 5-6.5 respectively (Burton *et al.*, 1993; Tappin *et al.*, 1995) on lithogenous particles presumably dominant at the mouth of the Humber Estuary. During the following spring and summer months the log K_D value decreases to approximately 3 thus implying a diminished association with estuarine derived particles and hence an increase in the percentage of Cd in the dissolved phase. It is likely that any associated increase in K_D during spring and summer months due to preferential adsorption onto biogenic surfaces, as implied in previous sections, is thus not observed due to the mass dominance of lithogenous particles at the mouth of the Humber. Comparison of the LOIS data set to the NSP data set (Figures 3.26a & b respectively) shows a general agreement in the magnitude of log K_D i.e. approximately 3 but does not reveal the distinct range in SPM concentrations with season as seen during the NSP surveys. The other difference to note between the two data sets is that the percentage Cd in the particulate phase is consistently higher during the LOIS surveys compared to those of the NSP project. This possibly reflects the increase in concentration of SPM obtained during the former sampling times as a consequence of

larger tidal ranges and residual water outflow at the mouth of the Humber Estuary (refer to section 3.3.2, Table 3.5).

3.5 The Humber Coastal Zone - Lead

3.5.1 Particulate Pb distributions

The Pb_p concentrations in the Humber coastal zone have been contoured and are shown in Figures 3.27 a-f representing distributions observed during winter'88 and spring'90 NSP surveys (insufficient data to contour Pb_p distributions during summer'90) and autumn'94, winter'95, spring'95 and summer'95 LOIS surveys. During winter'88 sampling was restricted to the Humber Plume and showed concentrations of $Pb_p > 100 \mu g g^{-1}$ extending to the north Norfolk coast. The lack of samples taken adjacent to the Holderness coastline and further offshore somewhat restricts any further interpretation. During spring'90 high concentrations of Pb_p (of the order $100 \mu g g^{-1}$) were still evident just east of the Humber mouth but a gradient of concentrations decreasing to $< 20 \mu g g^{-1}$ offshore was observed *cf.* Cu_p distributions Figure 3.13b. This data suggests that the Humber Estuary is a source of Pb_p to the nearshore coastal zone. However linear regression analysis of Pb_p vs. salinity for the NSP surveys (see Table 3.12) and indeed for the LOIS surveys in the Humber coastal zone did not reveal any significant ($P < 0.05$) relationships indicating the unconservative nature of Pb_p and the influence of non estuarine sources. Significant linear positive relationships were shown for all surveys except winter'88 and winter'95 between Pb_p and Fe_p . Similar relationships were also present between Pb_p and Mn_p for spring'90, winter'95, spring'95 and summer'95 surveys consistent with the fact that Fe and Mn oxhydroxides are highly efficient scavengers of Pb and thus markedly influence its solid phase distribution (Mart *et al.*, 1982; Balls, 1985:1988; James *et al.*, 1993). Lead is also known to rapidly adsorb onto particulate phases following input from riverine systems (Elbaz-Poulichet *et al.*, 1984).

The Pb_p distributions during autumn'94 were patchy in nature and generally showed

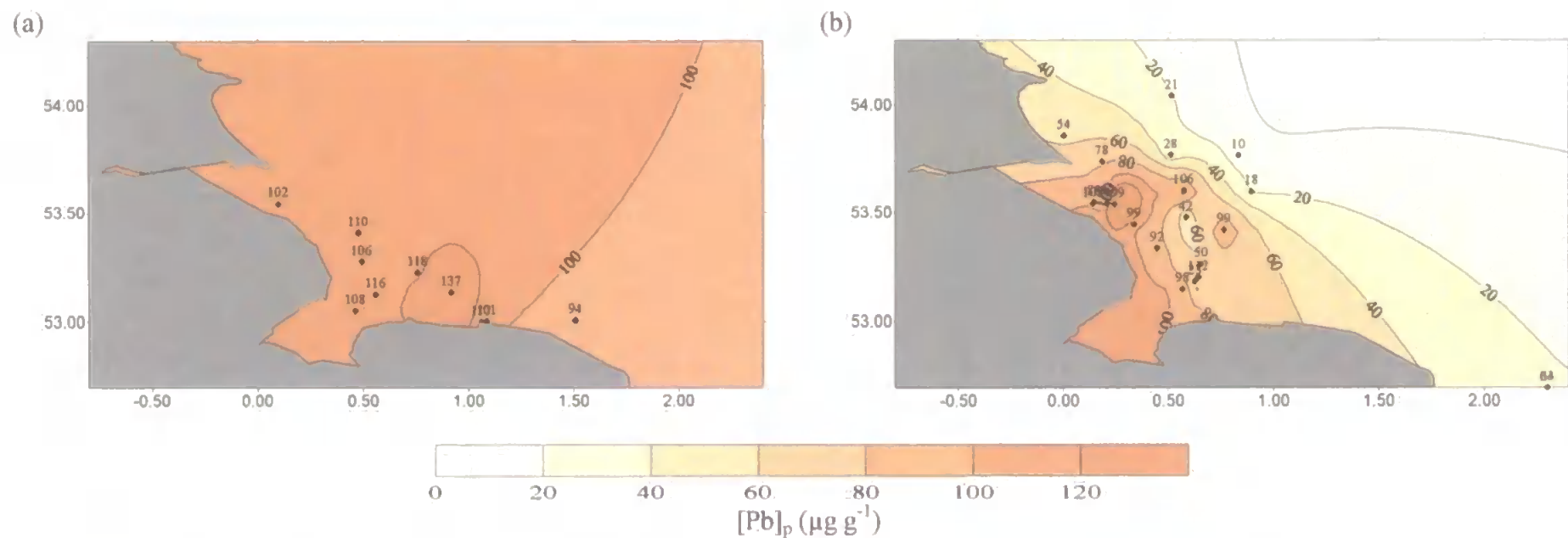


Figure 3.27 The contoured distributions of Pb_p in the Humber coastal zone during (a) winter '88 and (b) spring '90 NSP surveys. Insufficient data was available from the summer '90 survey to contour the Pb_p distributions. Data taken from the NERC North Sea project data set that is currently available on CD-ROM (Lowry *et al.*, 1992).

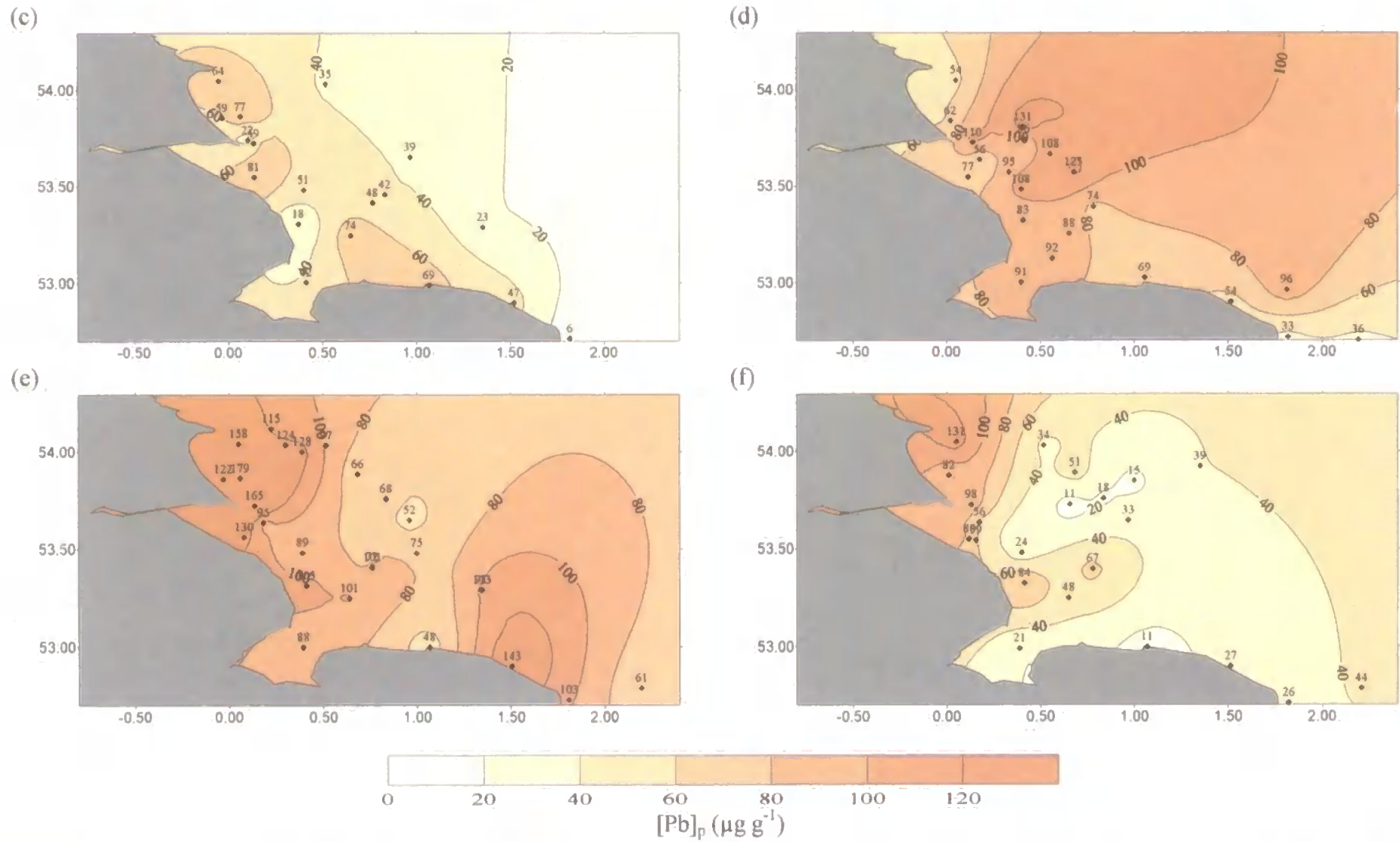


Figure 3.27 The distribution of Pb_p in the Humber coastal zone during (c) autumn '94, (d) winter '95, (e) spring '95 and (f) summer '95 present LOIS surveys.

Table 3.12 Values of r for relationships between the concentration of Pb_p vs. salinity and the concentrations of SPM, Fe_p and Mn_p in the Humber coastal zone. Statistically significant ($P < 0.05$) correlations are indicated in bold type.

Cruise	n	Salinity	SPM	Fe_p	Mn_p
Winter'88 ^a	9	0.30	-0.28	0.12	0.30
Spring'90 ^a	22	-0.30	0.12	0.53	0.48
Summer'90 ^{a,b}					
Autumn'94	17	0.26	-0.35	0.83	0.35
Winter'95	20	0.08	-0.55	0.14	0.62
Spring'95	25	0.06	0.07	0.61	0.71
Summer'95	21	-0.16	0.25	0.83	0.45

^aData taken from the NSP CD-ROM (Lowry *et al.*, 1992); ^bInsufficient data available for correlation statistics

concentrations $< 60 \mu\text{g g}^{-1}$ in the Humber coastal zone except for sampling locations in the mouth of the Humber Estuary and adjacent to the Holderness and Norfolk Cliffs i.e. sources of Pb_p , refer to Table 3.14 for corresponding flux data. Mart *et al.* (1980) also observed patchiness in their survey of Pb_p distributions in Belgian and Dutch coastal waters which they attributed to the tidal dispersion of lead inputs from rivers. During winter'95 Pb_p distributions interestingly showed enhanced concentrations ($> 100 \mu\text{g g}^{-1}$) further offshore that decreased with distance towards the Humber Estuary (to Pb_p concentrations $< 80 \mu\text{g g}^{-1}$). During this period the predominant winds originated from continental Europe (north easterly/easterly winds, 10-15 knots refer to Figure 3.3c & d) which have previously been shown to contain enhanced concentrations of trace metals, including Pb, relative to those from the north and west i.e. open North Sea and the UK respectively (Chester & Bradshaw, 1991; Rendell, 1992; Chester *et al.*, 1993). Atmospheric particulate matter from a continental dust-rich aerosol population was collected and analysed by Kersten *et al.* (1991a) who reported average Pb air concentrations of 52.6 ng m^{-3} . The average particle mass load was $50 \mu\text{g m}^{-3}$ thus giving particulate aerosol concentrations of the order $1052 \mu\text{g g}^{-1}$. Similar analysis by Fones (1997) similarly suggested that typical urban aerosols contained $2000 \mu\text{g g}^{-1}$ of Pb. Assuming that 87% of particulate aerosol Pb is leached by seawater (Fones, 1997) gives a typical seawater particulate concentration arising from atmospheric aerosol deposition between $137\text{-}260 \mu\text{g g}^{-1}$. This figure is very similar in magnitude to those observed offshore in the Humber coastal zone during spring'95 and suggests that atmospheric

deposition from continental winds could have augmented the observed Pb_p signal. This hypothesis is also in agreement with the findings of Tappin *et al.* (1995) for SPM samples taken in the southern North Sea during winter'88.

The following spring and summer'95 surveys, contrary to Cu_p and Cd_p distributions (see Figures 3.13f & g and 3.21f & g respectively) revealed plumes of Pb_p flowing out from the Humber Estuary. However highly elevated Pb_p concentrations ($>100 \mu g g^{-1}$) were also evident adjacent to the Holderness and Norfolk Cliffs during spring'95. Elevated concentrations of Cu_p were similarly reported in the aforementioned areas during spring'95 (refer to section 3.3.1, Figure 3.13f). It is feasible that the prevailing strong (15-20 knots) southerly winds dominate during this survey (see Figure 3.3e & f) could have assisted spreading the contaminated estuarine SPM (average Pb_p concentrations in the mouth of the Humber Estuary $130 \mu g g^{-1}$, see Figure 3.27e) north to areas neighbouring the Holderness Cliffs. Further enhancement of Pb_p concentrations due to inputs from the resuspension of Pb rich sediments (see Figure 3.12) are also possible, a process alluded to previously in section 3.3.1 to augment the Cu_p signals in the Humber coastal region. The Pb_p distributions during summer'95 are, similarly to autumn'94, patchy in nature reflecting the much reduced particulate flux from the Humber Estuary (see Table 3.14) and tidal state (Mart *et al.*, 1980).

The average concentrations of Pb_p in the Humber coastal zone for all the survey periods are shown in Table 3.13. For the NSP data it is difficult to assess the changes in the average concentration of Pb_p in the Humber coastal zone with season due to the severely limited number of samples taken during summer'90. Maximum concentrations ($112 \mu g g^{-1}$) were obtained during winter'88 with levels decreasing in spring'90 ($69 \mu g g^{-1}$).

For the LOIS data a clear seasonal trend was evident for the Humber coastal zone where average concentrations of Pb_p increased from autumn'94 to winter'95 and were greatest during spring'95 (45, 82 & $102 \mu g g^{-1}$ respectively) in agreement with the trend displayed for the entire LOIS coastal zone (refer to section 3.2.4). However this trend contrasts with the results published by Tappin *et al.* (1995) for the English coastal zone where maximum concentrations of Pb_p ($>250 \mu g g^{-1}$) were found during winter that decreased rapidly ($<50 \mu g g^{-1}$) in spring. The enhanced concentrations reported for the

Table 3.13 Mean and standard deviation (SD) of the concentration of Pb_p in the Humber coastal zone, Holderness Cliff material and in Humber Estuary sediments.

Cruise	N ^a samples	[Pb] _p ± SD (µg g ⁻¹) ^f	Coefficient of Variation (%)
SPM			
Winter'88 ^c	9	112 ± 12.3	11
Spring'90 ^e	22	69 ± 44	64
Summer'90 ^e	2	57 ± 34	60
Autumn'94	17	45 ± 20	44
Winter'95	20	82 ± 27	33
Spring'95	25	102 ± 34	33
Summer'95	21	47 ± 31	66
Holderness Cliff material ^b	10	13 ± 2.3	18
Humber sediments			
Humber mouth ^d	4	134 ± 41	31
Humber Estuary ^a	1	147	
Pre-industrial ^c	1	22	

^aSample number 6 taken from up the Humber estuary, refer to Figure 2.5; ^b10 samples of Holderness Cliff clay material, <63 µm particle size fraction; ^cMiddleton & Grant (1990); ^dAverage of all surface sediments collected from the mouth of the Humber Estuary (refer to Figure 3.12); ^eData taken from the NSP CD-ROM (Lowry *et al.*, 1992); ^fCompare with literature in Tables 1.4 & 1.6.

winter during the latter study were largely due to the incorporation of samples along the UK north-east coast including the Tees and Tyne estuaries, which have previously been identified in the LOIS coastal zone (refer to section 3.2.4) as exhibiting concentrations of Pb_p up to 200 µg g⁻¹. Indeed Balls (1985), Kersten *et al.* (1991) and Laslett (1995) similarly reported enhanced concentrations of Pb_p off the Tees and Tyne estuaries for summer'83, winter'87 and summer'91 respectively. The variability in Pb_p concentrations was highest during spring'90, summer'90 and summer'95 surveys whilst winter'88, winter'95 and spring'95 distributions were more uniform, possibly a consequence of the large Humber Estuary outflows (350, 425 & 345 m³ s⁻¹ respectively) and estuarine particulate matter dominating the Pb_p source to the coastal zone during these times.

The differences between average Pb_p concentrations obtained during winter for the NSP and LOIS surveys can not be easily reconciled by considering the respective output fluxes of Pb_p (see Table 3.14) from the Humber Estuary to the receiving coastal waters.

For example the flux of Pb_p from the mouth of the Humber Estuary during winter'95 is more than double that of winter'88 despite a lower average concentration of Pb_p in the Humber coastal zone. This implies that particulate matter emanating from the estuary has a high settling velocity and hence deposits quickly to nearshore sediments during winter'95. Indeed particle settling experiments from the mouth of the Humber Estuary (see Chapter 5) showed that particles obtained during the winter'95 ebb tide had a median settling velocity of 0.125 mm s^{-1} and hence under real field conditions in a 10 m water column i.e. typical of the mouth of the estuary and plume would settle to the bottom in <1 day. Thus particle settling of estuarine Pb_p inputs combined with subsequent dilution with Holderness and marine SPM of lower Pb_p concentrations (refer to Table 3.13) helps to explain the observed distributions. However, as previously mentioned, other inputs from atmospheric deposition and coastal cliff erosion are likely to have augmented the Pb_p signal during winter'95.

In summary the distributions of Pb_p in the Humber coastal zone are a complex function of the interaction of different particle sources characterised by different Pb_p concentrations. During each season the relative contribution of the different particle sources to the total SPM population are governed by the prevailing hydrodynamics and weather of the area.

3.5.2 Dissolved and particulate Pb at anchor stations

Typical particulate and dissolved Pb concentrations determined at the anchor stations in the Humber coastal zone for the LOIS surveys are shown in Figures 3.28a-f. Figures 3.28b & f show Pb_p distributions only (Pb_d concentrations were often very close to or below the detection limits in Figures 3.28a, c & e, refer to section 2.3.2, Table 2.8). A summary and discussion of the master variables for each anchor station including those performed during the NSP surveys has previously been given in Table 3.5 and section 3.3.2. The mean particulate and dissolved Pb concentrations determined at the anchor stations in the Humber coastal zone are shown in Table 3.14. The mean concentration of Pb_p ranged between $77\text{-}130 \mu\text{g g}^{-1}$ for the Humber anchor station and showed no distinct

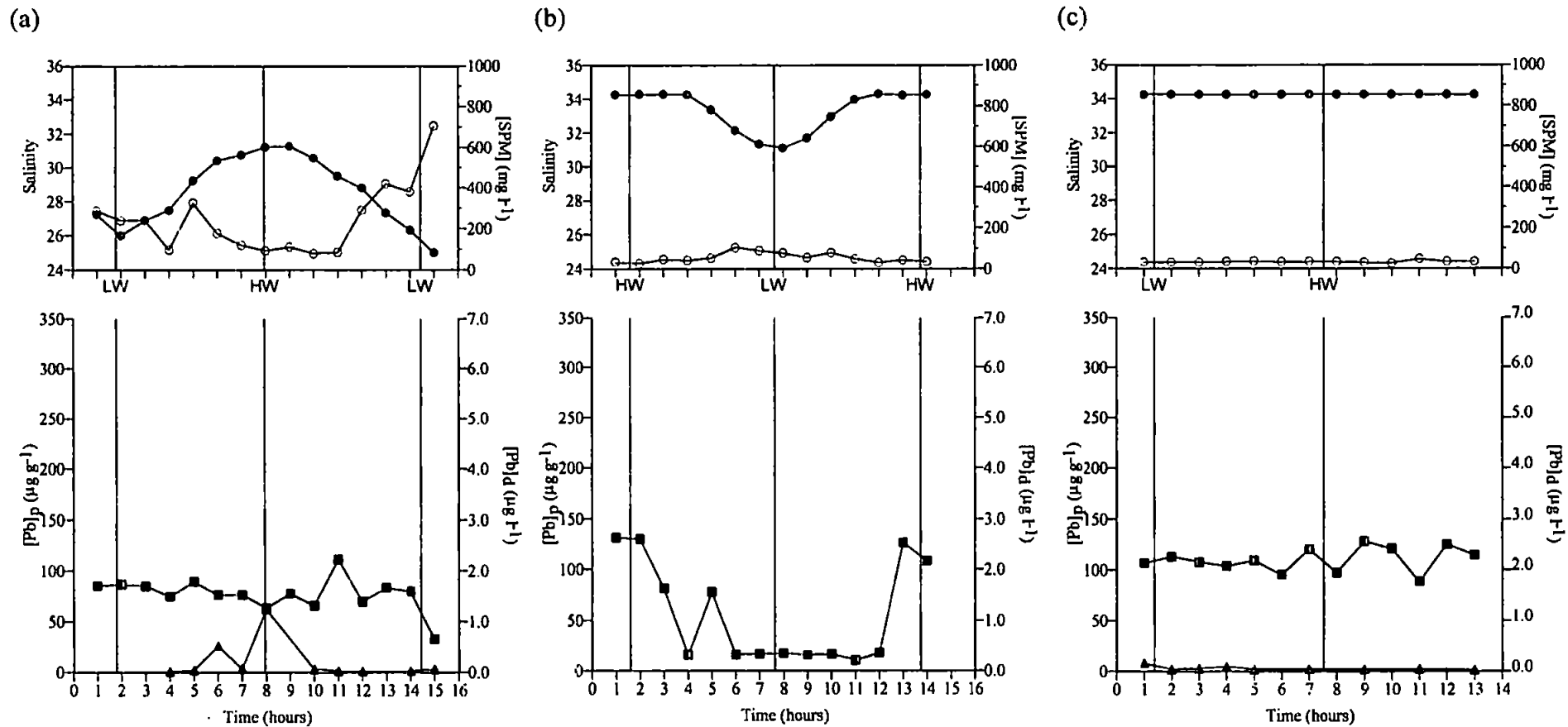


Figure 3.28 Salinity (●), concentration of SPM (○), Pb_p (■) and Pb_d (▲) as a function of time obtained during an anchor station (a) in the mouth of the Humber Estuary (HW5 - see Figure 2.3), (b) north of Spurn Head (HW3a - see Figure 2.3) and (c) adjacent to the Holderness Cliffs (S2 - see Figure 2.3) during winter'95.

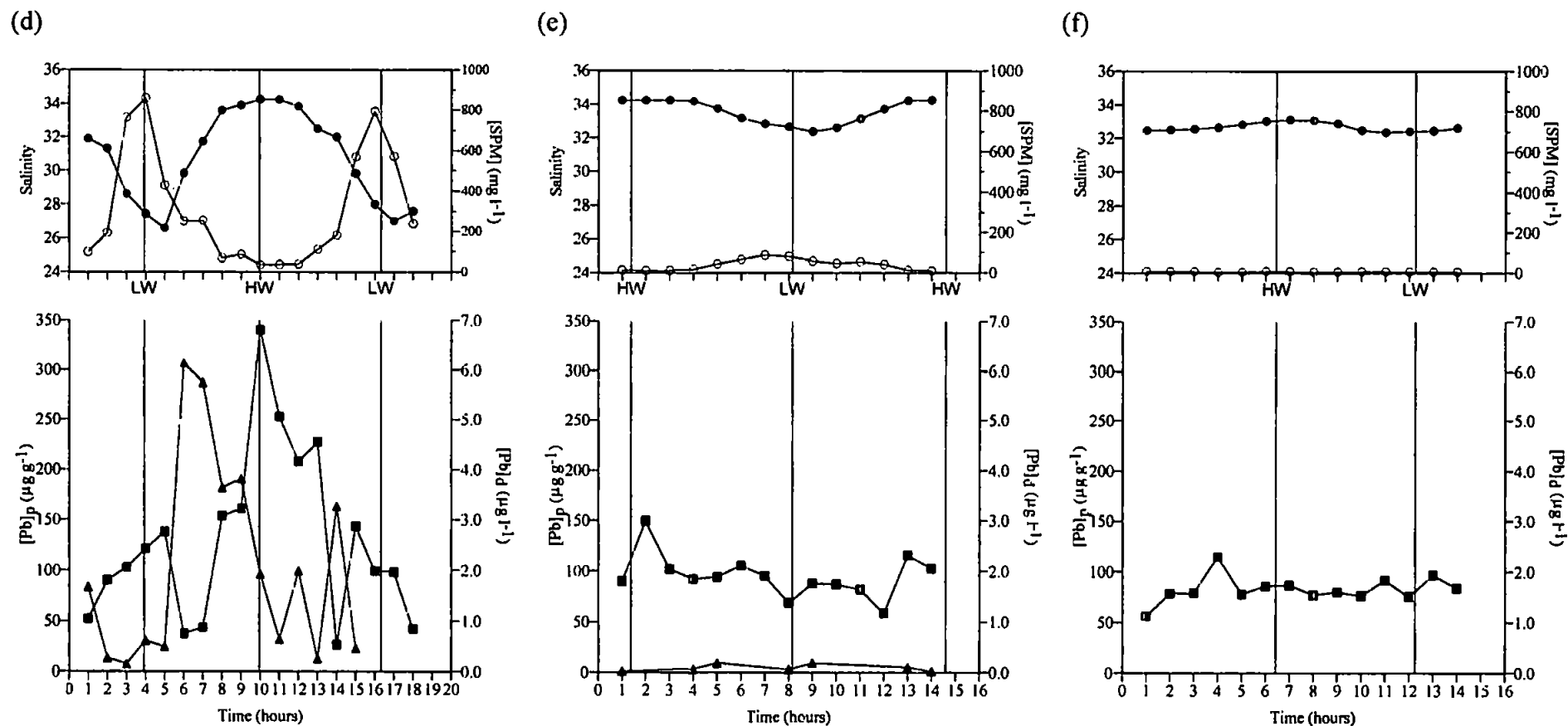


Figure 3.28 continued. Salinity (●), concentration of SPM (○), Pb_p (■) and Pb_d (▲) as a function of time obtained during an anchor station (d) in the mouth of the Humber estuary (HW5 - see Figure 2.3), (e) north of Spurn Head (HW3a - see Figure 2.3) and (f) in the Wash embayment (HW13 - see Figure 2.3) during spring'95.

Table 3.14 Mean Pb_p and Pb_d concentrations over the anchor stations including input and output fluxes of Pb to and from the Humber Estuary.

Survey	Location	Mean Pb concentrations		Pb Flux (kg day ⁻¹)		Humber estuary			
		Particulate (µg g ⁻¹)	Dissolved (µg l ⁻¹)	Particulate	Dissolved	Output IAA [†] (kg day ⁻¹)	Input [*] (kg day ⁻¹)	Output IAA [†] (kg day ⁻¹)	Input [†] (kg day ⁻¹)
Winter'88(1) ^a	HW5	96 ± 14	0.30 ± 0.20	167	9.0 (5)	<u>1988-90</u>		<u>1994-95</u>	
Winter'88(2) ^a	HW5	106 ± 7.9	0.04 ± 0.04	262	1.1 (0.4)	84	198-231	504	258
Spring'90 ^a	HW5	105 ± 29	0.04 ± 0.06	31	0.6 (2)				
Summer'90 ^a	HW5	81 ± 23	0.01 ± 0.01	1.7	0.1 (6)				
Autumn'94	HW5	81 ± 19	nd	313					
	S2	59 ± 28	nd						
Winter'95	HW5	77 ± 17	0.17 ± 0.37	618	6.3 (1)				
	HW3a	56 ± 50	n/a						
	S2	110 ± 12	0.06 ± 0.04						
Spring'95	HW5	130 ± 85	2.07 ± 2.01	983	62 (6)				
	HW3a	95 ± 21	0.09 ± 0.07						
	HW13	83 ± 13	n/a						
Summer'95	HW5	80 ± 31	0.07 ± 0.06	33	0.4 (1)				
	HW3a	56 ± 23	2.32 ± 1.78						
	Holderness Cliffs	13 ± 2.3 [‡]		50 [#]					

^aData previously shown in Millward & Glegg (1997) but fluxes have been recalculated due to revised residual outflows from the Humber Estuary, Wood, pers com; ^bFor sample locations refer to Figure 2.3; ^cAverage of 10 sample taken from the Holderness Cliffs during February'95 (see section 2.1.7); ^dAssuming a constant erosion rate of 140 x 10⁴ t a⁻¹ (McCave, 1987); ^eIntegrated annual average (IAA) of total Pb fluxes from the Humber Estuary to the North Sea. Calculated by assuming that for 1988-90 NSP data that each survey represented typical fluxes for a 4 month duration (an average was used for winter'88) and for the 1994-95 LOIS data that each survey represented typical rates for a 3 month duration; ^fTotal inputs into the Humber Estuary from rivers, industry and sewage sources - 1990 data (PARCOM, 1991) low and high loads respectively; ^gTotal inputs into the Humber Estuary from rivers, industry and sewage sources - 1992 data (NRA, 1993a & b). This was the most recent input flux data currently available for comparison with 1994-95 output flux data from the present LOIS study; nd denotes non detectable; n/a denotes data not available. Values in brackets indicate the % dissolved metal flux.

seasonal pattern. The maximum average concentration in the mouth of the Humber Estuary was obtained during spring'95 contrary to Cu_p and Cd_p (maximum average concentrations were found during summer'95 survey). The seasonal average concentrations of Pb_p were comparable between the NSP and LOIS surveys except perhaps during winter when concentrations during the latter study were approximately 30% lower than previously found. In general the mean Pb_p concentrations obtained during the anchor stations decreased with distance from the mouth of the Humber Estuary. This is illustrated in both winter'95 and spring'95 profiles when concentrations decreased from 77 and 130 $\mu g g^{-1}$ at the estuary mouth to 56 and 95 $\mu g g^{-1}$ respectively at Spurn Head. This presumably reflects the mixing and subsequent dilution of estuarine SPM with eroded Holderness Cliff material of lower Pb_p concentration (13 $\mu g g^{-1}$, see Table 3.13). There is however one exception to this trend during winter'95 when the average Pb_p concentration found at the anchor station adjacent to the Holderness Cliffs (S2) was approximately 43% greater than that found in the mouth of the Humber Estuary. The reason for this is not fully understood, however, further examination of the temporal trends (see Figure 3.28a & c respectively) reveals the lack of any discernible change in concentration with tidal state for either location. This suggests that the observed enhanced concentrations of Pb_p adjacent to the Holderness coast are not due to tidal pulsing events from the Humber Estuary but rather suggest alternative sources. The relatively low Pb_p concentration (13 $\mu g g^{-1}$, Table, 3.13) and associated daily flux (50 kg day⁻¹, Table 3.14) from the erosion of the Holderness Cliff material are unlikely to sustain the above increases in concentration. However the Pb_p SPM signal could have been further augmented by the resuspension of surface sediments (refer to Figure 3.12) or from diffuse atmospheric deposition arising from continental European air masses.

The concentration of Pb_d ranged between the limit of detection (0.012 $\mu g l^{-1}$, see Table 2.8) and 2.07 $\mu g l^{-1}$ for the Humber anchor stations (see Table 3.14). A clear seasonal trend was not evident from the NSP surveys due to the order of magnitude difference between the average Pb_d concentrations found at the Humber anchor station during the two surveys in winter'88. Otherwise the average concentrations for the NSP surveys were $\leq 0.04 \mu g l^{-1}$ and exhibited little short term temporal variability. This is in agreement with the findings of Tappin *et al.* (1995) for the southern North Sea and Balls (1985) for the English coastal zone. Indeed the aforementioned concentration of Pb_d is

very close to values reported for surface waters of the North Atlantic (e.g. Mart *et al.*, 1983; Schaule & Patterson, 1983; Boyle *et al.*, 1986). The average Pb_a concentrations found at the Humber anchor station during the recent LOIS surveys, in contrast to those of the NSP, showed a pronounced seasonal cycle of increasing concentrations from autumn'94 through to spring'95 before a decrease in summer'95. However the average concentrations found during spring were anomalously high ($2.07 \mu\text{g l}^{-1}$) compared to those of the former NSP surveys and the work of Balls (1985) and Tappin *et al.* (1995) in the Humber Estuary and coastal zone. Further examination of the temporal trend during spring'95 (see Figure 3.28d) revealed a sharp increase in Pb_a concentration (from <1.0 to $>6.0 \mu\text{g l}^{-1}$) just after low water with a gradual decrease on the subsequent flooding tide. The relatively small median particle size diameter of $54 \mu\text{m}$ obtained during the flood tide, (see Chapter 5, Table 5.4 & Figure 5.5f) perhaps indicates that some fine particulate matter ($<0.4 \mu\text{m}$) could have passed through the filter. This Pb could have been subsequently released into solution following acidification of the dissolved samples (refer to Chapter 2, section 2.1.3) and may explain the observed enhanced Pb_p concentrations (Duinker & Kramer, 1977). Anchor stations away from the Humber mouth generally displayed much lower average Pb_a concentrations although the uncertainty in spring'95 and to some extent winter'95 data makes subsequent comparisons questionable. Noticeably the average concentration of Pb_a at the anchor station near Spurn Head (HW3a, see Figure 2.3) during summer'95 ($2.32 \mu\text{g l}^{-1}$) was also significantly enhanced compared to other anchor stations. Concentrations $>3.0 \mu\text{g l}^{-1}$ were generally found during the flooding tide. However the lack of corresponding median particle size information and the somewhat haphazard temporal trend suggests methodological or analytical errors possibly contamination of samples.

The inter-parameter relationships between Pb_p and Pb_a vs. salinity, concentration of SPM, Fe_p and Mn_p for the Humber anchor stations are shown in Table 3.15. It is apparent that for Pb_a , unlike Cu_a and Cd_a (sections 3.3.2 & 3.4.2 respectively) there is no general relationship with salinity (in agreement with Balls, 1985), except during the summer'90 survey. In fact it is difficult to draw any trends or conclusions about the geochemistry of Pb from the correlation table due to the apparent randomness of all the significant inter-relationships. The surprising lack of significant correlations between the concentration of Pb_p and concentration of SPM i.e. Pb distributions are generally

Table 3.15 Values of *r* for linear relationships between the concentration of Pb_p and Pb_d vs. salinity and the concentrations of SPM, Fe_p and Mn_p in the mouth of the Humber Estuary. Statistically significant (*P*<0.05) correlation's are indicated in bold type.

Cruise		n	Salinity	SPM	Fe _p	Mn _p
Winter'88(1) ^a	Pb _p	9	-0.47	0.43	0.07	-0.55
	Pb _d	11	-0.32	0.14	-0.68	-0.13
Winter'88(2) ^a	Pb _p	13	-0.59	0.28	-0.46	-0.10
	Pb _d	13	0.25	-0.27	0.39	0.50
Spring'90 ^a	Pb _p	9	0.68	-0.85	0.84	0.72
	Pb _d	13	0.45	-0.54	0.38	0.01
Summer'90 ^a	Pb _p	9	-0.48	0.59	0.48	0.57
	Pb _d	15	0.90	-0.72	-0.90	-0.89
Autumn'94	Pb _p	16	0.26	-0.33	0.47	0.62
	Pb _d ^b					
Winter'95	Pb _p	15	0.16	-0.47	0.74	0.75
	Pb _d	12	0.48	-0.28	0.16	-0.06
Spring'95	Pb _p	18	0.52	-0.32	-0.70	-0.24
	Pb _d	15	0.25	-0.33	0.05	-0.70
Summer'95	Pb _p	14	-0.88	0.48	0.88	0.92
	Pb _d	12	0.11	-0.62	-0.32	-0.37

^aData taken from the NERC NSP CD-ROM (Lowry *et al.*, 1992; Millward *et al.*, 1996);

^bInsufficient data for correlation statistics.

dominated by the particulate phase (Balls, 1985) further suggests the importance of Pb_p sources other than those originating from the Humber Estuary itself i.e. aeolian deposition and the resuspension of bed sediments.

The particulate and dissolved fluxes of Pb have been calculated according to the method outlined in section 3.3.2 and are given in Table 3.14 . The flux of Pb_p decreased from winter'88 through to summer'90 for the NSP surveys as the mean concentration of SPM and residual outflow from the Humber mouth similarly decreased. This trend is in contrast to the LOIS surveys where the maximum Pb_p flux from the estuary occurred during spring'95. However this can similarly be explained by a much enhanced average concentration of SPM (310 mg l⁻¹, see Table 3.5) principally due to the large spring tidal range in combination with a relatively high residual outflow from the mouth of the estuary (345 m³ s⁻¹, see Table 3.5). Indeed similarly to Cu (refer to section 3.3.2), the fluxes of total Pb were between 2-30 times higher during LOIS surveys compared to their NSP counterparts. However unlike Cu and Cd, the % of Pb transported in the dissolved phase only ranged between 0.4-6% and showed no distinct variation with

season again inferring that the water column Pb budget was dominated by the particulate phase.

The fluxes of Pb_p and Pb_d have been plotted against the residual water outflow from the mouth of the Humber Estuary to the North Sea and are presented in Figure 3.29. A significant ($P < 0.05$) linear relationship was only observed between the flux of Pb_p and residual water outflow ($r = 0.67$). The Pb_d flux does not exhibit a significant correlation suggesting the influence of other factors e.g. tidal range. However if flux data from autumn'94 and spring'95 are excluded (as they both exhibit exceptionally large tidal ranges of 6.6 m compared to the other surveys, see Table 3.5) then (a) the correlation between the flux of Pb_d vs. outflow becomes significant ($r = 0.68$, $P < 0.05$) and (b) an increase in the significant correlation between Pb_p and outflow ($r = 0.82$) is observed. The fluxes of both Pb_p and Pb_d exhibit significant ($P < 0.05$) positive relationships when plotted against tidal range ($r = 0.66$ & 0.76 respectively) serving to illustrate the importance of tidal regime, in addition to residual water outflow, in explaining the variability in Pb fluxes. The observed relationship in Figure 3.29 is in agreement with Cu and Cd flux data (refer to Figures 3.15 & 3.23 respectively) implies no transport of Pb_p across the mouth of the Humber Estuary if residual flows drop below approximately $70 \text{ m}^3 \text{ s}^{-1}$ i.e. typical summer outflows (Table 3.5). NB. The absence of spring tidal flux data i.e. autumn'94 and spring'95 does not significantly change the value of the x intercept.

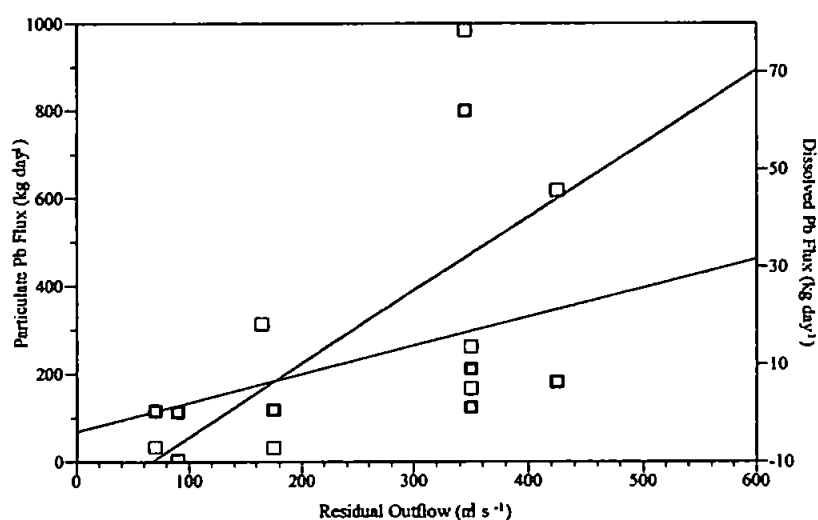


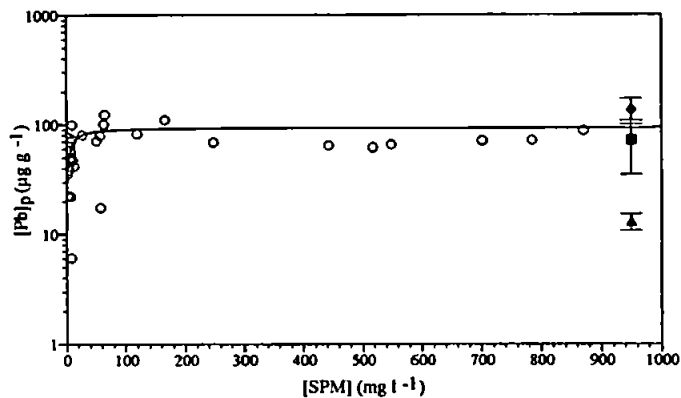
Figure 3.29 The flux of Pb_p (\square , red line) and Pb_d (\square , black line) as a function of residual water outflow from the mouth of the Humber Estuary.

A comparison of the IAA output (refer to section 3.3.2) of Pb from the Humber Estuary between the NSP and LOIS surveys periods reveals a 6 fold increase in the flux of total Pb emanating from the estuary during 1994/95 compared to 1988-89. The total inputs (rivers, industry and sewage sources) into the Humber Estuary have also slightly increased during 1992 compared to 1990 data (refer to Table 3.14). During the period 1988-90 comparison of input and output fluxes suggest substantial estuarine retention (58-63%) of Pb (Millward & Glegg, 1997). However, the highly elevated output Pb flux calculated during the LOIS surveys suggests that more Pb is being exported from the Humber Estuary to the North Sea than can be explained by inputs from rivers, industry and sewage sources. This suggests that the Humber Estuary is itself a source of Pb i.e. contaminated bed sediments resulting from years of anthropogenic/industrial waste deposition/discharge (Millward & Glegg, 1997). However to the contrary there is not any evidence of high Pb_p in Humber Estuary sediments shown in Figure 3.12.

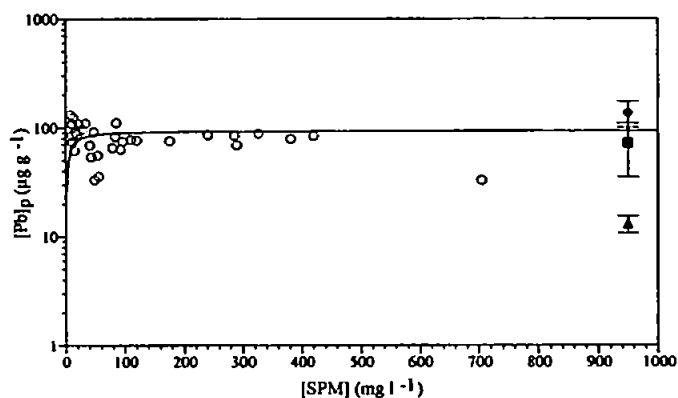
3.5.4 Predictive modelling of Pb concentrations in the coastal zone

In a similar manner to Cu_p and Cd_p the concentrations of Pb_p in the Humber coastal zone during the LOIS surveys have been plotted as a function of the concentration of SPM and are shown in Figure 3.30. The plot indicates that, in contrast to Cu_p and Cd_p, the concentrations of Pb_p exhibit Group II behaviour during autumn'94, winter'95 and summer'95 i.e. the larger denser SPM fraction has a higher content of Pb in agreement with the trend displayed by Fe_p (see Figure 3.18), but switch to a Group I type during the spring *cf.* Cd_p during spring'95 (see Figure 3.24c). This lends further support to the suggestion that Pb generally associates with Fe oxyhydroxide surfaces of particles (section 3.5.1). However clear deviation from this behaviour is apparent during spring'95 when concentrations of Pb_p >100 µg g⁻¹ occur at low SPM concentrations (<100 mg l⁻¹). These samples originated from the mouth of the Humber Estuary and at locations adjacent to the Holderness Cliffs (see Figures 3.28j & 3.27e respectively) and have previously been explained by an enhanced estuarine Pb_p flux (see section 3.5.2, Table 3.14) emanating from the mouth of the Humber Estuary and being pushed north adjacent to the Holderness Cliffs by the predominate strong southerly winds (see Figure 3.3e & f), in addition to the possible resuspension of estuarine bed sediments.

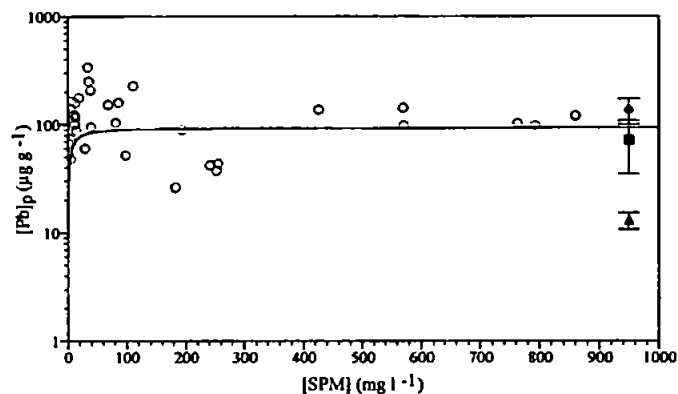
(a) Autumn



(b) Winter



(c) Spring



(d) Summer

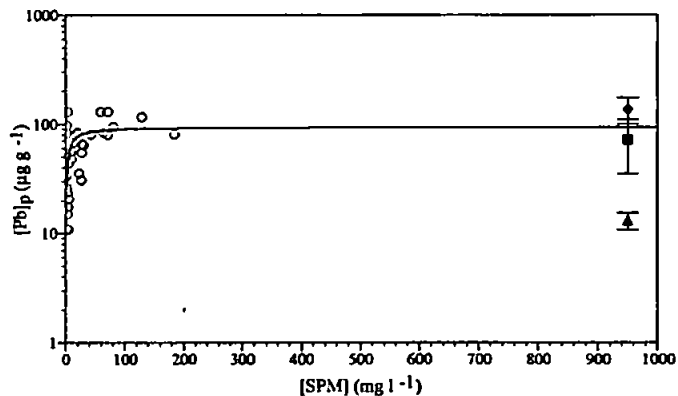


Figure 3.24 The concentration of Pb_p as a function of the concentration of SPM for samples collected in the Humber coastal zone (including Humber anchor station data) during (a) autumn'94, (b) winter'95, (c) spring'95 and (d) summer'95. Average Pb concentrations (± 1 SD) for the Humber Estuary (\blacklozenge), Plume (\blacksquare) and Holderness (\blacktriangle) sediments are also shown (see sediment data, Appendix D). The solid line represents modelled concentrations of Pb_p according to equation 3.2, see page 116 for the derivation of the 2 component end member model.

The concentrations of Pb_p were subsequently plotted as a function of Fe_p for all samples originating from the Humber coastal zone and anchor stations (Figure 3.31). However a number of samples collected during spring'95 at the Humber anchor station (as indicated by ● in Figure 3.31) showed a significant different Fe signature to the other surveys. Excluding this Pb_p data, a significant correlation ($P<0.05$) was found between Pb_p and Fe_p ($r=0.72$) and is shown by the solid line in Figure 3.31. Clearly a number of SPM samples taken during spring'95 have enhanced concentrations of Pb_p then can not be explained by association with Fe oxides again, inferring a different source signature of Pb.

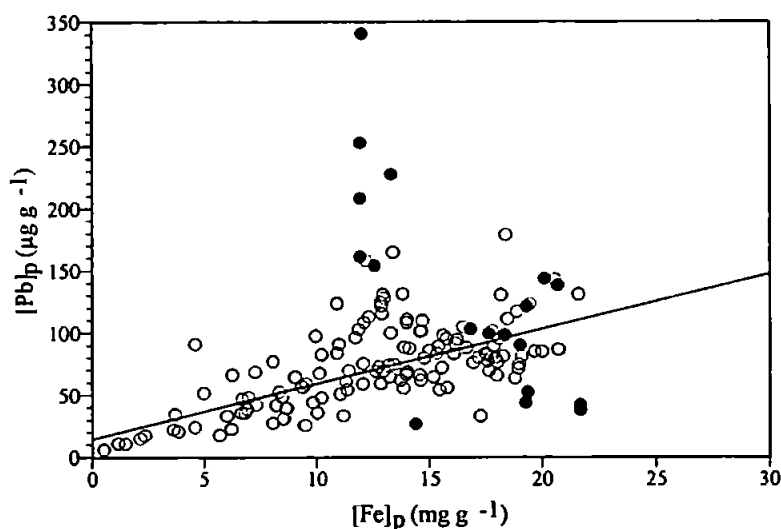


Figure 3.31 The concentration of Pb_p as a function of the concentration of Fe_p for samples collected in the Humber coastal zone (all seasons) where $r=0.63$ for $n=128$. (●) indicates data from the Humber Estuary anchor station from spring'95..

To investigate further, the concentrations of Pb_p were plotted as a function of Mn_p concentrations (Figure 3.32) and again indicated that some samples taken during spring'95 exhibited a different geochemical signature compared to the other surveys i.e. generally lower and more variable Mn_p concentrations. This figure also illustrates the significant ($P<0.05$) positive relationship found between Pb_p and Mn_p ($r=0.67$) (excluding spring'95 data) inferring, that in addition to Fe oxides, Mn oxides also appear to be highly efficient scavengers of Pb as previously mentioned in section 3.5.1.

The trend displayed in Figure 3.30 does suggest that, contrary to Cd_p (section 3.4.3), the distributions of Pb_p in the Humber coastal zone can largely be explained by the mixing of anthropogenically modified estuarine SPM rich in Pb_p with relatively uncontaminated

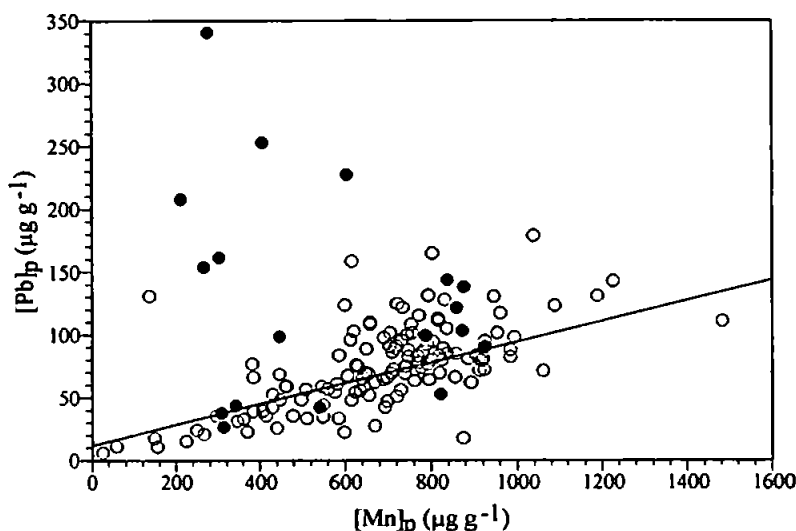


Figure 3.32 The concentration of Pb_p as a function of the concentration of Mn_p for samples collected in the Humber coastal zone (all seasons) where $r = 0.63$ for $n=128$ ($P < 0.05$). (●) indicates data from the Humber Estuary anchor station from spring'95..

eroded Holderness Cliff material ($13 \mu\text{g g}^{-1}$). Hence a good agreement was found between the modelled concentrations of Pb_p in the Humber coastal zone¹ (as indicated by the solid line in Figure 3.30) and the actual data for all seasons except spring. However, as with Cu_p distributions (section 3.3.3), caution is advised when attempting to use such a simple two component end member model to accurately predict the seasonal distribution of Pb_p as it neglects to include other inputs as clearly shown in the spring'95 data i.e. bed resuspension, diffuse atmospheric deposition etc.

3.5.3 The distributions of Pb between the dissolved and particulate phases

Figure 3.33a & b shows the partitioning (expressed as $\log K_D$) of Pb as a function of SPM for the anchor station located in the mouth of the Humber Estuary for the LOIS and NSP surveys respectively. The $\log K_D$ values were generally very high (of the order of 6 for the LOIS studies) and agree with the results of Tappin *et al.* (1995) for the southern North Sea who attributed the enhanced values to the markedly high concentrations of Pb_p in the water column. There is no distinct seasonal variation in K_D values in either data set and, in fact, if spring'95 data is neglected the partitioning of Pb

¹ the following end member concentrations were used based on the trace metal analysis of Holderness Clay material and average Pb_p and Fe_p concentrations observed at the Humber mouth anchor stations; $[SPM^{HC}] = 5 \text{ mg l}^{-1}$, $[Pb^{HC}] = 13 \mu\text{g g}^{-1}$, $[Pb^{HE}] = 94 \mu\text{g g}^{-1}$, $[Fe^{HC}] = 7.0 \text{ mg g}^{-1}$, $[Fe^{HE}] = 17 \text{ mg g}^{-1}$.

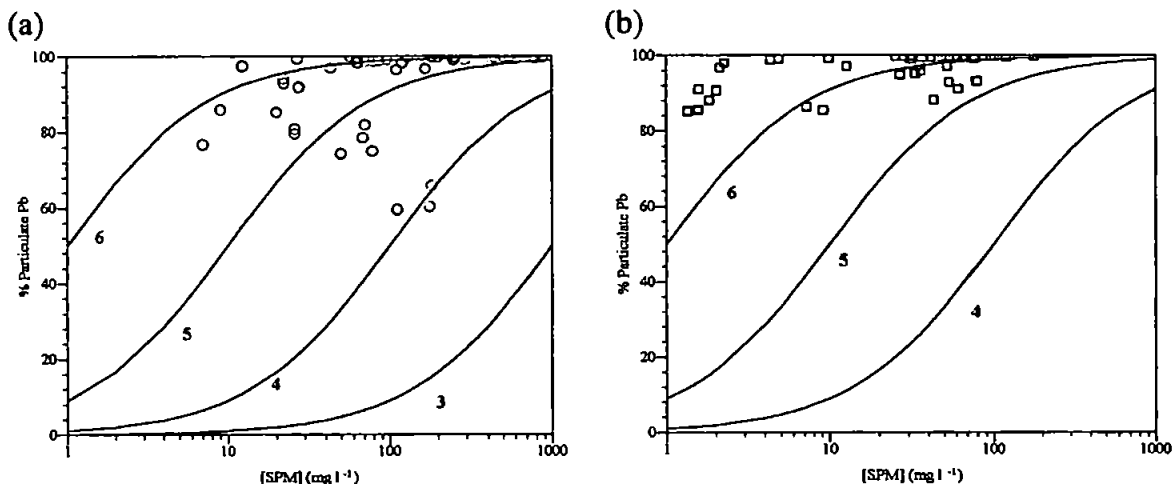


Figure 3.33 Percentage particle-bound Pb as a function of SPM concentration for samples collected at anchor stations in the mouth of the Humber Estuary during (a) the LOIS surveys autumn'94 (○), winter'95 (○), spring'95 (○) and summer'95 (○) and (b) the NSP surveys during winter'88 (□), spring'90 (□) and summer'90 (□). The lines represent log K_D values.

during the LOIS surveys can be described by a single value of K_D (of the order 10^6). It is interesting to note that the anomalous spring'95 data originating from samples taken around high water in the mouth of the Humber Estuary (as mentioned in section 3.5.2) have K_D 's at least one order of magnitude lower than the other samples again indicating the different nature and origin of these particles. The dominance of the particulate phase is also clearly illustrated for both NSP and LOIS data sets as mentioned in previous sections.

3.6 Comparative Behaviour of Copper, Cadmium and Lead in the Humber Coastal Zone

Distinct seasonal variations in the average concentrations of Cu_p , Cd_p and Pb_p were observed in the Humber coastal zone that were largely a consequence of the reactivity of the trace metal towards lithogenic and biogenic particles and their relative contributions to the total particulate matter in the water column. For example the average concentrations of both Cu_p and Cd_p increased from autumn'94 through to summer'95 reflecting the enhanced association of both metals with organic/biogenic matter i.e. phytoplankton and organic detritus that increased in relative proportion to lithogenic particles in the coastal zone during summer. In contrast the distribution of Pb_p was

clearly controlled by the quantity of SPM in the water column and hence enhanced concentrations were observed at times of maximum SPM concentrations i.e. winter'95 and spring'95. The calculated fluxes of particulate and dissolved Cu, Cd and Pb were shown to correspond to changes in residual water outflow and tidal regime at the mouth of the Humber Estuary. The relationship between the particulate fluxes of Cu, Cd and Pb and residual water outflow further inferred that during low residual water outflow regimes ($<80-100 \text{ m}^3 \text{ s}^{-1}$) e.g. those typically experienced during summer months the particulate flux of the aforementioned metals from the mouth of the Humber Estuary to the North Sea was effectively negligible. Hence there is an increase in the relative proportion of biogenic particles contributing to the total particle population in the Humber coastal zone during summer'95.

Application of the Duinker model to Cu_p , Cd_p and Pb_p in the Humber coastal zone also reflected the different reactivities of the trace metals. For example Cu_p demonstrated Groups II & III behaviour during autumn'94, winter'95 and spring'95. However a switch to Group I character was displayed during summer'95. This was attributed to an association of Cu with the organic fraction of the SPM population which is dominant only under low total SPM concentrations in the Humber coastal zone i.e. minimal estuarine SPM discharges as discussed above. Particulate Cd showed mixed responses that could not be ascribed to one Group during autumn'94 and winter'95. However during spring'95 and summer'95 Cd_p displayed Group I behaviour presumably reflecting preferential association with particulate organic fractions. Particulate Pb generally showed Group II behaviour for all seasons i.e. increasing Pb_p concentrations associated with increasing quantities of SPM but likewise to Cd_p clearly indicated a switch to Group I during spring. Deviations from the generalised behaviour trends were shown for all metals studied which were attributed to additional inputs of metals e.g. bed resuspension, aeolian deposition etc. not included in the model. Such additional sources occur with considerable seasonal and short term variability making their specific identification from present observations difficult (Burton *et al.*, 1993). The distribution of total metal concentration between the particulate and dissolved phase varied for the three elements. The distributions of Cu and Pb showed no change with season for samples taken at the mouth of the Humber Estuary. Lead was dominated by its association with particulate material ($\log K_D$ of 6), while Cu was more intermediate in behaviour ($\log K_D$ of 4).

Cadmium showed the reverse behaviour to Pb ($\log K_D$ of 4 during autumn and winter, $\log K_D$ 3 during spring and summer), existing almost totally in the dissolved phase (except during autumn'94 and winter'95) and displaying changes with season.

An extensive database derived from the concurrent seasonal sampling of both particulate and dissolved Cu, Cd and Pb in the nearshore coastal waters of the western North Sea has been reported. It is the most comprehensive seasonal trace metal database established for this coastal zone. This study has provided many new insights into the important factors that influence the biogeochemical pathways and their consequences for seasonal variability in the concentrations and distributions of Cu, Cd and Pb in the Humber coastal zone. Furthermore, to effectively model the fate of these trace metals in shelf seas such extensive high quality seasonal databases are required for the initialisation and testing of model simulations. The data presented here offer significant potential for the further development and refinement of coupled hydrodynamic-biogeochemical water quality models of the Humber coastal zone (Tappin *et al.*, 1997).

4 Trace Metal Reactivity: Radiochemical Experiments

4.1 Introduction

The gamma emitting radiotracers ^{54}Mn , ^{109}Cd and ^{137}Cs were used as analogues of their stable metal counterparts (Anderson *et al.*, 1987) for studying their behaviour in the coastal waters of the western North Sea. The advantages of using radioisotopes include the simplicity and specificity of the analysis (Amdurer *et al.*, 1982) which offers rapid, contamination free and multi element determinations. In addition the high sensitivity necessitates only a small spike (typically 20-30 μl , see section 2.5) of the radioisotopes to an enclosed system, thereby minimising perturbation to the natural conditions (Turner *et al.*, 1992a). However, the limitations of using radioisotopes must not be overlooked. Firstly is the assumption that radioisotope analogues behave in the same manner i.e. react as their stable counterparts, although this has been demonstrated for freshwater systems (Anderson *et al.*, 1987). Secondly is the assumption of instantaneous equilibration with natural ligands, unless pre-equilibrated before sediment/sample addition, which is practically difficult if natural unfiltered samples are being used as in this study.

The trace metal analogues of Mn and Cd were chosen to compliment their stable dissolved and particulate trace metal distributions. The gamma emitting analogues of Fe, Cu and Pb were unfortunately not available for use in this study. The irreversible sorption of ^{137}Cs onto clay minerals particles has been suggested by many authors (Li *et al.*, 1984a; Comans *et al.*, 1991; Turner *et al.*, 1992a:1993:1994; Williams, 1995) and

attributed to the migration of ^{137}Cs ions into wedge and/or interlattice sites of clay minerals where access by other seawater cations is very limited (Sawhney, 1972; Charles & Prime, 1983; Evans *et al.*, 1983; Nyffeler *et al.*, 1984). This process is often referred to as 'fixation' (Smith & Comans, 1996) and in particular Cs^+ is thought to compete with K^+ for particle sorption sites owing to its similar charge and ionic radius (Evans *et al.*, 1983). Cesium was therefore considered to be of interest due to the large particle flux (see Chapter 3) of Holderness quaternary clay material (McCave, 1987) that is being eroded into the Humber coastal zone and hence ^{137}Cs was also studied.

The particle affinity of the aforementioned trace metals was subsequently assessed by the radiochemically derived K_D 's (refer to section 2.5.7), from herein referred to as K_D^5 where superscript '5' denotes the time of incubation in days (except for the productivity experiments where the incubation time was 1 day, refer to section 2.5.6). A five day incubation period was selected because previous experiments have established that this is a suitable period for Cd and Cs to attain quasi-equilibrium (Turner *et al.*, 1992a; Turner & Millward, 1994; Williams, 1995), although a more protracted first order reaction (with respect to Mn_d) has been shown for Mn in estuarine waters (Morris & Bale, 1979). Manganese, Cd and Cs display widely contrasting particulate and dissolved reactivities in seawater (Turner *et al.*, 1981; Turner *et al.*, 1992a; Turner & Millward, 1994). For example Mn is known to be relatively particle reactive in comparison to Cd and Cs as shown by typically higher K_D^5 's of 10^4 (Mn) compared to 10^2 (Cd & Cs) (Turner *et al.*, 1992a). The isotope ^{109}Cd has also shown significantly enhanced K_D^5 's during diatom and *Phaeocystis* blooms. Radioactive ^{137}Cs , despite having a similar K_D^5 to ^{109}Cd could not be detected in the plankton dominated samples (Turner *et al.*, 1992a). Interestingly ^{54}Mn displayed a marked contrast between its affinity for diatoms and *Phaeocystis*, the former showing K_D 's of an order of magnitude higher (Turner *et al.*, 1992a).

Previous studies (Turner *et al.*, 1992a;1993; Williams, 1995) have examined the partitioning of the ^{54}Mn , ^{109}Cd and ^{137}Cs in the southern North Sea and Humber-Wash coastal zone providing a good historical framework of reference. The current study compliments this work by providing a novel insight into the concurrent seasonal variation in K_D^5 's off the mouths of the Humber, Tees, Tyne and Tweed estuaries (see Figure 2.1 for locations). The variation of trace metal partitioning with particles differentiated by

their settling velocities is then examined in detail at the mouth of the Humber Estuary. Subsequently novel mixing experiments designed to investigate changes in particle reactivity as a function of the proportion of end member waters (refer to section 2.5.5 for further details) are reported. Finally novel productivity incubations designed to investigate the significance of biological uptake of trace metals in the highly turbid and dynamic Humber coastal zone are discussed. Experimental details for all radiochemical experiments performed are given in section 2.5.

4.2 Spatial And Seasonal Changes In K_D^5 For The Western North Sea

The outflow regions of estuaries including the mouth and plume represent the final stages of mixing between river water and seawater and hence warrant special attention when considering the land ocean interaction of trace metals (Turner *et al.*, 1992a). The differences in particle affinity, expressed in terms of the K_D^5 , off the mouths of the Humber, Tees, Tyne and Tweed estuaries have been tabulated and are compared with those representing other nearshore environments in Table 4.1. Significant differences are shown in the range of K_D^5 observed for the metals studied, i.e. 10^2 - 10^5 for ^{54}Mn and 10^1 - 10^2 for ^{109}Cd and ^{137}Cs for the recent LOIS data, which gives the following ranking of elemental particle affinities:

$$^{54}\text{Mn} > ^{109}\text{Cd} \geq ^{137}\text{Cs}$$

This is consistent with results derived from other natural seawater-sediment partitioning investigations using these radioisotopes (Aston & Duursma, 1973; Li *et al.*, 1984a & b; Nyffeler *et al.*, 1984; Santschi *et al.*, 1984:1987; Turner *et al.*, 1992a; Williams, 1995). The implied reduction in sorptive removal of ^{109}Cd and ^{137}Cs relative to ^{54}Mn is attributed to the formation of highly soluble and stable chloro complexes for ^{109}Cd (Edmond *et al.*, 1985; Bourg, 1987; Elbaz-Poulichet *et al.*, 1987; Turner *et al.*, 1992a) and competition for ^{137}Cs occupied adsorption sites on particle surfaces by major seawater cations for (Aston & Dursma, 1973; Patel *et al.*, 1978; Zucker *et al.*, 1984; Turner *et al.*, 1992a). A decrease in the K_D^5 of ^{109}Cd and ^{137}Cs with increasing salinity for the Humber Estuary has also been reported by Turner *et al.* (1993) although the

Table 4.1 A summary of the seasonal changes in K_D^5 's off the mouths of the Humber, Tees, Tyne and Tweed estuaries with subsequent comparison with other nearshore environments.

Location	Season	K_D^5 ($\times 10^3$)		
		^{54}Mn	^{109}Cd	^{137}Cs
Humber Estuary	spring'90 ^c	108	0.75	0.62
	winter'92 ^d	63	0.33	0.20
	winter'95	91	0.31	0.37
	spring'95	151	0.79	0.37
	summer'95	500	0.66	0.26
Humber Plume	winter'88 ^c	53	0.40	0.51
	spring'90 ^e	70	0.95	0.56
Holderness seawater	winter'92 ^d	0.8	0.05	0.43
	winter'95	9.8	0.05	0.03
	summer'95	5.3	0.09	0.05
Tees Estuary (S) ^a	winter'95	0.65	0.03	0.04
	spring'95	3.05	0.19	0.05
	summer'95	11.49	0.62	0.03
Tees Estuary (N) ^b	winter'95	2.82	0.05	0.04
	spring'95	1.18	0.16	0.05
	summer'95	2.61	0.15	0.04
Tyne Estuary	winter'95	2.49	0.05	0.04
	spring'95	1.32	0.12	0.04
	summer'95	3.88	0.22	0.04
Tweed Estuary	winter'95	1.28	0.03	0.06
	spring'95	2.71	1.42	0.04
	summer'95	2.40	0.16	0.03
Thames Plume	winter'88 ^c	33	0.53	0.31
Dee Estuary	autumn'91 ^f	675	0.55	0.25

^asouth station, site C12 refer to Figure 2.2; ^bnorth station, site C14 refer to Figure 2.2; ^cTurner *et al.* (1993); ^dWilliams (1995). ^eTurner *et al.* (1992a); ^fTurner & Millward (1994).

reduction was greatest below a salinity of 9 and did not significantly change between 20-30 (salinity range of the present experiments was 28.5-34.3, see Table 4.2). During

winter'92 Williams (1995) reported a greater particle affinity of ^{137}Cs for Holderness material compared to Humber particles (see Table 4.1) which was attributed to the interstitial replacement of K^+ with Cs^+ in clay lattices. This was not evident in winter'95 and summer'95 K_D^5 data from seawater collected off the Holderness coast, presumably because these samples were considerably diluted with seawater compared to the pure end member Holderness clay material.

The radioisotopes ^{54}Mn , ^{109}Cd and ^{137}Cs also displayed significant spatial variations in K_D^5 possibly reflecting the different particle populations and associated surface characteristics dominating the water column at each location. For the LOIS data ^{54}Mn K_D^5 's decreased in the following order (refer to Table 4.2):

Humber Estuary > Holderness seawater \geq Tees, Tyne and Tweed Estuaries.

The formation of particulate Mn is principally the result of the precipitation of oxidised Mn species (Turner *et al.*, 1992a). Although theoretically a kinetically slow process in aquatic systems, rapid observed oxidation rates have been attributed to pronounced autocatalysis by MnO_x ($1.5 \leq x \leq 2$) or mixed Mn-Fe oxide phases. These phases may occur as superficial coatings on particles which subsequently act as self-maintaining catalytic sites for continued uptake of dissolved Mn (Morris & Bale, 1979; Yeats & Strain, 1990). In addition effective microbially mediated oxidation of dissolved Mn has also been suggested (Emerson *et al.*, 1982; Vojak *et al.*, 1985; Sunda & Huntsman, 1987). The Humber Estuary has previously been identified as a primary source of dissolved Fe (see section 1.2.2.4) which upon mixing with seawater results in its removal to the particulate phase by flocculation and/or precipitation (Millward *et al.*, 1996). This mechanism provides fresh active new surfaces upon which dissolved trace metals, such as Mn, can adsorb (Millward & Moore, 1982). This process may explain the greater K_D^5 obtained at the mouth of the Humber Estuary compared to those observed in other locations for the present study (see Table 4.2). The sampling locations for the Tees, Tyne and Tweed estuaries were further offshore compared to those of the Humber Estuary as evident by higher observed salinities (see Table 4.2). The rate of removal of dissolved Mn decreases with increasing salinity (Morris & Bale, 1979; Millward &

Table 4.2 Summary of the spatial K_D^5 values determined during the LOIS surveys with corresponding master variables and concentrations of Fe_p , Mn_p and Cd_p .

Location	Season	$K_D^5 (x 10^3)$			Salinity	Temp ³ (°C)	[SPM] (mg l ⁻¹)	[Fe _p] (mg g ⁻¹)	[Mn _p] (µg g ⁻¹)	[Cd _p] (µg g ⁻¹)	Chla ⁴ (µg l ⁻¹)	%POC ⁵ (%)
		⁵⁴ Mn	¹⁰⁹ Cd	¹³⁷ Cs								
Humber ¹	winter'95	91	0.31	0.37	28.53	4.8	243	18.4	768	0.44	-	-
	spring'95	151	0.79	0.37	30.79	8.6	310	16.8	556	0.19	1.40	15.0
	summer'95	500	0.66	0.26	32.59	14.7	60.4	15.6	767	0.42	1.10	14.1
Holderness ²	winter'95	9.8	0.05	0.03	34.34	6.2	14.1	13.8	670	nd	0.70	-
	summer'95	5.3	0.09	0.05	34.06	12.7	1.5	10.2	747	0.14	1.30	33.0
Tees (S) ¹	winter'95	0.65	0.03	0.04	34.10	6.6	6.6	17.1	598	nd	0.08	23.3
	spring'95	3.05	0.19	0.05	33.96	6.7	4.4	13.9	612	0.38	1.04	-
	summer'95	11.49	0.62	0.03	33.89	13.1	1.5	8.4	743	0.73	2.01	27.5
Tees (N) ¹	winter'95	2.82	0.05	0.04	34.28	6.5	9.0	15.2	514	nd	0.35	19.5
	spring'95	1.18	0.16	0.05	33.73	7.6	5.3	14.6	605	0.19	0.64	-
	summer'95	2.61	0.15	0.04	33.98	12.9	1.3	4.1	341	0.44	1.22	34.9
Tyne ¹	winter'95	2.49	0.05	0.04	33.20	6.4	7.8	15.0	634	0.30	0.02	28.8
	spring'95	1.32	0.12	0.04	34.02	6.5	1.4	29.1	1383	nd	1.30	25.8
	summer'95	3.88	0.22	0.04	34.03	12.5	2.1	4.8	284	0.72	0.72	31.9
Tweed ¹	winter'95	1.28	0.03	0.06	33.46	6.7	2.0	8.7	591	nd	0.20	-
	spring'95	2.71	1.42	0.04	33.89	6.8	3.1	3.5	280	0.18	4.40	84.8
	summer'95	2.40	0.16	0.03	34.01	12.4	0.7	0.5	104	2.21	0.68	34.5

¹Humber Estuary (HWS), Tees Estuary (south-C12), Tees Estuary (north-C14), Tyne Estuary (C18), Tweed Estuary (C26), refer to Figure 2.2 for sample locations; ²Holderness seawater collected at C2 and HW1 during winter'95 and summer'95 respectively, see Figure 2.2; ³Temperature of the seawater; ⁴Chlorophyll a concentration (courtesy of BODC, LOIS core data); ⁵Particulate organic carbon by Loss on Ignition (refer to section 2.2.5); nd denotes not detectable; - denotes data not available.

Moore, 1982) and hence the observed decreases in K_D^5 could be partially due to elevated salinities. The decrease in K_D^5 between samples taken in the mouth of the Humber Estuary compared to those taken adjacent to the Holderness coast presumably reflect the decrease in the amount of estuarine particulate matter or rather the dilution of active Fe and Mn oxyhydroxide surfaces with seawater as evident by the decrease in SPM concentrations observed (see Table 4.2).

Significant seasonal variations in K_D^5 for ^{54}Mn , previously undocumented in the literature, are also shown at the mouth of the Humber Estuary and just south of the Tees Estuary. This implies increasing removal of dissolved Mn to the particulate phase i.e. increasing K_D^5 from winter through spring to summer'95. This trend is not fully understood. However increasing temperature has been reported by Morris & Bale (1979) to accelerate the rate of removal of dissolved Mn and hence could partially explain the above results (see Table 4.2). However this hypothesis does not explain why the above trend was not seen north of the Tees Estuary or adjacent to the Tyne and Tweed estuaries. The oxidation of dissolved Mn has also been shown to be catalysed by bacteria (Emerson *et al.*, 1982; Vojak *et al.*, 1985; Sunda & Huntsman, 1987) but lack of supporting data i.e. bacterial production or biomass renders such explanations purely speculative.

It is difficult to establish the relative particle affinity of ^{109}Cd between the different sampling locations due to the changes in K_D^5 with season. Indeed the Humber and Tweed estuaries show enhanced K_D^5 's during spring'95 in comparison to the Tees (S) and Tyne who show maximum K_D^5 's during summer'95. Interestingly enhanced uptake of dissolved Cd shows a significant positive correlation ($P < 0.05$) with chlorophyll a concentrations ($r = 0.88$) inferring the relative affinity of Cd to biogenic particles compared to lithogenic particles as previously mentioned in sections 3.2.8 & 3.4.1.

The K_D^5 obtained for ^{137}Cs are approximately an order of magnitude greater for samples obtained in the mouth of the Humber Estuary compared to all other locations sampled and hence particle affinity in the following order (refer to Table 4.2):

Humber Estuary > Holderness seawater \cong Tees, Tyne and Tweed Estuaries.

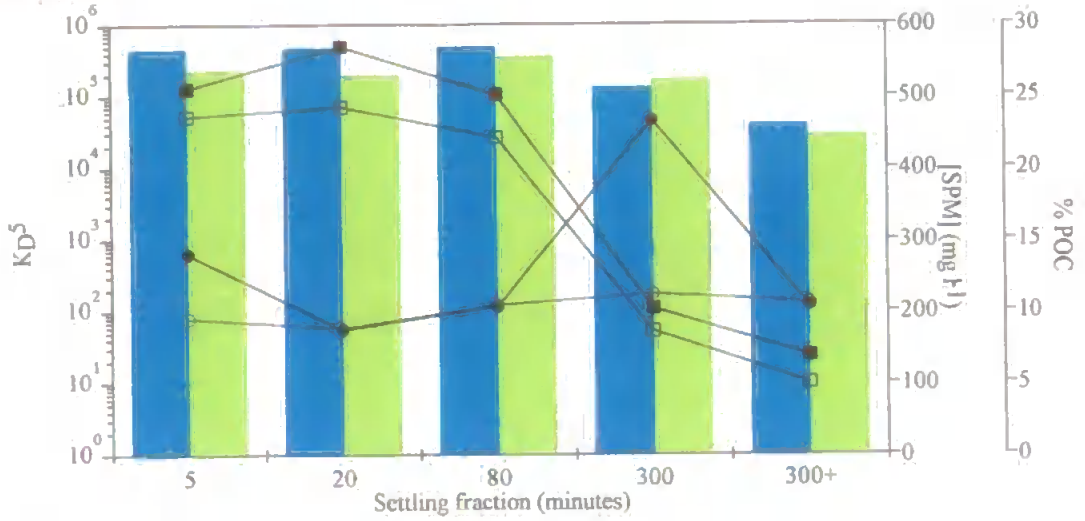
which is comparable to the trend observed for ^{54}Mn . A positive ($P < 0.05$) correlation was obtained between the K_D^5 's for ^{137}Cs and the concentration of SPM ($r = 0.94$) suggesting that the uptake of dissolved Cs was a function of the number of adsorption sites available. In contrast to ^{54}Mn and ^{109}Cd , the K_D^5 's obtained for ^{137}Cs displayed little changes with season thus implying no biological mediation. The importance of clay minerals in providing irreversible sorption sites for ^{137}Cs ions has previously been mentioned however the above findings imply that solid phases other than clay surfaces i.e. Fe and Mn hydroxide coatings of estuarine particles are also important sites.

4.3 Partitioning Experiments with Particles of Different Settling Velocities

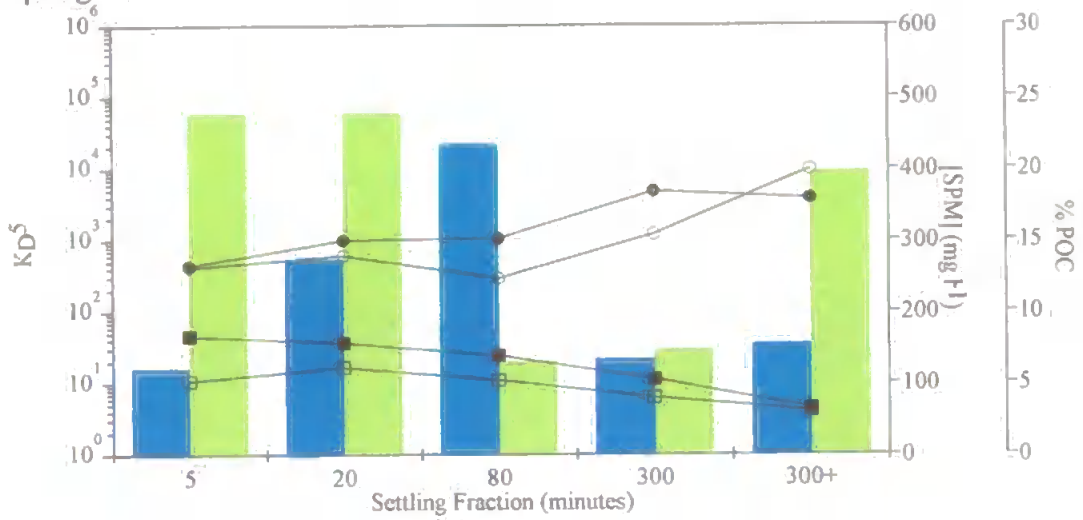
An aliquot of the water from each settling fraction of the QUISSET experiments undertaken in winter'95, spring'95 and summer'95 was taken and the trace metal reactivity of ^{54}Mn , ^{109}Cd and ^{137}Cs investigated using radioisotope incubation experiments (see section 2.5.4, Table 2.11 for experimental details). The results expressed as K_D^5 's with corresponding concentrations of SPM and %POC are displayed in Figures 4.1-4.3 for ^{54}Mn , ^{109}Cd and ^{137}Cs respectively.

During winter'95 little variation in K_D^5 was displayed for ^{54}Mn between successive flood and ebb tides. The magnitude of K_D^5 showed slightly lower values with the slower settling fractions (≥ 300 minutes) coincident with lower concentrations of SPM. Indeed regression analysis of the empirically derived K_D^5 for ^{54}Mn against the concentration of SPM showed a significant ($P < 0.05$) positive relationship ($r = 0.54$, $n = 30$) suggesting that the uptake of dissolved Mn from solution was a function of the concentration of suspended solids. The following spring K_D^5 values were between 1-4 orders of magnitude lower and displayed significant variation both with settling fraction and tidal state. During the ebb tide K_D^5 's of the order 10^4 cf. 10^5 during winter'95 were found during the fastest settling fractions (5 & 20 minutes) and the residual fraction (> 300 minutes) which is attributed to the different nature of the fractions (Williams, 1995) i.e. the residual fraction is characterised by a lower concentration of SPM but higher %POC

(a) Winter'95



(b) Spring'95



(c) Summer'95

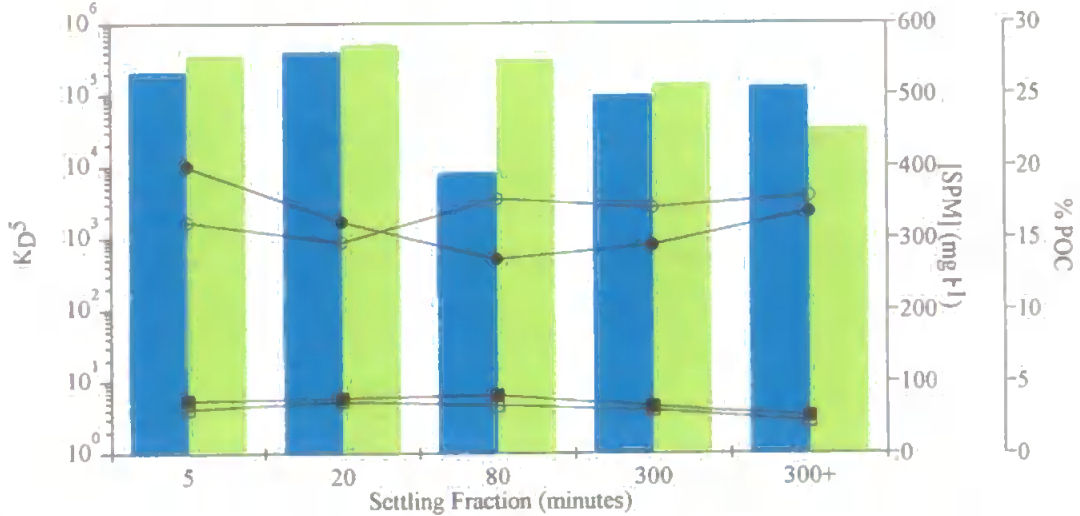


Figure 4.1 A comparison of K_D^5 's determined for ^{54}Mn in each time fraction particle population yielded from the QUISSET tube experiments during maximum flood (■) and ebb tides (■) in (a) winter'95, (b) spring'95 and (c) summer'95. Corresponding concentration of SPM (■ flood, □ ebb) and %POC (● flood, ○ ebb) are also depicted for each particle settling fraction.

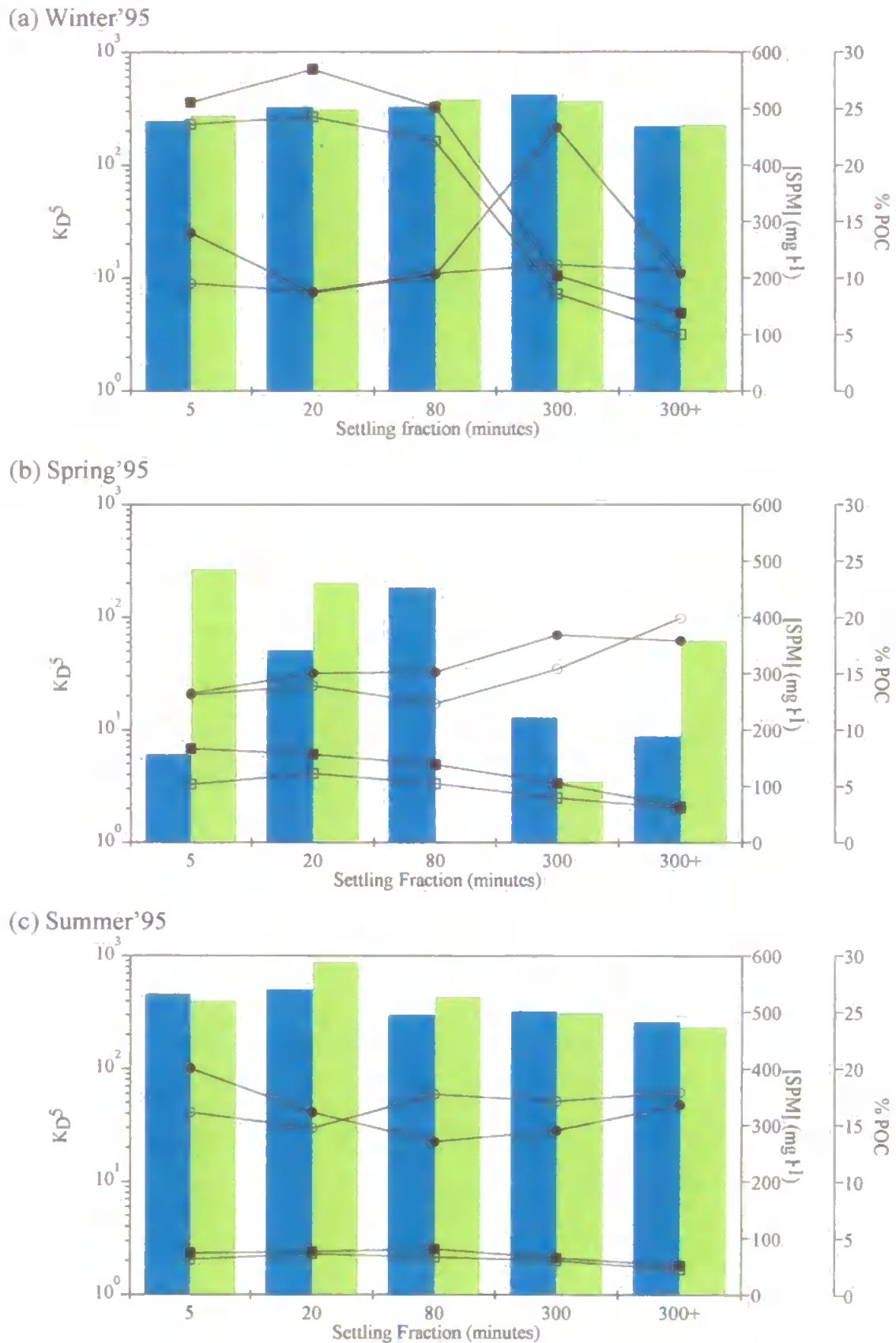


Figure 4.2 A comparison of K_D^5 's determined for ^{109}Cd in each time fraction particle population yielded from the QUISSET tube experiments during maximum flood (■) and ebb tides (■) in (a) winter'95, (b) spring'95 and (c) summer'95. Corresponding concentration of SPM (■ flood, □ ebb) and %POC (● flood, ○ ebb) are also depicted for each particle settling fraction.

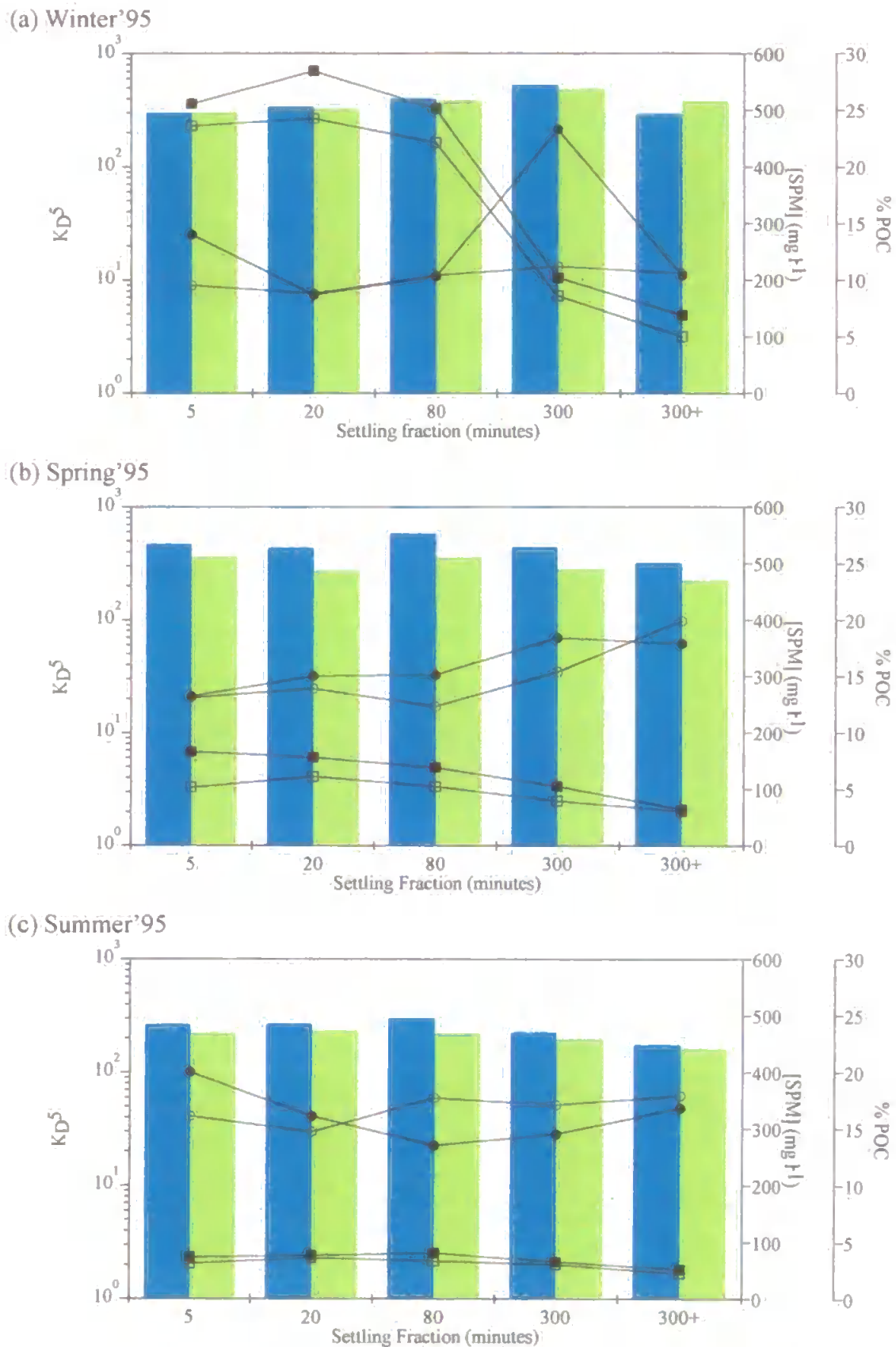


Figure 4.3 A comparison of K_D^5 's determined for ^{137}Cs in each time fraction particle population yielded from the QUISSET tube experiments during maximum flood (■) and ebb tides (■) in (a) winter'95, (b) spring'95 and (c) summer'95. Corresponding concentration of SPM (■ flood, □ ebb) and %POC (● flood, ○ ebb) are also depicted for each particle settling fraction.

possibly indicating enhanced association of Mn with organic ligands/surfaces compared to the heavy, possibly resuspended estuarine bed sediments (see Chapter 5). However during the flood tide the greatest K_D^5 was found during the 80 minute settling fraction. Interestingly the concentration of Mn_p obtained in each fraction during the spring flood tide (see Figure 5.6d) mirrors the trend found in the radiochemically derived K_D^5 's. This suggests that the uptake of dissolved Mn is directly related to the amount of Mn_p or rather the number of self maintaining surface catalytic sites as previously mentioned in section 4.2. This process is further implied by the positive ($P < 0.05$) correlation found between all K_D^5 's obtained for ^{54}Mn and the concentration of Mn_p ($r = 0.50$, $n = 30$). During summer'95 the magnitude of the K_D^5 obtained for ^{54}Mn returned to previous winter levels of the order 10^5 and similarly displayed little variation between the flood and ebb tides (except the 80 minutes settling fraction) despite lower concentrations of SPM. However the enhanced %POC data may reflect more organic-particle surface interactions ultimately leading to similar ^{54}Mn uptake rates compared to winter'95.

The K_D^5 data obtained for ^{109}Cd are shown in Figure 4.2 and, despite a lower particle affinity, show the same trends both with season and particle settling fraction to those of ^{54}Mn . Indeed the uptake of ^{109}Cd and ^{54}Mn show a strong inter-correlation ($r = 0.73$ for $n = 30$, $P < 0.05$) indicating similar adsorption mechanisms for particle populations sampled in the mouth of the Humber Estuary. This is attributed to the high adsorption capacity of fresh active Fe and Mn oxyhydroxide surfaces of lithogenic particles that dominate the SPM at the mouth of the Humber Estuary. This mechanism is corroborated by the linear relationship obtained between the K_D^5 's derived for ^{109}Cd and the concentration of Mn_p (see section 5.5.1, Figure 5.6d) found in each settling fraction of each experiment ($r = 0.63$ for $n = 30$, $P < 0.05$) *cf.* K_D^5 's obtained for ^{54}Mn .

In comparison ^{137}Cs (see Figure 4.3) despite showing K_D^5 similar in magnitude to those of ^{109}Cd i.e. approximately 10^2 revealed no significant variations with particle settling fraction, tidal state or season. This suggests that the uptake of dissolved Cs was not affected by changes in SPM concentration, particle size, density or composition.

4.4 Mixing Experiments

These experiments were designed to simulate the mixing of particles derived from the erosion of Holderness clay material and those originating from the Humber Estuary in the Humber Plume. Inherent in this is the assumption that these two end members are the mass dominant particle sources to the plume (Millward *et al.*, 1996). Full experimental details have been previously given in sections 2.5. Previously in section 3.3.3 the concentration of trace metals in plume particles, M^P , were predicted from the following equation;

$$[M^P] = \frac{[SPM^{HE}][M^{HE}] + [SPM^{HC}][M^{HC}]}{[SPM^P]} \quad 4.1$$

where M^{HE} and M^{HC} are, respectively, the concentration of trace metal in the Humber Estuary and Holderness Cliff material and SPM^P , SPM^{HE} and SPM^{HC} are the SPM concentrations in the Humber Plume, Estuary and Holderness nearshore environments, respectively.

If P is equal to the proportion of Humber Estuary material contributing to the total particle population in the plume then;

$$P = \frac{[SPM^{HE}]}{[SPM^{HE}] + [SPM^{HC}]} \quad 4.2$$

and assuming that;

$$[SPM^P] = [SPM^{HE}] + [SPM^{HC}] \quad 4.3$$

the proportion of Holderness material contributing to the plume particle population is;

$$1 - P = \frac{[SPM^{HC}]}{[SPM^{HC}] + [SPM^{HE}]} \quad 4.4$$

Equations 4.2, 4.3 and 4.4 can then be substituted into equation 4.1 to give;

$$[M^P] = P[M^{HE}] + (1 - P)[M^{HC}] \quad 4.5$$

However from the definition of the partition coefficient K_D , where M_p denotes the concentration of metal in the particulate phase (w/w) and M_s concentration of metal in the dissolved phase (w/v);

$$K_D = \frac{M_p}{M_s} \quad 4.6$$

The concentration of particulate metal from the Humber Estuary, Holderness Cliffs and Plume can therefore be described in terms of the K_D for each particle type therefore;

$$[M_p^P] = K_D^P [M_s] \quad 4.7$$

$$[M_p^{HE}] = K_D^{HE} [M_s] \quad 4.8$$

$$[M_p^{HC}] = K_D^{HC} [M_s] \quad 4.9$$

This assumes that the concentration of M_s is constant and does not change between water samples obtained from the mouth of the Humber Estuary, adjacent to the Holderness Cliffs and in the Plume. Equations 4.7, 4.8 and 4.9 can be substituted into equation 4.5 to give;

$$K_D^P [M_s] = PK_D^{HE} [M_s] + (1 - P)K_D^{HC} [M_s] \quad 4.10$$

$$K_D^P = PK_D^{HE} + (1 - P)K_D^{HC} \quad 4.11$$

$$K_D^P = K_D^{HC} + P(K_D^{HE} - K_D^{HC}) \quad 4.12$$

The value P assumes that the particles add together in a linear fashion and do not flocculate (Williams, 1995) or rather that particles derived from the Humber Estuary and Holderness Cliffs exist as individual particles in the Plume and do not interact. It was found by trial and error that to fit the above algorithm (Equation 4.12) to the observed

data it was necessary to raise P to the power A, where A therefore represented an ‘additivity factor’ (Millward *et al.*, 1994). Thus equation 4.12 became a ‘mixing equation’ describing the behaviour of particulate metals in the Humber Plume;

$$K_D^P = K_D^{HC} + (K_D^{HE} - K_D^{HC})P^A \quad 4.13$$

By rearranging and taking the logarithms of Equation 4.13 the theoretical value of A can be determined;

$$\log(K_D^P - K_D^{HC}) = \log(K_D^{HE} - K_D^{HC}) + A \log P \quad 4.14$$

An example plot is shown in Figure 4.4.

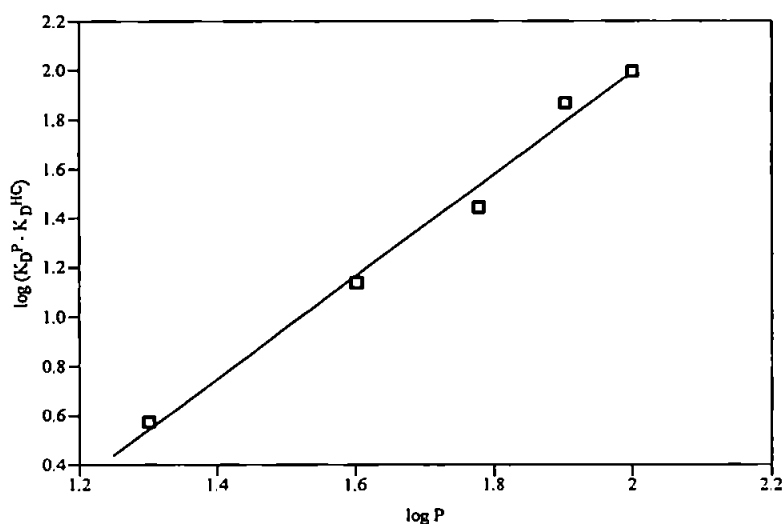


Figure 4.4 A representative plot of $\log(K_D^P - K_D^{HC})$ vs. $\log P$ to find the additivity factor, A for Cs during winter'95 ($A=2.1$, $r=0.99$).

If the mixing of the end member particles and associated particulate trace metals are assumed to be conservative and particulate to dissolved reactions negligible, then the partition coefficient of trace metals in the plume, K_D^P , can also be calculated by the following equation where x denotes the proportion of particles from the Humber Estuary;

$$K_D^P = xK_D^{HE} + (1-x)K_D^{HC} \quad 4.15$$

This relationship also assumes that particle inputs from sources other than the Humber Estuary and Holderness coast are negligible e.g. atmospheric deposition, biogenic particles and resuspension of bed particles.

The results of the mixing experiments performed in winter'95 and summer'95 for ^{54}Mn , ^{109}Cd and ^{137}Cs are shown in Figure 4.5. It is immediately apparent that none of the metals studied behaved in a conservative manner or one that was additive (Millward *et al.*, 1994) i.e. deviation from straight line as predicted from equation 4.15. As found in section 4.2, generally all K_D^5 's derived for ^{54}Mn and ^{109}Cd during winter'95 were lower than those during summer'95. During winter'95 the K_D^5 's for all metals studied were less than those predicted by simple conservative mixing. This is presumably because the relatively low Mn_p content of Holderness clay material ($412 \pm 58 \mu\text{g g}^{-1}$ cf. Humber Estuary SPM values in Table 4.2) suppressed the effective promotion of the autocatalytic removal of dissolved Mn onto particle sources (Millward *et al.*, 1994). Such behaviour was also observed for ^{109}Cd and ^{137}Cs which could similarly be caused by depleted Mn_p and/or Fe_p (concentration of Fe_p in pure Holderness Cliff material is $7.5 \pm 0.8 \mu\text{g g}^{-1}$ compared to $15.6\text{-}18.4 \mu\text{g g}^{-1}$ in SPM sampled in the mouth of the Humber Estuary) (Millward & Moore, 1982; Davies-Colley *et al.*, 1984).

Interestingly during the following summer the opposite trend were observed for all metals i.e. enhanced K_D^5 's than could be predicted from conservative/additive mixing of Humber and Holderness particles. This trend was exaggerated in ^{54}Mn and ^{109}Cd values. Previously in sections 3.4.1 and 4.2 the enhanced affinity of Cd with biogenic particles was noted. Results from the productivity experiments (see section 4.5) also revealed enhanced K_D^5 's for ^{54}Mn and ^{109}Cd during summer'95 compared to spring'95 which was subsequently attributed biological mediation. These results suggest that in the Humber coastal zone or Plume, represented in the mixing experiments by particle compositions comprising between 20-80% Humber material, the enhanced K_D^5 's could be explained by an increased affinity of ^{54}Mn and ^{109}Cd with seasonally active biogenic particles, a population that was not taken into account in the above model formulation.

Equation 4.14 did not always give the best solution for A and it was necessary to use

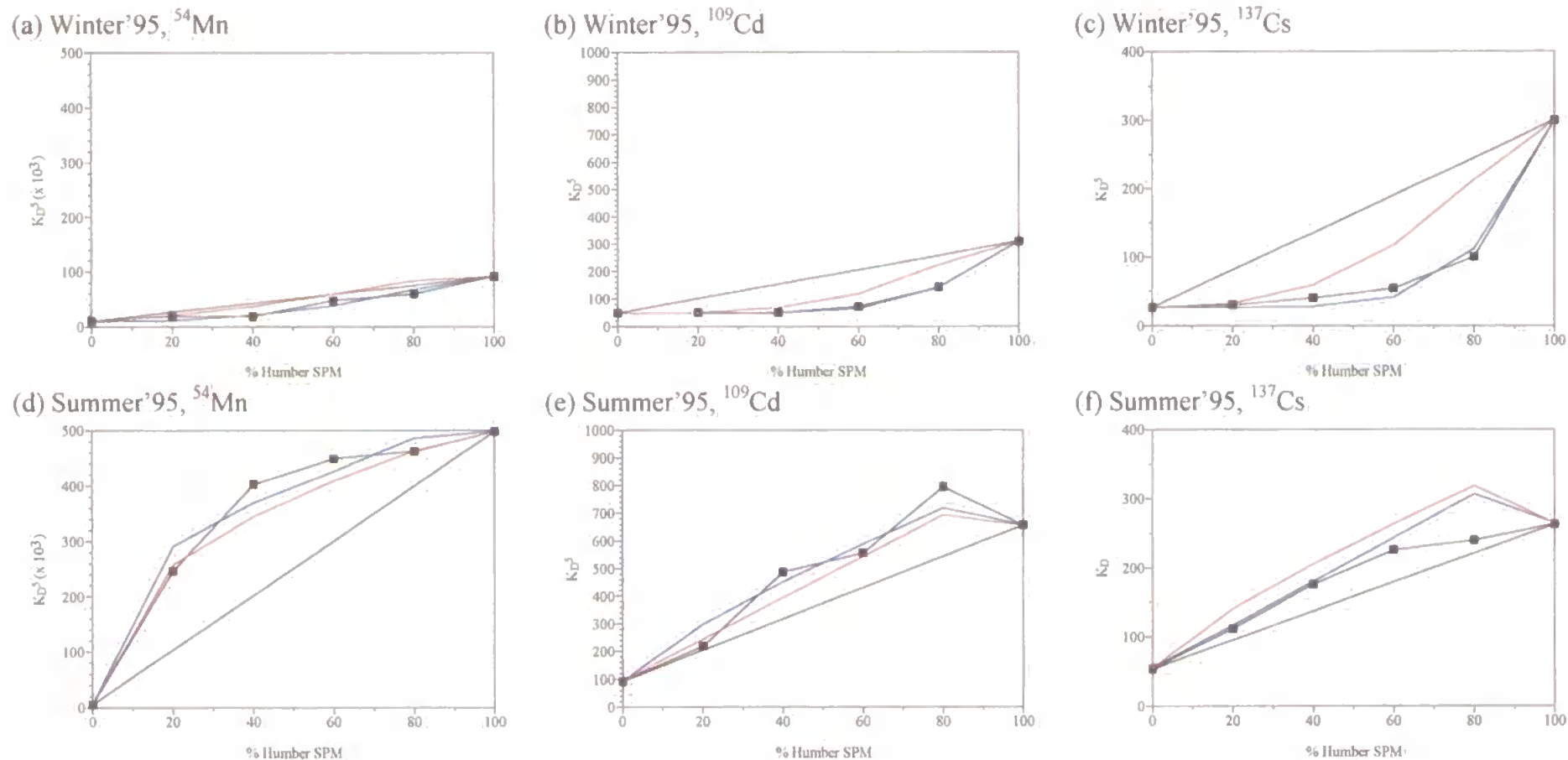


Figure 4.5 K_D^5 (-■-) as a function of % Humber water mixed in varying proportions with water collected adjacent to the Holderness coast (see section 2.5.5) during winter'95 for (a) ^{54}Mn , (b) ^{109}Cd , (c) ^{137}Cs and summer'95 for (d) ^{54}Mn , (e) ^{109}Cd , (f) ^{137}Cs . The black solid lines represents the theoretical K_D^5 as predicted from Equation 4.15. The K_D^5 's represented by the red and blue lines are those determined by equation 4.13. Red line where A = determined by equation 4.14, and blue line by the best iterative fit.

iterative methods to find a better fit to the experimental data (as indicated by the red and blue lines respectively in Figure 4.5). A comparison between the two methods is given in Table 4.3. The practical application of Equations 4.13 and 4.15 as a tool for predicting particulate trace metal concentrations and subsequent transport requires the knowledge of P or x. The values of the $^{206/207}\text{Pb}$ isotopic ratios developed in section 6.5.1 gave approximately 30% anthropogenic contamination of Pb in SPM of the Humber Plume during autumn'94 and summer'95 seasons and 37% during spring'95. If one assumed that these figures were representative of the contamination of other anthropogenic trace metals, it would be possible to theoretically determine the K_D^5 from Equation 4.13 for the metal in the plume with a knowledge of the end member particle trace metal K_D^5 's. Unfortunately no actual radiochemical incubation experiments were performed during the LOIS cruises in the Humber Plume (due to limited resources) to enable direct comparison and subsequent validation of the above model.

Table 4.3 A comparison of the methods used for determining the additivity constant (A) for the Humber/Holderness mixing experiments.

Metal	Additivity constant (A)			
	Calculated	Iterative	Calculated ^a	Iterative ^a
Mn				
winter'95	1.41	2.5	2.1	2.6
summer'95	0.43	0.35		
Cd				
winter'95	3.2	6.0	1.5	1.9
summer'95	0.99	0.80		
Cs				
winter'95	2.7	4.8	1.3	1.0
summer'95	0.8	0.98		

^aComparative data from Williams (1995) for samples taken during winter'92.

4.5 Productivity Experiments

4.5.1 Introduction

Phytoplankton affect trace metal chemistry in natural and oceanic waters not only by surface reactions (passive adsorption) but also by metal uptake (active assimilation) and

by production of extracellular organic matter with high metal complexing properties (González-Dávila, 1995). Concentrations of many trace metal micronutrients (e.g. Fe, Mn, Cu, Zn) and nutrient analogs (e.g. Cd, Ni) have often been shown to increase with depth in the ocean and covary with the concentration of major nutrients (Boyle *et al.*, 1976; Bruland 1980; Bruland & Franks, 1983; Martin & Gordon, 1988). This covariance has led to speculation that the concentration of these metals within the oceanic nutricline are largely regulated by uptake and regeneration cycles similar to those of the major nutrients (Morel & Hudson, 1984; Sunda & Huntsman, 1995).

However little is known as to whether such processes occur in shelf waters and, if so, the consequences on the observed particulate and dissolved trace metal distributions and their subsequent transport in coastal regimes. These experiments were therefore designed to investigate the role of the biota in the uptake and subsequent distribution of Mn, Cd and Cs in the dynamic regime of the Humber coastal zone. Full details of the experimental procedure and sampling locations have been given in section 2.5.6.1.

4.5.2 Results

A summary of the average K_D values for ^{54}Mn , ^{109}Cd and ^{137}Cs with corresponding master variables and chemical parameters for each productivity experiment are presented in Table 4.4. The changes in K_D with incubation conditions and corresponding primary productivity rates, chlorophyll a and SPM concentrations are also depicted for spring and summer in Figures 4.6-8 for ^{54}Mn , ^{109}Cd and ^{137}Cs respectively. Water column conditions are noticeably different between seasons. Results obtained during spring'95 (Figure 4.6-8a) showed SPM concentrations varying between 4-14 mg l^{-1} with relatively high chlorophyll a concentrations of 5-10 $\mu\text{g l}^{-1}$ at all three sites. Primary production measurements carried out on the same samples (see section 2.5.6.1) using the standard ^{14}C inoculation procedure (for an overview see Joint & Pomroy, 1993) ranged between 273-1500 $\text{mgC m}^3 \text{ day}^{-1}$ which is in agreement with production figures from Joint & Pomroy (1993) for the Humber coastal zone in spring. Examination of the surface nutrient time series (see Figure 4.9a) for the spring survey revealed typically enhanced

Table 4.4 Summary of average (± 1 SD) ^{54}Mn , ^{109}Cd and ^{137}Cs K_D values determined in each productivity experiment performed in spring'95 and summer'95. Corresponding master variables and concentrations of SPM, Fe_p , Mn_p and Cd_p determined in surface water samples are also presented.

Site number [†]	Spring'95			Summer'95		
	1	2	3	4	5	6
Water depth (m)	5.45	4.90	4.58	3.63	4.23	4.33
Temperature ($^{\circ}\text{C}$)	6.1	6.3	6.4	13.3	12.2	16.8
Salinity	33.54	33.12	34.48	33.88	34.17	33.61
[SPM] (mg l^{-1})	11.2	13.7	3.7	12.0	1.9	1.07
[Fe_p] (mg g^{-1})	13.6 ± 0.1	14.0 ± 0.1	12.5 ± 0.1	10.1 ± 0.1	1.2 ± 1	8.9 ± 0.1
[Mn_p] ($\mu\text{g g}^{-1}$)	635 ± 10	689 ± 12	712 ± 24	606 ± 9	58 ± 3	nd
[Cd_p] ($\mu\text{g g}^{-1}$)	0.180 ± 0.002	0.616 ± 0.006	0.599 ± 0.006	0.117 ± 0.001	0.553 ± 0.005	0.305 ± 0.003
Chl a ($\mu\text{g l}^{-1}$)	9.85	5.08	7.02	0.63	1.06	4.02
$^{54}\text{Mn } K_D$ ($\times 10^3$)						
Light	2.42 ± 0.04	3.95 ± 0.42	4.92 ± 0.54	13.3 ± 0.71	25.4 ± 32.8	24.3 ± 10.8
Dark	2.67 ± 0.62	4.20 ± 0.49	6.11 ± 0.82	33.3 ± 6.17	6.9 ± 0.22	41.5 ± 21.2
Poisoned	2.16	4.35	3.90	15.5	5.2	19.0
$^{109}\text{Cd } K_D$						
Light	0	31 ± 5.0	63 ± 16	220 ± 123	365 ± 101	807 ± 88
Dark	25 ± 16	54 ± 6.0	0	298 ± 132	440 ± 158	678 ± 378
Poisoned	1	85	0	69	124	0
$^{137}\text{Cs } K_D$ ($\times 10^2$)						
Light	3.00 ± 0.20	2.81 ± 0.45	8.00 ± 9.51	2.03 ± 0.59	1.42 ± 0.42	1.43 ± 0.82
Dark	2.88 ± 0.57	2.66 ± 0.42	1.81 ± 0.23	1.85 ± 0.26	2.29 ± 120	1.40 ± 0.40
Poisoned	2.83	2.87	1.48	2.16	1.94	1.03

^{*}Chlorophyll a concentrations (courtesy of BODC LOIS RACS core data); [†]for site location see section 2.5.6.1, Figure 2,9; nd denotes non detectable; K_D performed under light and dark conditions are the average of 3 replicates. Due to practical constraints only 1 poisoned samples was taken.

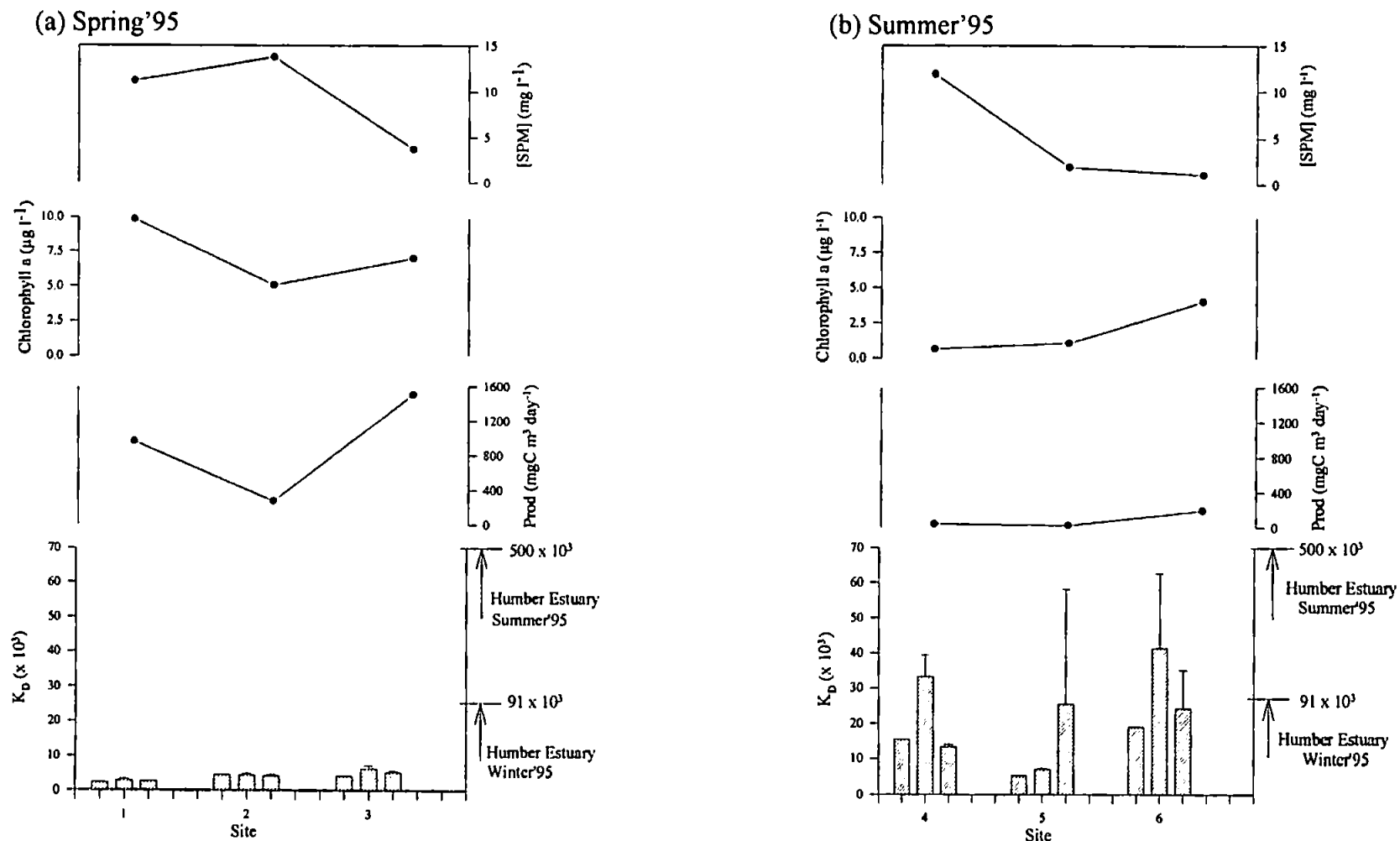


Figure 4.6 The uptake of dissolved ^{54}Mn expressed as K_D for samples poisoned (▨) and incubated under light (▤) and dark (□) conditions with corresponding concentrations of SPM, chlorophyll a and production rates for each experiment during (a) spring'95 and (b) summer'95. For site locations refer to section 2.5.6.1, Figure 2.9.

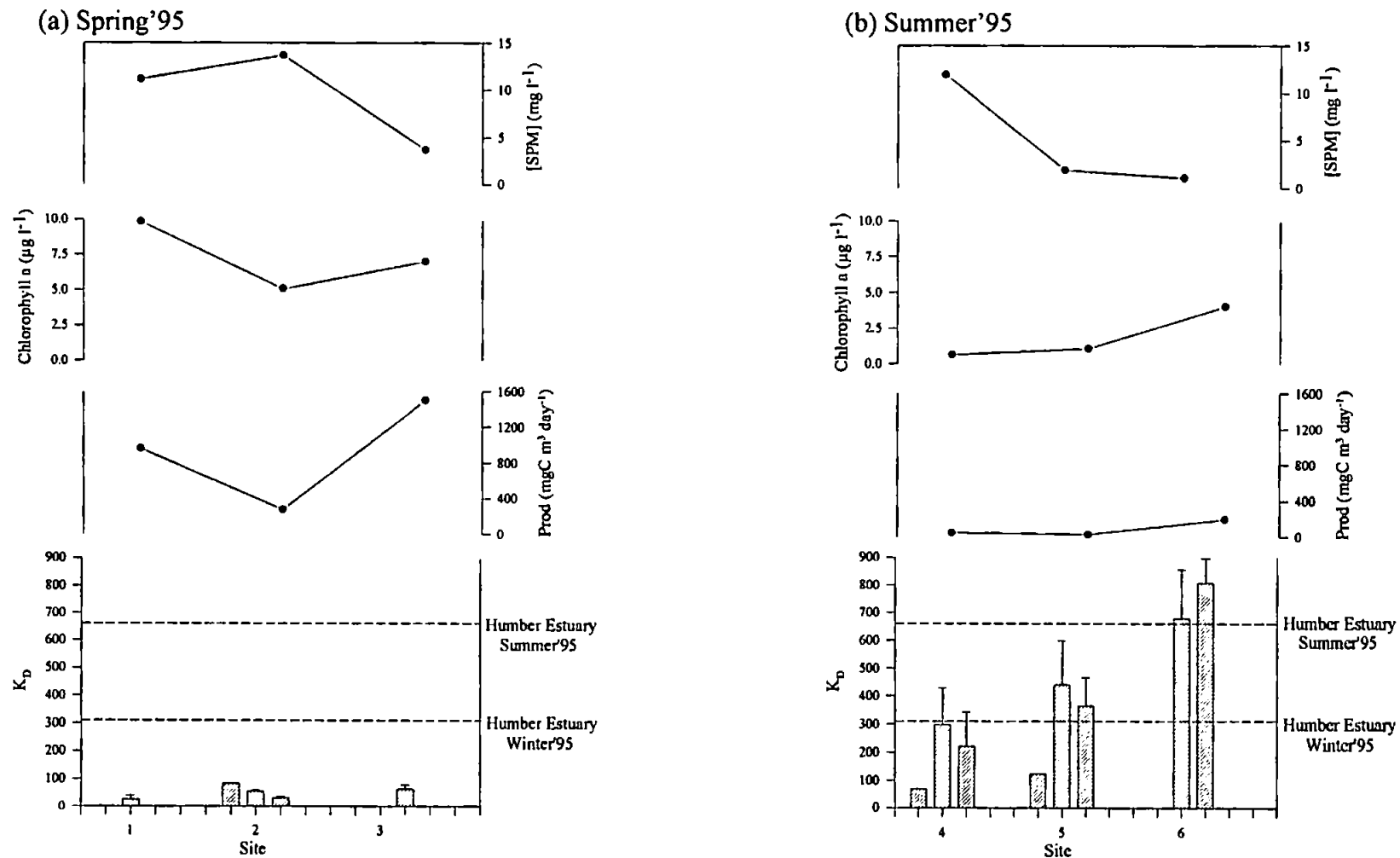


Figure 4.7 The uptake of dissolved ^{109}Cd expressed as K_D for samples poisoned (▨) and incubated under light (▤) and dark (▥) conditions with corresponding concentrations of SPM, chlorophyll a and production rates for each experiment during (a) spring'95 and (b) summer'95. For site locations refer to section 2.5.6.1, Figure 2.9.

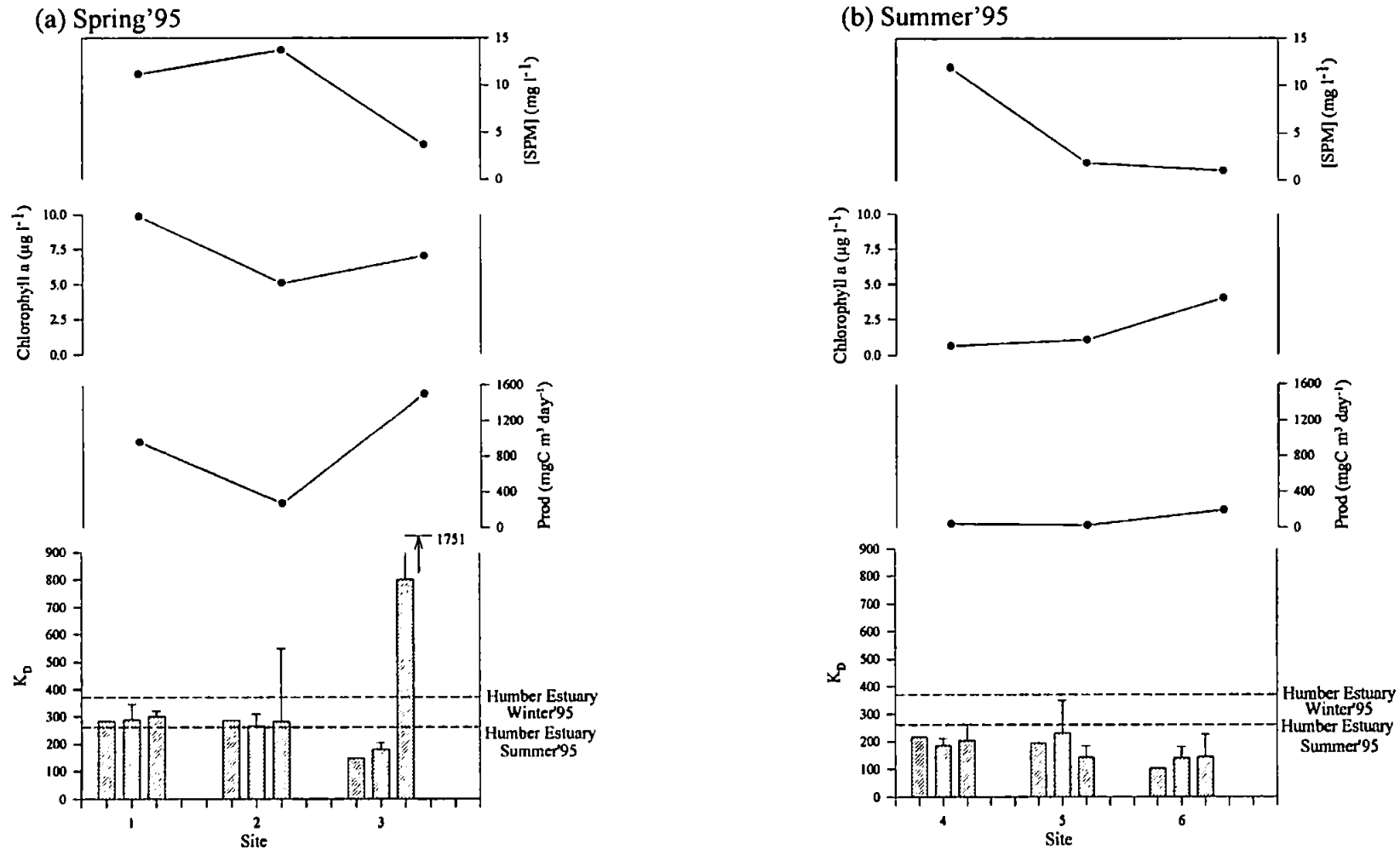


Figure 4.8 The uptake of dissolved ¹³⁷Cs expressed as K_D for samples poisoned (▨) and incubated under light (▧) and dark (□) conditions with corresponding concentrations of SPM, chlorophyll a and production rates for each experiment during (a) spring'95 and (b) summer'95. For site locations refer to section 2.5.6.1, Figure 2.9.

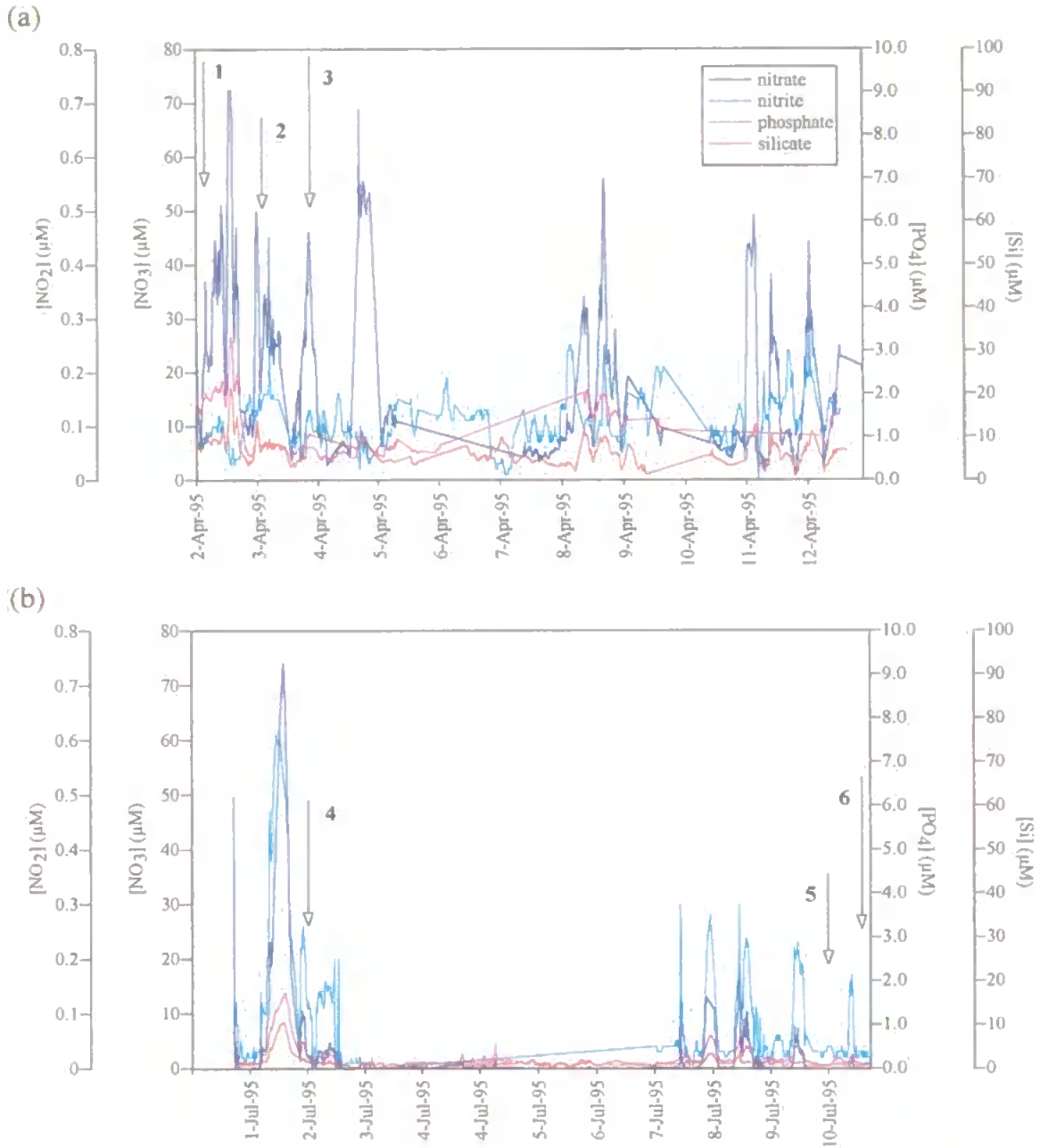


Figure 4.9 Surface concentration of dissolved nitrate, nitrite, phosphate and silicate (averaged over 5 minute bursts) during the LOIS surveys in (a) spring'95 and (b) summer'95. The numbers 1-6 correspond to the productivity experiments (see Figure 2.9) and represent the approximate time of water collection.

surface nitrate concentrations ($>40 \mu\text{M}$) which were high enough to support the growth of algae. Surface water temperatures during spring averaged $6.3 \pm 0.2^\circ\text{C}$.

The uptake of ^{54}Mn and ^{137}Cs during spring'95 (as defined by K_D 's) was $<10^4$ and $<10^3$ respectively, regardless of sampling location or incubation conditions i.e. light, dark or

poisoned. There was also no systematic pattern observed in Mn or Cs uptake for the three sites and no statistical difference (calculated by student t-test, degrees of freedom=4) demonstrated between K_D 's. When compared to typical K_D values for predominantly lithogenic matter in the mouth of the Humber Estuary in winter and summer, the uptake of ^{54}Mn , despite high primary productivity, was very small and well below typical values experienced for estuarine material. This suggests that the biota played little role in the recycling or transport of particulate Mn during spring conditions. The K_D 's derived for ^{137}Cs exhibited levels very similar to those obtained for estuarine material indicating similar passive adsorption rates onto particle surfaces irrespective of particle nature. However during productivity experiment 3 (see Figure 4.8a) ^{137}Cs does show enhanced uptake for samples incubated in the light but the large error associated renders the measurement suspect and indeed when calculated not statistically different from the samples incubated in the dark.

The uptake of ^{109}Cd produced K_D 's $<10^2$. However during experiment 2 and 3 (see Figure 4.7a) statistical differences were observed between samples incubated under light and dark conditions but they implied reverse trends i.e. K_D (dark) $>$ K_D (light) for experiment 2 and vice versa for experiment 3, making the results inconclusive. However when typical K_D values for predominantly lithogenic matter in the mouth of the Humber Estuary in winter and summer are compared to those found in the productivity experiments, despite high primary productivity, ^{109}Cd uptake was very small indicating negligible active biological mediation during spring conditions in agreement with the uptake of ^{54}Mn .

The incubation experiments were repeated in the following summer at slightly different sites but within the same area (experiments 4-6, see Figure 2.9). Firstly average water temperatures had increased i.e. $14.1 \pm 2.4^\circ\text{C}$ *cf.* $6.3 \pm 0.2^\circ\text{C}$. However the concentrations of SPM and chlorophyll a were generally (except SPM concentration for experiment 4) much lower than the former spring ($1\text{-}2 \text{ mg l}^{-1}$ and $0.6\text{-}4 \text{ } \mu\text{g l}^{-1}$ respectively). Primary productivity had also decreased significantly to levels between $26\text{-}196 \text{ mgC m}^3 \text{ day}^{-1}$. However the uptake of ^{54}Mn and ^{109}Cd generally showed an increase in the derived K_D 's of at least one order of magnitude (see Table 4.4 and Figures 4.6 & 4.7 respectively) independent of incubation conditions. Despite the observed relative

increases in summer compared to spring values, the K_D 's obtained for both ^{54}Mn and ^{109}Cd were similar to those obtained for Humber estuarine material in summer'95. One could therefore reason that simple passive adsorptive processes could account for the observed uptake. However comparison of the SPM concentrations obtained in the mouth of the Humber Estuary of 60 mg l^{-1} to the incubation sites of between $1\text{-}10 \text{ mg l}^{-1}$ possibly indicates different processes or surface reactions. The difference between poisoned and not-poisoned samples was generally noticeable indicating some kind of active uptake process but one that was not directly related to photosynthesis since there was no statistical difference between ^{54}Mn or ^{109}Cd uptake under light and dark incubation conditions (except for ^{54}Mn during experiment 4 when K_D (dark) > (light)). In contrast the uptake of dissolved ^{137}Cs was comparable to former spring values and again indicated no statistical differences between samples that had been poisoned or incubated in the light or dark. The values of K_D were also very similar, within experimental error, to those obtained for samples taken in the mouth of the Humber Estuary (see Figure 4.8b).

In summary the uptake of dissolved radio-labelled ^{54}Mn , ^{109}Cd and ^{137}Cs by biota was negligible in spring'95. However substantial increases in K_D values observed for ^{54}Mn and ^{109}Cd during summer'95 indicated some 'active' biological intervention but one not directly related to photosynthesis or chlorophyll a concentrations and hence the need for further consideration.

The uptake of trace metals by phytoplankton occurs via binding to a surface ligand i.e. active or passive assimilation, in the first instance followed by subsequent transfer across the cell membrane. However it is also recognised that subsequent production of particulate organic matter with high, and sometimes specific, metal complexing properties also plays a role in decreasing the concentration of free metal ions thereby increasing the K_D (Ahner & Morel, 1995; González-Dávila, 1995). Mineralisation of phytoplankton has also shown subsequent associated increases in trace metal uptake. For example Koelmans *et al.* (1996) reported that the remineralisation of the cyanobacterium *Anabaena* spp. resulted in an increase in K_D for Cd (factor 4), Cu (factor 8) and Pb (factor 10-20). This was attributed to either (a) decomposition of algal cells leading to an increase in the surface area available for sorption or alternatively providing

surfaces for which metals have a higher affinity or (b) sorption maybe from the growth of bacteria responsible for the remineralisation of the algae. It has previously been demonstrated that bacterial exopolymers used in bacterial attachment to surfaces (Marshall *et al.*, 1971) can be involved in binding metal ions (Brown & Lester, 1979). Loaec *et al.* (1997) subsequently demonstrated that the bacterial exopolysaccharide from *Alteromonas macleodii* showed a strong ability to bind Cd^{2+} ions (although Zn^{2+} ions competed for the same binding sites). It is therefore possible that the increase in K_D 's observed for ^{54}Mn and ^{109}Cd during summer'95 when production and chlorophyll a concentration were low was either due to enhanced association with phytodetritus or with extracellular particulate products previously exuded by phytoplankton or bacteria.

However metal uptake has been shown by some authors to depend on the plankton species (Mandelli, 1969; Sakaguchi *et al.*, 1979; Hårdstedt-Roméo & Gnassia-Barelli, 1980; Romeo & Gnassia-Barelli, 1985; Fisher & Wentz, 1993). Although there are conflicting arguments in the literature (Sunda & Hunstman, 1985; Fisher, 1986; Harrison & Morel, 1986) which suggest that the concentration of metals by marine phytoplankton is not correlated to taxonomy. Fisher (1986) reported that the concentration factors of trace metals by algal species showed less than an order of magnitude difference between species and that at equilibrium, regression analysis ($P < 0.001$) showed that the logarithms of the concentration factors were related to the solubility products of metal hydroxides and to cytotoxicity. In order to investigate the effect of different plankton species on the uptake of dissolved ^{54}Mn , ^{109}Cd and ^{137}Cs the phytoplankton species present and relative abundance were analysed for water samples taken at each productivity site. The results are summarised in Table 4.5.

Despite lower primary productivity rates the total carbon was substantially greater during experiments 5 & 6 in summer'95. This was coincident with the higher K_D values calculated for ^{54}Mn and ^{109}Cd (refer to Figures 4.6 & 4.7 respectively). Regression analysis of light and dark K_D 's for ^{109}Cd vs. total carbon yields significant ($P < 0.05$) positive relationships again inferring the enhanced affinity of Cd for biogenic particles (see sections 3.2.3 & 3.4). However the similarity in K_D values between light and dark incubation conditions does not suggest an active photosynthetic uptake mechanism. The

Table 4.5 Summary of cell biomass ($\mu\text{gC l}^{-1}$) and percentage contribution to total carbon biomass (indicated in brackets) in water samples obtained during the 6 productivity experiments in spring'95 and summer'95.

Site number ⁸	Cell numbers ($\mu\text{gC l}^{-1}$)					
	Spring'95			Summer'95		
	1	2	3	4	5	6
Diatoms	3.49 (60)	0.20 (8)	3.70 (42)	1.82 (20)	8.33 (44)	81.62 (88)
Dinoflagellates			0.08 (1)	1.25 (14)	1.23 (7)	
Flagellates	1.99 (34)	2.12 (85)	4.42 (50)	4.14 (46)	5.78 (31)	4.77 (5)
Coccolithophorids						
Others						0.01
Ciliates	0.36 (6)	0.14 (6)	0.12 (1)	0.56 (6)	1.97 (11)	1.72 (2)
Heterotrophic Dinoflagellates		0.02 (1)	0.43 (5)	1.20 (13)	1.48 (5)	4.94 (5)
Total Carbon	5.83	2.49	8.75	8.97	18.79	93.06

⁸Refer to Figure 2.9 for site locations

dominant species during experiments 4 & 5 in the summer were diatoms (although in terms of percentage contribution, flagellates were significant during experiment 5) specifically *Rhizosolenia alata* during experiment 5 and *Rhizosolenia delicatula* and *Leptocylindrus danicus* during experiment 6. Considering the dominating numbers of diatoms in these two experiments it was not surprising that a significant ($P < 0.05$) linear relationship was also found between the ^{109}Cd K_D 's and the carbon biomass of diatoms present ($r = 0.92$ & 0.85 for light and dark incubations respectively). Under conditions of dissolved Zn limitation (Zn_d), Cd_d has been shown to enhance the growth of the marine diatom *Thalassiosira weissflogii* (Price & Morel, 1990; Lee *et al.*, 1995). This was attributed by Lee *et al.* (1995) to the replacement of Zn by inorganic Cd, so restoring the activity of carbonic anhydrase, thought to be the key enzyme limiting growth of *T. weissflogii* at low Zn_d concentrations. It is therefore possible that the enhanced K_D 's observed for ^{109}Cd during the summer were due to active uptake by coastal diatoms, although the lack of free Zn ion concentrations render such explanations merely speculative. Typical total Zn_d concentrations found during summer'95 in the Humber coastal zone were $0.78 \pm 0.55 \mu\text{g l}^{-1}$ or 11.9 nM (Sands, pers comm). The free Zn^{2+} concentration was calculated using MINEQL and typical concentrations of Zn organic

complexing ligands found in coastal waters (van den Berg, 1985). The computations yielded typical free Zn ion concentrations of 3.8 nM (4.9 nM excluding the species ZnOHCl from the calculation). However the reported free Zn concentrations at which free Cd is thought to replace Zn in diatoms ranges between 0.02-0.014 nM (Lee *et al.*, 1995) therefore making this process unlikely in the Humber coastal zone.

However this is not the only possible explanation as Ahner *et al.* (1995) and Ahner & Morel (1995) reported that phytochelatin production by *T. weissflogii* was rapidly induced after exposure to free Cd ions at concentrations as low as 12 pM. It is believed that production of this peptide is a general metal detoxification system although Cd has been found to be the most effective inducer of phytochelatin synthase (Grill *et al.*, 1989). This alternatively suggests that the greater ^{109}Cd K_D 's observed could be due to enhanced complexation with particulate phase phytochelatin produced by coastal diatoms, more abundant during summer'95. The free ion concentration of Cd for these samples have been calculated using the computer modelling program MINEQL. Typical total Cd_d concentrations found in this study during summer'95 in the Humber coastal zone were $0.045 \pm 0.020 \mu\text{g l}^{-1}$ or 0.40 nM (see section 3.4.2). The free Cd^{2+} concentration computed was of the order 12 pM. This suggests that the increased ^{109}Cd K_D 's observed during summer'95, particularly experiments at sites 5 & 6, could have been due to enhanced complexation of Cd_d with particulate phytochelatin produced by coastal marine diatoms that were abundant in the water column at these sites (assuming phytochelatin remained attached to the diatom surfaces).

Manganese on the other hand is essential to all organisms and has particular importance in plant nutrition because of its role in the oxidation of water during photosynthesis (Cheniae & Martin, 1969; Diner & Joliot, 1976). There is evidence that low Mn concentrations may limit plankton growth in certain oceanic regions (Sunda *et al.*, 1981; Brand *et al.*, 1983; Sunda & Hunstman, 1996). However contrary to the proposed mechanisms to account for the increase in summer'95 ^{109}Cd K_D 's, the uptake of Mn in the unicellular alga *Chlamydomonas* was reported by Sunda & Hunstman (1985) to be related to the free Mn ion concentration i.e. an increase in K_D or particulate uptake with increasing free Mn ion concentrations. A similar mechanism of uptake for Fe was proposed by Harrison & Morel (1986) for the coastal diatom *T. weissflogii*. In

agreement with the present results for ^{54}Mn and ^{109}Cd the Fe uptake was not directly related to photosynthetic or respiratory activity (Anderson & Morel, 1982) and thus the observed increase in the maximum rate of Fe uptake was thought to reflect the number of porter sites and not an increase in turnover rates. It is therefore possible that the observed increases in K_D 's derived for ^{54}Mn during summer incubations were due to higher concentrations of free Mn ions in the water column (as a results of lower SPM concentrations). Concentrations of dissolved Mn (Mn_d) were not analysed during the present study but Tappin *et al.* (1995) reported that total concentrations during winter'88 in the Humber Plume were 1.97 nM. Using this concentration, speciation calculations using MINEQL indicated that 55.8% would exist as the free Mn^{2+} ion or rather 1.10 nM. Sunda & Huntsman (1985) suggested that cellular Mn increased with free Mn ion concentrations in the range 0.22-25.8 nM indicating the possibility that the increase in K_D 's observed for ^{54}Mn during summer'95 could be due to algae uptake.

4.6 Summary

The use of radioisotopes in the present study has not only given the following indication of particle affinity in the order:

$$^{54}\text{Mn} > ^{109}\text{Cd} \geq ^{137}\text{Cs}$$

but has established significant seasonal variations in K_D ⁵ values that have not previously been reported. For the Humber and Tees (south site) estuaries the uptake of ^{54}Mn increased more than 5 fold during summer'95 compared to the previous winter. In agreement the uptake of ^{109}Cd similarly increased by an order of 2 and 20 for the Humber and Tees (south site) estuaries respectively, whilst ^{137}Cs demonstrated little change with season. The observed seasonal increases in K_D ⁵ were not fully understood but were attributed to an enhanced affinity of ^{54}Mn and ^{109}Cd with particles of a more biogenic nature.

The use of QUISSET tubes investigated the changes in K_D^5 at the mouth of the Humber Estuary not only with season but with tidal state and particle settling times. During winter'95 and summer'95 all metals studied displayed little variation in K_D^5 with tidal state or settling time. However during the spring significant variations were found for ^{54}Mn and ^{109}Cd . The calculated K_D^5 's were substantially lower and exhibited significant variation between flood and ebb tides and with particle settling times. Linear regression analysis indicated that (a) ^{54}Mn and ^{109}Cd uptake was a linear function of the number of self maintaining surface Mn oxide catalytic sites and (b) that the uptake of ^{54}Mn and ^{109}Cd were significantly inter-correlated again inferring similar uptake mechanisms for particle populations occurring in the Humber mouth. Subsequent mixing experiments of Humber Estuary SPM and Holderness material during winter'95 showed K_D^5 's for all metals studied were less than those predicted by simple conservative mixing of the two end member particle populations. This was attributed to the depleted Mn_p content of Holderness clay material suppressing the effective promotion of the autocatalytic removal of dissolved Mn, Cd and Cs. The converse trend in predicted K_D^5 's was observed for the trace metals during summer'95 which was attributed to biological enhancement of uptake.

Productivity experiments confirmed the biological enhancement of ^{54}Mn and ^{109}Cd uptake during summer'95 compared to the former spring. However such processes were not directly related to photosynthetic activity since there was no statistical difference between uptake under light and dark conditions. Phytoplankton biomass in surface waters revealed a considerable increase in the number of diatoms and total carbon in the summer experiments where enhanced ^{54}Mn and ^{109}Cd K_D 's were found. The enhanced uptake of Cd_d was attributed to (a) an increased affinity to diatom surfaces, (b) increased production of organic complexes i.e. phytochelatin production by diatoms as indicated by relevant speciation calculations or (c) increased mineralisation of phytoplankton thus increasing the surface area available for sorption or increasing the number of bacteria responsible for the mineralisation. In contrast the increased uptake of Mn_d has been attributed to uptake by algae under conditions of increasing free Mn ion concentrations in the water column although lack of Mn_d or free Mn ion concentrations in the Humber coastal zone during summer'95 renders such explanations speculative.

These results indicate the large variation in K_D 's with particle type which itself is a function of the season and prevailing meteorological and hydrodynamic climates. However in the multivariate modelling of trace metals a single K_D is often used (or one that is purely a function of the change in salinity) to describe the particulate to dissolved phase (and vice versa) transitions for each trace metal under study. This work therefore suggests that K_D should itself be incorporated into such models as a function of particle type and composition i.e. POC content.

5 Particle Settling Velocity

Experiments

5.1 Introduction

Understanding the behaviour and transport of suspended sediments in estuarine and coastal waters is of importance on both engineering and environmental grounds (Bale, 1996). In highly dynamic estuarine and nearshore coastal regimes, the varying current velocities and the change of current direction in tidal areas result in a complex cycle of sedimentation and resuspension of particles and it is principally these processes that are the predominate factors controlling SPM transport (Niedergesäß *et al.*, 1994). The mathematical modelling of the transport of SPM and associated contaminants, e.g. trace metals, requires the settling velocity distribution of the SPM masses and the specific concentrations of particulate trace metals in the different fractions of the SPM (Niedergesäß *et al.*, 1994; Williams, 1995). A number of studies have investigated the settling behaviour of particles in estuarine (Owen, 1971, 1976; Gibbs, 1985; Puls *et al.*, 1988; Burban *et al.*, 1990; Fennessy *et al.*, 1994; Prochnow *et al.*, 1994; Dearnaley, 1996; Dyer *et al.*, 1996; Jones & Jago, 1996; Pejrup & Edelvang, 1996; van Leussen, 1996; Wolfstein, 1996) and coastal environments (Kineke & Sternberg, 1989; Kineke *et al.*, 1989; Jago *et al.*, 1993) but few have addressed the associated transport of particle-associated contaminants (Niedergesäß *et al.*, 1987, 1994; Williams, 1995). The median settling velocity of trace metals can only be treated in the same respect as that of the SPM within predictive modelling if the respective settling velocities are comparable. Hence there is a need to quantify trace metal settling velocities in order to refine long range fine-sediment chemistry transport models. Williams (1995) conducted preliminary

investigations into the settling velocities of trace elements in the Humber nearshore coastal zone and showed that the median settling velocities of all particulate metals studied (Fe, Mn, Zn, Ca, Co, Cu & Pb) varied according to tidal state and year and were often different to the settling velocity of the mass SPM. The aims of this study are to build upon the trace metal settling velocities previously evaluated for the Humber coastal zone and to provide, for the first time, an investigation into the seasonal variation in the settling velocities of Fe, Mn, Cu, Cd, Pb. The variation in $^{206/207}\text{Pb}$ isotopic ratios with particles of different settling velocities have also been investigated to determine whether anthropogenically derived Pb preferentially associates with any particular settling fraction of the SPM population and whether any seasonal variations are evident.

All particle settling experiments were performed using QUISSET's as described in section 2.1.5. There are a number of different instruments and handling techniques employed in the measurement of settling velocities ranging from an array of settling tubes, often referred to as 'Owen Tubes' (Owen, 1971, 1976; Kineke *et al.*, 1989; Kineke & Sternberg, 1989; Cornelisse, 1996; Dearnaley, 1996; Jones & Jago, 1996; Pejrup & Edelvang, 1996; van Leussen, 1996; Wolfstein, 1996) to direct measurement systems using visual aids (Kineke *et al.*, 1989; van Leussen & Cornelisse, 1993; Fennessy *et al.*, 1994; Fennessy & Dyer, 1996) e.g. high magnification video cameras, direct video measurements of flocs settling within tubes. Recent concern over the comparability of settling velocity data derived from the different available techniques has led to the instigation of an international intercomparison study funded by the European Commission as part of the MAST II project. This study showed that the different instruments used, including the QUISSET, gave quite different SPM concentrations but in general displayed the same broad trends. The differences observed between systems were attributed to (a) SPM patchiness in highly turbid estuarine environments such as those sampled in the Elbe intercomparison experiment, (b) sampling a rapidly varying turbulent field, with small variations in location and sampling instant being significant and (c) different tube handling procedures. The measured median settling velocities (W_s^{50}) showed a scatter of up to an order of magnitude between the different systems. Of those considered the QUISSET system showed the smallest scatter in data (greatest precision). QUISSET samples in general exhibited lower median settling velocities (W_s^{50}) when compared to other Owen tubes. This difference was accentuated at SPM concentrations $<100 \text{ mg l}^{-1}$. Several possible reasons were suggested for these differences including (a)

the QUISSET system broke up flocs to a greater extent than the other systems, (b) the thermal insulation of the QUISSET (see section 2.1.5) led to a more accurate measure of settling velocity at low concentrations and (c) the contrasting methods of calculating settling velocities. It was also concluded that the hourly collected samples were not sufficient to achieve an adequate definition of the changing concentrations of SPM. For a complete summary of the results of the intercomparison study the reader is referred to Dyer *et al.* (1996).

There are a variety of problems inherent in the use of settling tube technology. These are reviewed in detail by Syvitski *et al.* (1991) with particular emphasis on sample introduction. A problem perceived with Owen tubes in general is that the material is captured while flowing horizontally through the tube, with possible effects due to shearing in the boundary layer created by wall friction (Dyer *et al.*, 1996). The QUISSET system, to some extent, counteracts this problem by moving the tube rapidly across a volume of water during collection (Jones & Jago, 1996). This does not entirely remove the problem of wall friction but helps to collect a more representative sample. However the actual movement of the tube closing causes a pressure pulse that can disrupt flocs. Nevertheless at present the QUISSET system is the most appropriate method for determining the settling velocities of trace metals as it allows the collection of sufficient SPM within each settling fraction facilitating the accurate determination of particulate trace metal concentrations.

5.2 Sampling Strategy

Typically settling velocity experiments were performed in the mouth of the Humber Estuary (HW5, refer to Figure 2.3) during maximum tidal streaming on the flood tide in autumn'94 and subsequently during maximum flood and ebb tides in winter'95, spring'95 and summer'95 (see Table 5.1). Two further QUISSET deployments were performed at a sampling location adjacent to the Holderness Cliffs (S2, refer to Figure 2.3) during maximum flood and ebb tide in autumn'94. The primary focus of the investigation was on the settling characteristics and subsequent transport of particulate bound trace metals from anthropogenically modified SPM emanating from the Humber Estuary (Grant &

Middleton, 1990; Turner *et al.*, 1991) to the nearshore coastal environment. However the mass dominant source of SPM arises from the erosion of the boulder clay cliffs of Holderness (Wilmot & Collins, 1981) and hence therefore the importance of examining the settling behaviour of particles from both end member SPM sources to the receiving Humber coastal zone. Tidal resuspension of bed sediments is generally greatest at times of maximum flood and ebb currents. The deployment time of the QUISSET tubes was chosen to ensure that a complete particle spectrum was sub-sampled. Sampling during both the maximum flood and ebb tide (a) guaranteed the collection of temporally and permanently suspended particles and (b) allowed any differences in particle settling velocities between successive tidal states to be elucidated. Concurrent seasonal sampling at the mouth of the Humber Estuary also investigated possible changes in the composition of the SPM population owing to seasonal processes such as phytoplankton blooms.

5.3 Calculation of SPM Settling Velocity

The settling velocity distribution of suspended particles is a complex function of a large number of factors including (a) particle size, (b) mineralogical composition, (c) concentration of SPM, (d) salinity, (e) temperature and (f) flow turbulence. There are several methods of determining the settling velocity of particles¹ which tend to give different results (Owen, 1976; Dyer *et al.*, 1996) depending upon which of the above influencing factors are included. For the current study an actual seawater sample is used in the QUISSET experiments, therefore the effects of SPM concentration and salinity are automatically included in the determination of the particle settling velocity spectra. The QUISSET was also designed to collect an 'undisturbed' sample of the suspension (see Jones & Jago, 1996 & section 5.1) and because the settling velocity of the suspended particles are measured immediately after collection and the *in-situ* temperature maintained by a thermally insulating jacket pumped with seawater the effects of temperature are also included².

¹ The QUISSET tubes measure particle settling velocity indirectly via Stokes Law (see section 5.4)

² Because the sample is collected relatively undisturbed the floc sizes and effective densities are those determined by the natural flow turbulence. However for the present study the particle diameters were obtained by an *in-situ* laser particle sizer (see section 2.1.8).

Settling velocities were obtained graphically following the method described by Owen (1976). Water samples were decanted from the bottom of the QUISSET tube at 5, 20, 80, 320 minutes plus the residual fraction (greater than 320 minutes) and subsequently filtered through pre-weighed, acid washed, 0.4 μm Nuclepore filters from which the weight of SPM in each fraction was recorded (see section 2.1.5). A table was subsequently compiled first calculating the cumulative weight of SPM at the respective time intervals. A depth factor was then calculated by dividing the length of the QUISSET tube (1 m) by the actual depth of fall of each particle settling fraction³. The depth factor was then used to correct the cumulative weights and times to those required for a full 1 m height of settling of each withdrawn sample. The true corrected SPM weights were then divided by the total sediment weight to give corrected % cumulative weights which were subsequently plotted against corrected time on semilogarithmic graph paper. An example of which is shown in Figure 5.1.

The settling velocity of dispersed particles (and mud flocs) in water greatly depends on the water temperature, mainly because of the large changes in viscosity (Owen, 1976). Therefore the temperature of the first withdrawn fraction is rounded off to the nearest degree, and the times required to settle 1 m at that temperature (tabulated in Owen, 1976) plotted along the abscissa, as in Figure 5.1 for a temperature of 5°C. A piece of tracing paper is then laid on the graph paper and horizontal lines are drawn at the 0 and 100% cumulative weight levels. Two vertical lines are then drawn, one at time 1.0 and the other at time e (2.718) minutes (e is the base of Napierian logarithms) i.e. the distance between the two lines is $\log e - \log 1 (=a)$. The tracing paper is then moved horizontally until the right hand vertical line coincides with one of the marked standard times and a tangent to the curve is now drawn at this point (T on Figure 5.1) to intercept the left hand vertical line. The percentage at which this interception occurs is then read from the ordinate and gives the percentage by weight of the suspension which has a settling velocity less than that defined by the time T (Figure 5.1).

³ From a knowledge of the cross sectional area of the tube and volume of each particle fraction the height of each settling fraction can be calculated. The depth of fall of each particle fraction can then be calculated by addition of later fractions i.e. the actual depth of fall of fraction 1 is the addition of the heights of all fractions 1-5.

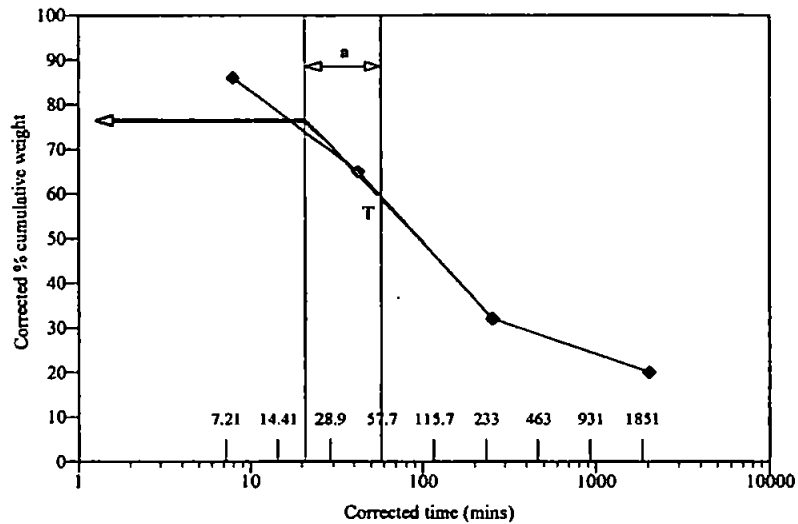


Figure 5.1 An example of a plot of corrected % cumulative weight against corrected time for a QUISSET tube deployed in the mouth of the Humber Estuary during an ebb tide in winter'95. Times of known standard settling velocities at the temperature of the water sample (5°C) are marked on the abscissa. The two vertical lines are a distance of $\log e - \log 1$ apart ($=a$). The right hand line has been aligned with a standard settling velocity time of 57.7 minutes and a tangent drawn to the curve at this point. At the intercept of this tangent with the left hand line the % cumulative weight values are obtained.

The above procedure was repeated for each of the selected times marked on the time axis and a graph plotted of % cumulative weight as a function of settling velocity on semilogarithmic graph paper (for example see Figure 5.2). The W_s^{50} was then read from the x-axis at the point of intersection of the 50% cumulative weight with the curve.

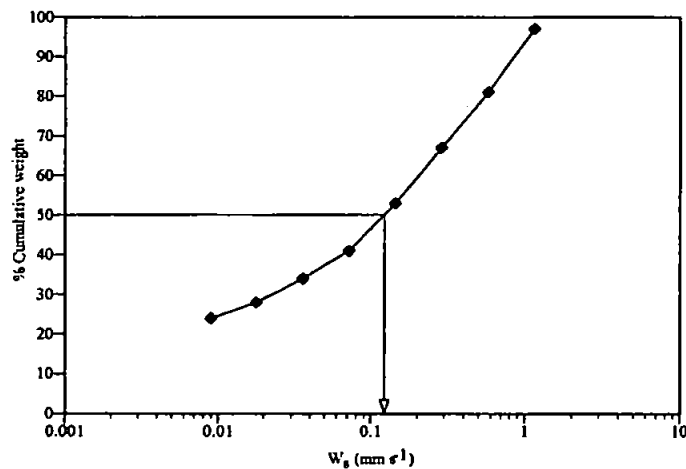


Figure 5.2 An example of a semilogarithmic plot of % cumulative weight as a function of particle settling velocity for the QUISSET deployment in the mouth of the Humber Estuary during winter'95, ebb tide.

The W_s^{50} were determined for each QUISSET deployment using the above method and ranged between 10^{-4} to 10^{-1} mm s^{-1} as summarised in Table 5.1. In good agreement with this data set, Williams (1995) reported median settling velocities between 10^{-3} to 10^{-1} mm

s⁻¹ for QUISSET samples taken in the mouth of the Humber Estuary, Plume and the Holderness regions in winter 1992 and 1993.

The W_s^{50} 's obtained for the nearshore Holderness region are shown in Table 5.2 and reveal a median settling velocity two orders of magnitude greater during maximum ebb tide compared to maximum flood tide. The magnitude of W_s^{50} during maximum flood of approximately 10^{-4} mm s⁻¹ is comparable to typical background settling velocities of seston components in permanent suspension in the south-east North Sea (Jago *et al.*, 1993). This data suggests that there is significant variation in W_s^{50} over the tidal cycle for SPM samples located nearshore to the Holderness Cliffs but the data only covers the autumn season of one year making any subsequent explanation of processes merely speculative in nature. However, it is conceivable that during maximum ebb tide the resuspension of bed material was observed that mostly settled out during low water slack. Whilst the returning flood waters saw the advection of background concentrations of SPM in permanent suspension from further offshore. Consideration of the hydrodynamics of the Holderness nearshore region i.e. the tide ebbs to the north-west and floods to the south-east would alternatively suggest during the ebb tide possible transport of material derived from the Humber Estuary to the Holderness coast. Estuarine derived particles typically have greater W_s^{50} (refer to Table 5.1) than those sampled adjacent to the Holderness Cliffs and would hence increase the W_s^{50} of the particle population. The material obtained during the flood tide is also likely to include fine boulder clay material derived from the erosion of the Holderness Cliffs in addition to background SPM in permanent suspension.

A similar study carried out in waters adjacent to the Holderness Cliffs by Williams (1995) reported a W_s^{50} of 3×10^{-3} mm s⁻¹ during low water slack in autumn '93. If you consider this data to be representative of general low water conditions in autumn, irrespective of year, and compare the median settling velocities from Holderness samples (see Table 5.2) the data reveals a decrease in W_s^{50} from maximum ebb tide to low water slack i.e. lower proportion of heavy estuarine material in water column during slack water, a trend previously noted before for QUISSET samples in the south-east North Sea by Jago *et al.* (1993).

The median settling velocity data from QUISSET tubes deployed in the mouth of the

Table 5.1 Summary of QUISSET deployments and associated W_s^{50} .

Cruise	Location	Tidal Conditions		Salinity	Temperature (°C)	[SPM] (mg l ⁻¹)		W_s^{50} (mm s ⁻¹)	Chlorophyll a ⁶ (µg l ⁻¹)	POC ⁴ (%)	Humber Outflow ⁷ (m ³ s ⁻¹)
		Range ⁵ (m)	State			QUISSET ²	Go-Flo ³				
Autumn'94	Holderness ¹		Flood	34.291	11.1	26.7	7.9	<0.0001	-	*	
	Holderness ¹		Ebb	34.297	11.1	17.4	5.3	0.027	-	*	
Winter'95	Humber Mouth	6.6	Flood	33.819	10.6	47.3	50.4	0.003	-	*	165
	Humber mouth	5.0	Flood	29.215	4.8	284.3	325.8	0.095	-	13.3 ± 5.9	425
Spring'95	Humber Mouth	5.0	Ebb	28.810	4.7	338.6	290.4	0.125	-	10.1 ± 0.9	425
	Humber mouth	6.6	Flood	33.581	8.3	113.58	85.4	0.035	0.81	15.9 ± 2.2	345
Summer'95	Humber Mouth	6.6	Ebb	32.493	8.4	123.5	110.5	0.170	0.83	14.9 ± 3.0	345
	Humber mouth	4.9	Flood	32.030	15.0	56.5	70.6	0.0009	4.16	16.2 ± 2.5	70
	Humber Mouth	4.9	Ebb	33.095	14.5	39.2	27.6	0.0004	0.86	16.7 ± 1.3	70

¹Anchor station at S2 due east of the Holderness Cliffs (refer to Figure 2.3 for location); ²SPM values were determined by the ratio of the total cumulative weight of SPM filtered and the total volume of seawater filtered; ³SPM values were calculated gravimetrically from water samples taken using Go-Flo water sample bottles; ⁴Particulate organic carbon content obtained from Loss On Ignition; ⁵Tidal range at Spurn Head (53.583N 0.117E), spring range 5.7 m, neap range, 2.8 m; ⁶Chlorophyll a data courtesy of BODC, LOIS RACS(C) core data; ⁷Residual water flow estimated by a hydrodynamical model (Wood, 1993); - Data not available; * Samples not taken.

Table 5.2 Median settling velocities of particulate material nearshore to the Holderness Cliffs.

	W_s^{50} (mm s ⁻¹)		
	Autumn'93 ^a	Autumn'94	
	low water	max. flood	max. ebb
Holderness nearshore	0.003	<0.0001	0.027

^aData from Williams (1995)

Humber Estuary are given in Table 5.1. Some seasonal differences in W_s^{50} were apparent with winter'95 and spring'95 (ebb tide only) showing the greatest settling velocities of approximately 10^{-1} mm s⁻¹. Summer settling velocities were the lowest values ranging 10^{-3} to 10^{-4} mm s⁻¹. Spring (flood tide) and autumn values were found to be intermediate. Generally there were little differences between flood and ebb tides except in spring'95 when settling velocities decreased from 170×10^{-3} mm s⁻¹ on the ebb tide to 35×10^{-3} mm s⁻¹ on the flood. Highest W_s^{50} observed in winter and spring (ebb tide only) also coincided with periods of elevated estuarine outflow indicating the likelihood of a dominant estuarine particle source with characteristic settling velocities of the order 10^{-1} mm s⁻¹ (refer to Table 5.1). These findings are consistent with recent data from the Elbe Estuary where a W_s^{50} of 7.9×10^{-1} mm s⁻¹ was observed during maximum current flow by Jones & Jago (1996) and a value of 1.6×10^{-1} mm s⁻¹ was similarly reported by Niedergesäß *et al.* (1994). Fennessy *et al.* (1994) also observed minimum values of approximately 10^{-1} mm s⁻¹ for the Tamar Estuary while Burban *et al.* (1990) quoted an average settling speed of 8×10^{-2} mm s⁻¹ for all flocs. Particle populations sampled during the summer showed markedly decreased W_s^{50} 's of 9×10^{-4} and 4×10^{-4} mm s⁻¹ for flood and ebb tides respectively. These are comparable to those of Prochnow *et al.* (1994) who during spring and summer seasons for the Spree river reported settling velocities $<3.5 \times 10^{-3}$ mm s⁻¹ which was attributed to phytoplankton growth. Similarly Jago *et al.* (1993) also reported settling fractions of 10^{-2} mm s⁻¹ during plankton blooms in May'92 in the south-east North Sea, which coupled with high values of POC and low C/N ratios suggested that the fractions consisted of living and degrading cells and aggregates of *Phaeocystis*. Chlorophyll a concentrations during the summer flood tide (refer to Table 5.1) support this hypothesis when concentrations peak at $4.16 \mu\text{g l}^{-1}$ but ebbing waters display a relatively low chlorophyll a concentration of $0.86 \mu\text{g l}^{-1}$ *cf.* spring values which were perhaps more indicative of typical background settling velocities of

particles in permanent suspension (Jago *et al.*, 1993), although the high values of % POC values suggest some organic component.

It is perhaps more informative to consider the relative importance of the various particle sources when attempting to explain the current seasonal data set. Winter displays the highest W_s^{50} 's of the order 10^{-1} mm s⁻¹, with the exception of the flood tide during the following spring, and displays little variation between successive flood and ebb tides. This information in combination with an elevated estuarine outflow of 425 m³s⁻¹ and enhanced SPM concentrations (284-339 mg l⁻¹, refer to Table 5.1) suggests that estuarine particulate material dominates the particle population. The lower flood W_s^{50} is perhaps indicative of the dilution of estuarine particulate material by marine or Holderness SPM of characteristically lower W_s^{50} . The following spring values as previously mentioned revealed a W_s^{50} during the ebb tide much greater than the flood and indeed greater than the ebb tide during the previous winter. This is attributed to the enhanced tidal spring range experienced during the spring compared to the winter survey increasing (a) the relative proportion of estuarine derived particulate material and (b) the amount of resuspended bed sediments in the total SPM population sampled. This data suggests that most of the particles are a re-suspended mixture of river and sea derived particles, the percentage contribution of each source being a complex function of estuarine outflow, SPM concentration and tidal range. The concentration of chlorophyll a and % POC of the SPM indicate little difference between successive tidal states (in the order of 0.8 µg l⁻¹ and 15% respectively) but values do nevertheless suggest the presence of biogenic particles during both the flood and ebb tide but perhaps not in sufficient quantities to dominate either population.

During the following summer a much depressed river outflow of 70 m³s⁻¹ yields a lower contribution of riverine particulate matter to the total SPM. This results in a higher percentage of marine particulate matter at the mouth of the Humber Estuary (Dyer, pers comm) of lower W_s^{50} in the range 10^{-3} - 10^{-4} mm s⁻¹. The variation in W_s^{50} between flood and ebb tides is insignificant *cf.* spring values which is probably enhanced by a smaller tidal range (see Table 5.1). The magnitude of the W_s^{50} 's suggest typical background SPM in permanent suspension of marine origin, however, the noticeably high chlorophyll a concentration of 4.16 µg l⁻¹ obtained during the flood tide suggests a particle

population composed of a relatively greater proportion of biogenic material, most probably attributable to phytoplankton growth (Prochnow *et al.*, 1994).

The W_s^{50} determined in this study imply that particles of low settling velocity in the range 10^{-3} - 10^{-4} mm s⁻¹ obtained in the Humber mouth in summer and Holderness coast (flood tide) in autumn are likely to settle so slowly that, even under the most quiescent conditions, rarely encountered in the North Sea, significant proportions are likely to remain in suspension in the water column and undergo significant advective transport. For example, assuming an average water depth of 25 m, the absence of flocculation processes and particles behaving according to Stokes Law (Williams, 1995), a SPM population with a W_s^{50} of 10^{-4} mm s⁻¹ would take approximately 2800 days to settle to the bottom of the water column under conditions of low turbulence. Estimates by Jago *et al.* (1993) suggest that settling velocities in the range 2-0.2 mm s⁻¹ would be required to allow particles to settle during slack water. The highest W_s^{50} of 0.125 mm s⁻¹ and 0.170 mm s⁻¹ obtained during ebb tides in winter and spring respectively are therefore those most likely to deposit on the bed. However, a similar calculation to the one above, with a water depth of 10 m (average water depth in the mouth of the Humber estuary) and a W_s^{50} between 0.125-0.170 mm s⁻¹, gives estuarine particle deposition times between 16-22 hours for spring and winter ebb flows respectively.

To summarise it would appear that during winter and spring (ebb only) periods particles with the greatest settling velocities are encountered coincident with enhanced SPM concentrations and elevated river discharges. Hence there are higher flow velocities (Niedergesäß *et al.*, 1994) which possibly resuspend bed particulates (themselves of high settling velocities) which are consequently deposited back to the seabed again in <24 hours. Conversely during summer particles with lower settling velocities are attributed to an interaction of particles of a biogenic nature (plankton), with advection of background seston in permanent suspension (Jago *et al.*, 1993).

The relationship between W_s^{50} and total SPM concentration has been investigated by many authors (Owen, 1971; van Leussen, 1988; Fennessy *et al.*, 1994; Puls *et al.*, 1988; Williams, 1995; Dyer *et al.*, 1996; Jones & Jago, 1996; Pejrup & Edelvang, 1996; van Leussen, 1996) in the form:

$$W_s^{50} = k.C^m$$

5.1

where W_s^{50} =median settling velocity in mm s^{-1} , C =total concentration of SPM in mg l^{-1} , K is an empirical constant and m is an empirical exponent.

Figure 5.3 illustrates the observed relationship between W_s^{50} and SPM concentration from the present study and implies that variations in W_s^{50} are a function of the total SPM concentration. However from Chapter 3, section 3.3.2, it was reported that the concentration of SPM at the mouth of the Humber Estuary was related to tidal range ($r=0.83$, $P<0.05$) and to some degree residual water outflow indicating their likely 'indirect effect' on the W_s^{50} of particle population sampled. The QUISSET deployed adjacent to the Holderness coast on the flood tide has not been included on the plot because a W_s^{50} could not be obtained due to % cumulative weight never falling below 50% (refer to Figure 5.2). Extrapolation of the curve was not possible because of levelling at 80% cumulative weight implying that 80% of the SPM had a settling velocity $<0.0001 \text{ mm s}^{-1}$.

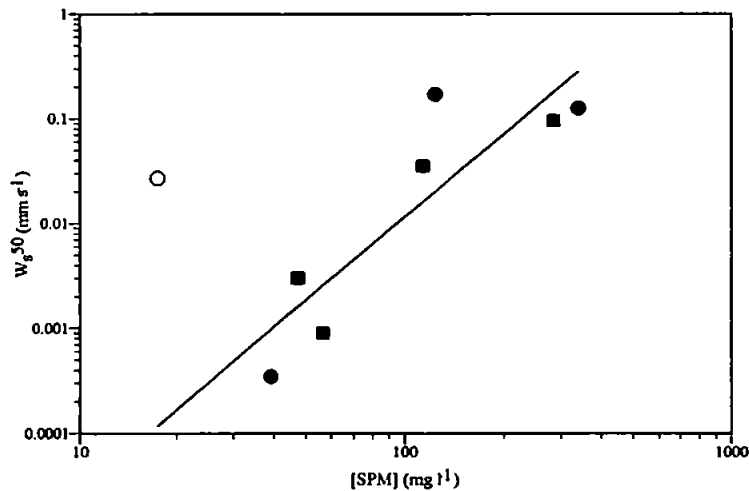


Figure 5.3 W_s^{50} as a function of SPM concentration for QUISSET deployments at the Holderness Cliffs autumn '94 ebb tide (○) and in the Humber mouth autumn '94 flood tide (■); winter '95 at flood (■) and ebb (●) tide; spring '95 at flood (■) and ebb (●) tide and summer '95 at flood (■) and ebb (●) tide, using Equation 5.1 (Jones & Jago, 1996).

The geometric fit as in Equation 5.1 applied to the data in Figure 5.3 excludes the one value obtained at the Holderness Cliffs (○) and gives values of $m=2.62$ and $k=6 \times 10^{-8}$ ($n=7$) with a correlation coefficient $r=0.88$ which is significant at 99% confidence limits ($P<0.01$). Table 5.3 shows a comparison of the values of the empirical constants found in the literature and indicates good agreement with the results for the present study.

Values for m generally range between 0.6-2.6 for estuary environments (Jones & Jago, 1996) although a maximum value of 2.92 has been quoted by van Leussen (1988). Results from the recent inter-comparison experiment in the Elbe Estuary have indicated that inter-estuarine differences in the value of m reported in the literature may be partly the result of different handling techniques (Dyer *et al.*, 1996). However changes in the values of m have also been attributed to varying floc density and/or organic matter (Dyer, 1994) which could partly explain the scatter in Figure 5.3 (refer to changes in chlorophyll a concentration and % POC values in Table 5.1). However it is interesting that the scatter in Figure 5.3 could also be partially explained on the basis of tidal range i.e. the W_s^{50} obtained during winter and summer seasons only show much less scatter in the data and correspond to approximately the same tidal limits (5.0 & 4.9 m respectively, refer to Table 5.1) *cf.* autumn and spring values when strong spring tides (6.6 m range) were evident.

Table 5.3 Comparison of the empirically derived constants m and k in equation 5.1.

	Humber mouth	Humber flood data	Humber neap data ¹	Elbe estuary ²	Elbe estuary ³	Weser mouth ⁴
N ^o samples	7	4	4	23	22	22
m	2.62	2.41	1.96	2.36	0.69	1.04
k	6×10^{-8}	2×10^{-7}	4.5×10^{-2}	5×10^{-7}	4.1×10^{-2}	1.4×10^{-1}

¹Data from Williams (1995) from the mouth of the Humber Estuary during neap tides only;

²Jones & Jago (1996); ³Cornelisse (1996); ⁴Puls *et al.* (1988).

5.4 Particle Sizes and Densities of SPM

In marine environments particle diameters and effective densities are difficult parameters to determine due to flocculation and deflocculation processes of often irregular shaped particles with low densities⁴ (Williams, 1995). However, recent advances in technology have led to the development and application of an *in-situ* particle sizer (see section 2.1.8) to more accurately determine the diameter of particles. The measurement of particle diameter combined with the calculation of particle settling velocity allows an estimate of effective particle density through the application of Stokes Law.

⁴ Individual particles that have high densities often include organic material in variably open structures that result in lower densities for flocs.

A dense particle released in a column of water will start to fall, and within a distance of a few particle diameters, its fall velocity will be constant. This is the terminal fall velocity and is achieved when the drag forces equal the immersed weight of the sphere (Dyer, 1986). At a settling Reynolds number <1 the drag forces (F_D) can be calculated as;

$$F_D = 3\pi\mu DW_s \quad 5.2$$

where μ =molecular viscosity ($\text{kg m}^{-1} \text{s}^{-1}$), D =diameter of particle (m) and W_s =settling velocity (m s^{-1}) (Dyer, 1986). The immersed weight (I) of the particle is the difference between the force of gravity acting downwards and buoyancy force acting upwards. This is expressed as;

$$I = \frac{4}{3} \pi \frac{D^3}{8} (\rho_s - \rho)g \quad 5.3$$

where ρ_s and ρ are the particle and water density (kg m^{-3}) respectively and g is the gravitational acceleration (m s^{-2}) (Dyer, 1986). Assuming that terminal fall velocity of the particle has been attained the above forces must be equal. Combining equations 5.2 and 5.3, W_s can be expressed in terms of the particle diameter and is known in this form as Stokes Law (Allen, 1985);

$$W_s = \frac{D^2}{18} \left(\frac{\rho_s - \rho}{\mu} \right) g \quad 5.4$$

The settling Reynolds number (Re_s) is a ratio of the inertial and viscous forces (Allen, 1985) and distinguishes between laminar and turbulent flows (Pye, 1994). A Reynolds number can be formed from the settling velocity and particle diameter as a measure of these effects such that;

$$Re_s = \frac{\rho DW_s}{\mu} \quad 5.5$$

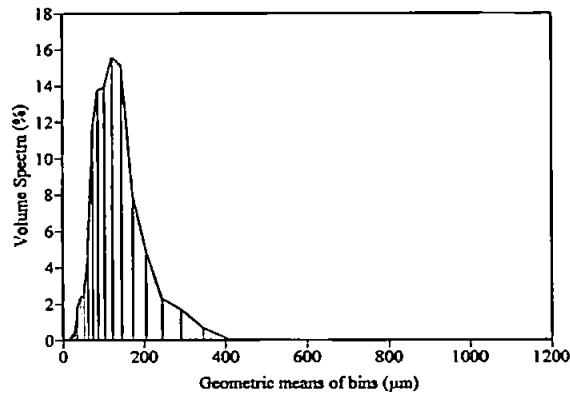
Following the deployment of each QUISSET tube the *in situ* particle sizer (Par-tec 100, refer to section 2.1.8) stored particle size distribution data (Law *et al.*, 1997) of the sampled water column. The particle size spectra for all the QUISSET experiments are shown in Figure 5.4, whilst median particle sizes (D^{50}) are summarised in Table 5.4.

Table 5.4 Median particle diameter, D^{50} for each QUISSET experiment.

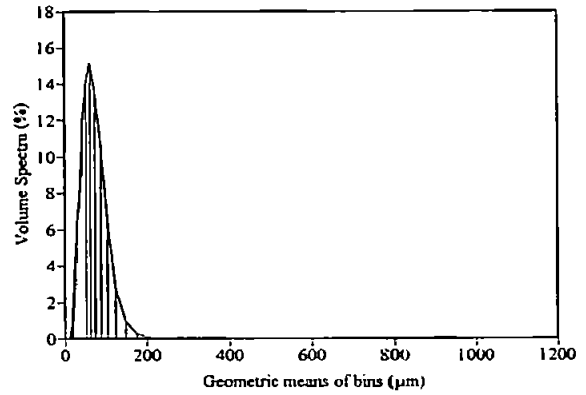
Season	Location	Tidal state	D^{50} (μm)
Autumn'94	Holderness	flood	86
	Holderness	ebb	92
	Humber mouth	flood	49
Winter'95	Humber mouth	flood	166
	Humber mouth	ebb	90
Spring'95	Humber mouth	flood	54
	Humber mouth	ebb	52
Summer'95	Humber mouth	flood	120
	Humber mouth	ebb	74

The largest median particle diameters were observed during flood tides in winter'95 (166 μm) and summer'95 (120 μm) in the mouth of the Humber Estuary. In contrast, the smallest D^{50} 's were recorded during spring'95 flood and ebb tides (54 and 52 μm respectively) and autumn'94, flood tide (49 μm) in the Humber mouth. Interestingly Holderness material displayed intermediate D^{50} ranging between 86-92 μm . The composition of eroded Holderness quaternary material has been estimated at 67% mud (<63 μm) (McCave, 1987). Recent studies conducted in this study by the wet sieving of collected Holderness terrestrial samples (refer to section 2.1.7) similarly showed 70% of the material was <63 μm . The increase in D^{50} observed nearshore to the Holderness Cliffs is attributed to either (a) flocculation of primary clay sized particles (Fennessy *et al.*, 1994), (b) entrained estuarine derived particles of increased particle diameter, (c) resuspension of coarser bed material or (d) a combination of all three processes. Both winter'95 and summer'95 deployments displayed large differences in D^{50} between successive flood and ebb tides. During winter'95 it is possible that flood tides advected Holderness derived material past the anchor station in the mouth of the Humber Estuary. This material, as explained above, comprises of mostly clays which exhibit electrostatic charges, causing them to be attracted to one another (Fennessy *et al.*, 1994) i.e. flocculation. It is therefore foreseeable that the increase in D^{50} observed on the flood tide in winter'95 is a result of flocculated material, principally derived from Holderness being driven past the anchor station by the flooding tide. The tide floods to the south-east along the Holderness coast which, combined with moderate (10-15 knots) north-easterly winds during the winter cruise (see Figure 3.3c & d) could provide a suitable transport mechanism for Holderness derived material. However this hypothesis is purely

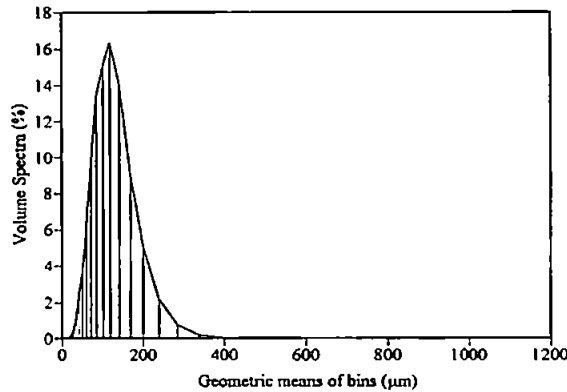
(a) Holderness, ebb tide



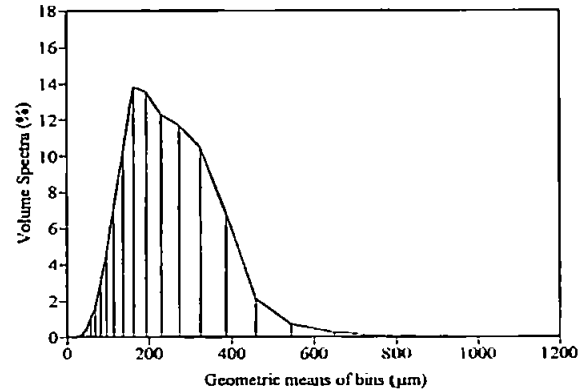
(b) Humber mouth, flood tide



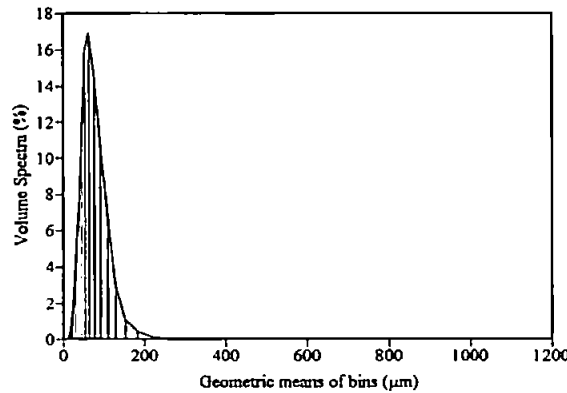
(c) ebb tide



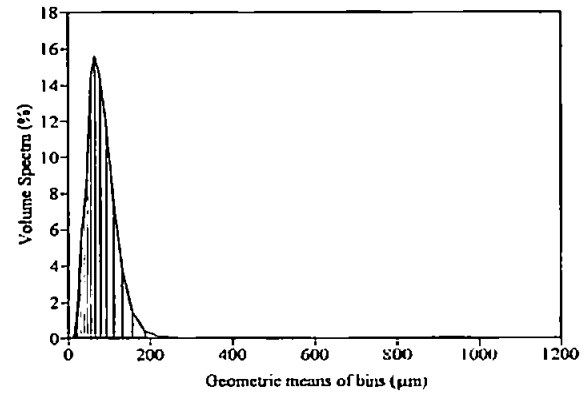
(d) flood tide



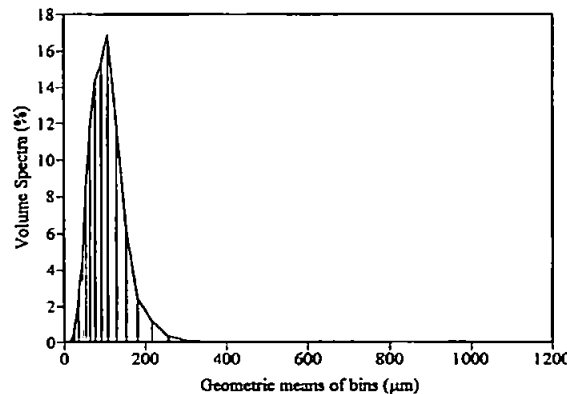
(e) ebb tide



(f) flood tide



(g) ebb tide



(h) flood tide

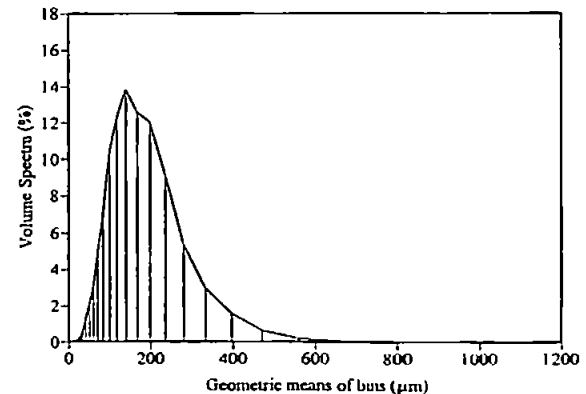


Figure 5.4 Particle size distributions obtained from the *in situ* deployment of the Par-tec 100 laser (refer to section 2.1.8) during (a) & (b) Autumn'94; (c) & (d) Winter'95 at the Humber mouth; (e) & (f) Spring'95 at the Humber mouth and (g) & (h) Summer'95 at the Humber mouth on the ebb and flood tides as labelled. Data courtesy of D. Law (see acknowledgements).

speculative and results could also be explained by resuspension of coarser bed sediments during maximum flood tide. Indeed recent results from the NERC LOIS Littoral Investigation of Sediment Properties (LISP-UK) study for sites in the Humber Estuary have shown that maximum bottom sediment entrainment and subsequent sediment transport occurs during the passage of a shallow, turbulent, bore-like flood front (Dyer, pers comm; Black *et al.*, 1997).

The increase in D^{50} observed during the flood tide of the following summer could be due to aggregated material of a more biogenic nature brought into the mouth of the Humber Estuary from nearshore coastal waters as indicated by high chlorophyll a concentrations and % POC values ($4.16 \mu\text{g l}^{-1}$ & 16.2% respectively, please refer to Table 5.1). Biological material enhances flocculation processes by providing fibrous structures around which clay particles can build (Fennessy *et al.*, 1994) and subsequently cementing these structures with bacterially active compounds such as mucopolysaccharides (Linley & Field, 1982). The wind direction during the summer was more mixed (see Figure 3.3g & h) but was mainly either from the north-east or south-west, the former of which could have also transported flocculated Holderness material past the Humber anchor station *cf.* previous winter. It is difficult to establish whether the enhanced D^{50} observed during the flood tide in summer is due solely to biogenic matter or whether the signal is augmented by Holderness material. However the differences in W_s^{50} observed between the Holderness and Humber sites, in addition to the enhanced chlorophyll a concentration and %POC values observed (see Table 5.1), suggest that the increase in D^{50} reported is more likely to be due to an increase in the amount of biogenic matter contributing to the total SPM population. Similar processes may explain why a difference was not observed between the flood and ebb tides for the D^{50} obtained during the spring survey i.e. chlorophyll a concentrations were low ($0.81\text{-}0.83 \mu\text{g l}^{-1}$) in addition to strong southerly winds (15-20 knots, see Figure 3.3e & f) which would have tended to hinder material emanating from the Holderness region being advected into the mouth of the Humber Estuary.

Many studies have shown that larger flocs generally have lower effective densities than smaller flocs (see Dyer, 1989; Fennessy *et al.*, 1994). Effective densities being defined as the difference between the floc bulk density and the water density ($(\rho_s - \rho)$, see Stokes Law, Equation 5.4). Stokes Law is only applicable for settling Reynolds numbers < 1 ,

indicative of laminar flow conditions where the particles creep through the water, distorting the flow for relatively large distances from the particle and leaving no wake (Dyer, 1986). Assuming that the molecular viscosity of seawater (μ) is equal to $0.001 \text{ kg m}^{-1} \text{ s}^{-1}$, the density of seawater (ρ) is equal to 1025 kg m^{-3} and substituting the W_s^{50} for W_s and D^{50} for D , for each QUISSET experiment into Equation 5.5 gives settling Reynolds numbers between 10^{-2} and 10^{-5} i.e. <1 . Therefore the use of Stokes law to calculate the effective densities of the particles from a knowledge of the W_s^{50} 's and D^{50} 's is valid. Figure 5.5 shows the relationship between W_s^{50} and D^{50} , where the diagonal lines represent effective constant density obtained from the application of Stokes Law (Equation 5.4).

The calculated effective densities thus obtained should be treated as estimates rather than absolute values since W_s^{50} and D^{50} may not adequately represent the whole particle population (Williams, 1995). The assumptions inherent in the application of Stokes Law should also be recognised, i.e. it assumes that particles are uniform density, smooth spheres with diameters $<100 \text{ }\mu\text{m}$ (equivalent to that of fine sand) that settle alone in an unbounded fluid (Allen, 1985) i.e. unrealistic in dynamic estuarine and coastal zones.

The calculated particle densities shown in Figure 5.5 range between $1025 - 1185 \text{ kg m}^{-3}$. The density of pure clay minerals ranges between $2000 - 3300 \text{ kg m}^{-3}$ (Allen, 1985) *cf.* the density of kaolinite and quartz minerals of 2600 kg m^{-3} and 2650 kg m^{-3} respectively. Puls *et al.* (1988) reported that the density of mud flocs ranged between $1048 - 1367 \text{ kg m}^{-3}$ indicating that particles in the mouth of the Humber Estuary and nearshore Holderness region are likely to comprise of low density mud flocs. This data compares well with observed floc densities in the Tamar (Fennessy *et al.*, 1994) and Elbe (Dyer *et al.*, 1996) estuaries where the majority of samples ranged between $1041 - 1185 \text{ kg m}^{-3}$. It is interesting to note that particles observed off the Holderness Cliffs in autumn'94 during the ebb tide had the same density (approximately 1031 kg m^{-3}) as those recorded at the mouth of the Humber Estuary during flood tide in winter'95. This supports the process suggested earlier that the enhanced D^{50} obtained in winter'95 during the flood tide in the mouth of the Humber could have been due to some flocculated material originating from the Holderness region being advected into the estuary on the flooding tide. The highest particle densities were recorded during the ebb

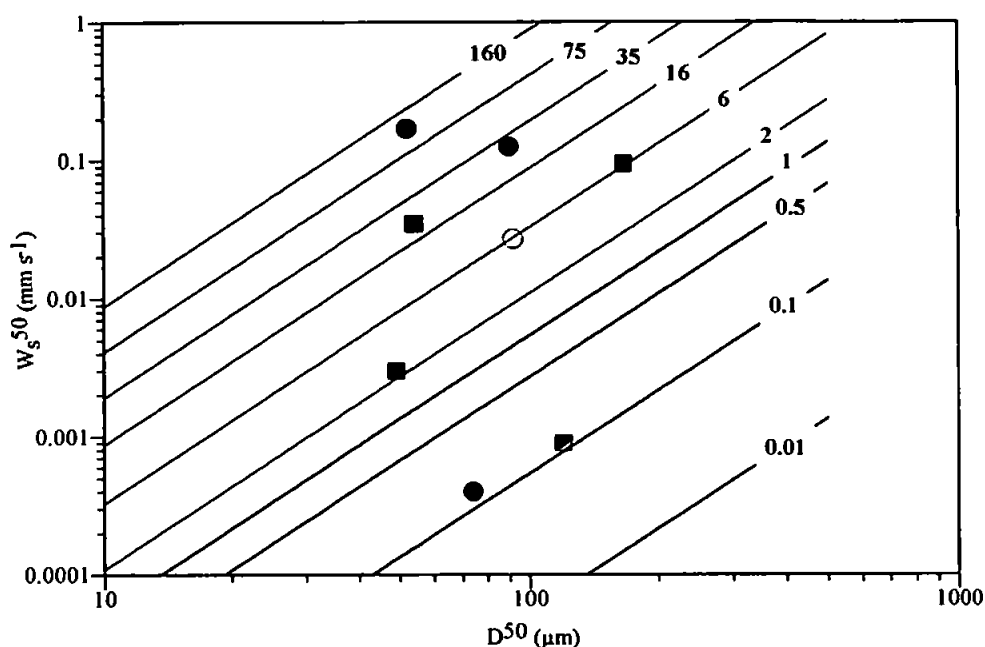


Figure 5.5 Median particle settling velocity as a function of median particle diameter for each QUISSET settling experiment ((○) Holderness Cliffs autumn'94 ebb tide; (■) Humber mouth autumn'94 flood tide; (■) Humber mouth winter'95 flood tide; (●) Humber mouth winter'95 ebb tide; (■) Humber mouth spring'95 flood tide; (●) Humber mouth spring'95 ebb tide; (■) Humber mouth summer'95 flood tide; (●) Humber mouth summer'95 ebb tide). The diagonal solid lines are calculated effective density (kg m^{-3}) using Stokes Law, where the numbers represent $(\rho_s - \rho)$ in Equation 5.4.

tide in winter'95 (approximately 1060 kg m^{-3}) and in the following spring (approximately 1045 & 1185 kg m^{-3} for the flood and ebb tide respectively) coincident with elevated SPM concentrations and periods of maximum estuarine outflow (425 and $345 \text{ m}^3 \text{ s}^{-1}$ respectively). This reinforces the hypothesis that dense estuarine derived particles, possibly resuspended bed material, contributed significantly to the particle population during these times. Summer displayed particles whose densities approached those of seawater supporting the suggestion that they were permanently suspended in the water column (see W_s^{50} values in Table 5.1). The large median particle sizes (see Table 5.4) coupled with high % POC and chlorophyll a concentrations (see Table 5.1) during the flood tide, previously implied large aggregates of material biological in nature. This view is supported further by the low density they exhibit and agrees with the general concept that larger flocs (as evident by high D^{50}) have lower bulk densities (Dyer, 1989). In agreement Jago *et al.* (1993) reported a seston category of particles such as those sampled during summer'95 that were relatively rich in organic carbon with low settling velocities, in long term suspension. Puls *et al.* (1988) also observed that slow flocs (W_s

<2.1 mm s⁻¹) had higher contents of combustible organic carbon compared to fast flocs ($W_s > 2.1 \text{ mm s}^{-1}$).

The present results at the mouth of the Humber Estuary have shown relatively large variations in W_s^{50} , D^{50} and effective density with tidal state and season. The variation in W_s^{50} have been largely explained by the total concentration of SPM which is in itself a function of tidal regime and estuarine outflow. The observed changes in D^{50} were subsequently influenced by the relative proportions of particles originating from estuarine and marine sources, i.e. resuspended bed sediments and biogenic particles or flocculated Holderness material respectively. The relative proportion of which changes considerably according to season, tidal state and prevailing meteorological conditions. However the resulting calculated effective densities of the particle populations in the mouth of the Humber Estuary and adjacent to the Holderness coastline in general suggest low density mud flocs that are periodically enhanced by the resuspension of estuarine bed sediments. These changes in W_s^{50} , D^{50} and effective density of the particle population will undoubtedly have profound effects on the transport potential of the particulate matter and associated contaminants (e.g. trace metals) down the water column and spatially throughout the southern North Sea.

5.5 Trace Metal Analysis of Settling Fractions.

This section considers the concentrations of Fe, Mn, Cu, Cd and Pb in each settling fraction collected from the QUISSET tubes. The median settling velocity for each trace metal was determined for each experiment in a similar manner to that used for the SPM, and subsequently compared to the particulate W_s^{50} . These results were then used to assign the trace metals into broad settling categories according to whether the metal (i) settled faster, (ii) equal to or (iii) slower than the SPM. The trace metal settling velocities indicate the possible deposition times to the bed sediment and hence likely spatial transport in relation to the SPM. This knowledge is essential when developing and refining contaminant transport models especially in cases when the metal or contaminant under study settles at a notably different rate to the mass SPM.

5.5.1 Particulate trace metal concentrations of each settling fraction

The %POC and concentrations of SPM, Fe_p, Mn_p, Cu_p, Cd_p, Pb_p and ^{206/207}Pb isotopic ratios are shown in Figure 5.6 a-h. The concentration of particulate metals are presented on a w/w basis. Please refer to Appendix E for a tabulated list of the results for each experiment. The five settling fractions labelled 1-5 in Figure 5.6 represent the individually collected QUISSET fractions at 5, 20, 80, 300 and greater than 300 minutes respectively (see section 2.1.5). Therefore a progressive increase in trace metal concentration from fraction 1 to fraction 5, i.e. left to right, indicates an increasing association of the metal with the slower settling SPM fractions. To provide a means of assessing the integrity of the trace metal data derived from QUISSET tubes compared to that from traditional Go-Flo bottles (see section 2.1.2), immediately prior to the deployment of a QUISSET tube a water sample was also collected at the same station using Go-Flo bottles. The unfractionated SPM sample collected from the Go-Flo (as described in section 2.1.2) bottle was similarly analysed for particulate metals and compared to the sum of the trace metals obtained from the five QUISSET fractions. Assuming that the concentrations in the QUISSET fractions behave in an additive manner (Williams, 1995) they should be approximately equal to the concentration obtained from the unfractionated sample. The results from the QUISSET tubes, expressed as a percentage of the respective trace metal concentration obtained from the Go-Flo bottle sampling, gave an average of 107%, 100%, 109%, 99.6% and 104% for Fe, Mn, Cu, Cd and Pb. These results were in keeping with those obtained by Williams (1995) who quoted a comparable range between 80-140% for Fe, Mn and Zn and were considered acceptable given the smaller sample volumes of the QUISSET tubes and errors involved in the addition of trace metal concentrations from the five different sample fractions.

The QUISSET experiments performed adjacent to the Holderness coast in autumn'94 during maximum flood and ebb tides are discussed initially (see Figure 5.6) before the seasonal cycles at the mouth of the Humber Estuary are considered in more detail. The lowest concentrations of SPM, Fe_p, Mn_p, Cu_p and Pb_p were found adjacent to the Holderness cliffs (compare the average metal concentration as shown by the lines in Figure 5.6) reflecting the relatively uncontaminated nature of the eroded lithogenic clay

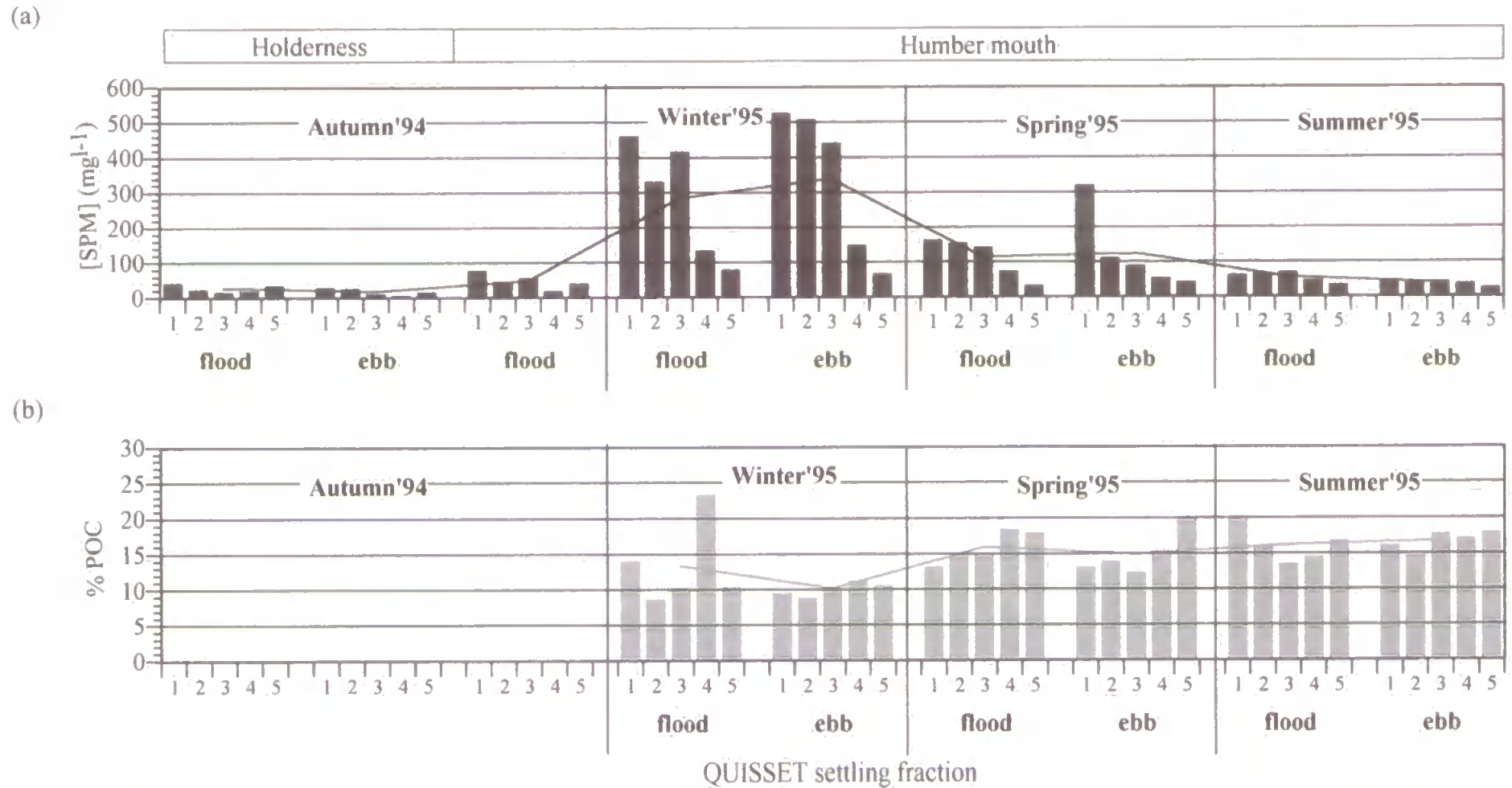


Figure 5.6 Concentrations of (a) SPM and (b) % POC determined in each of the five sample fractions derived from the deployment of the QUISSET tubes. The QUISSET fractions 1-5 were collected at 5, 20, 80, 300 and 300+ minutes, respectively, after the QUISSET was stood in the vertical position. The lines show the average SPM concentration or %POC for each QUISSET experiment.

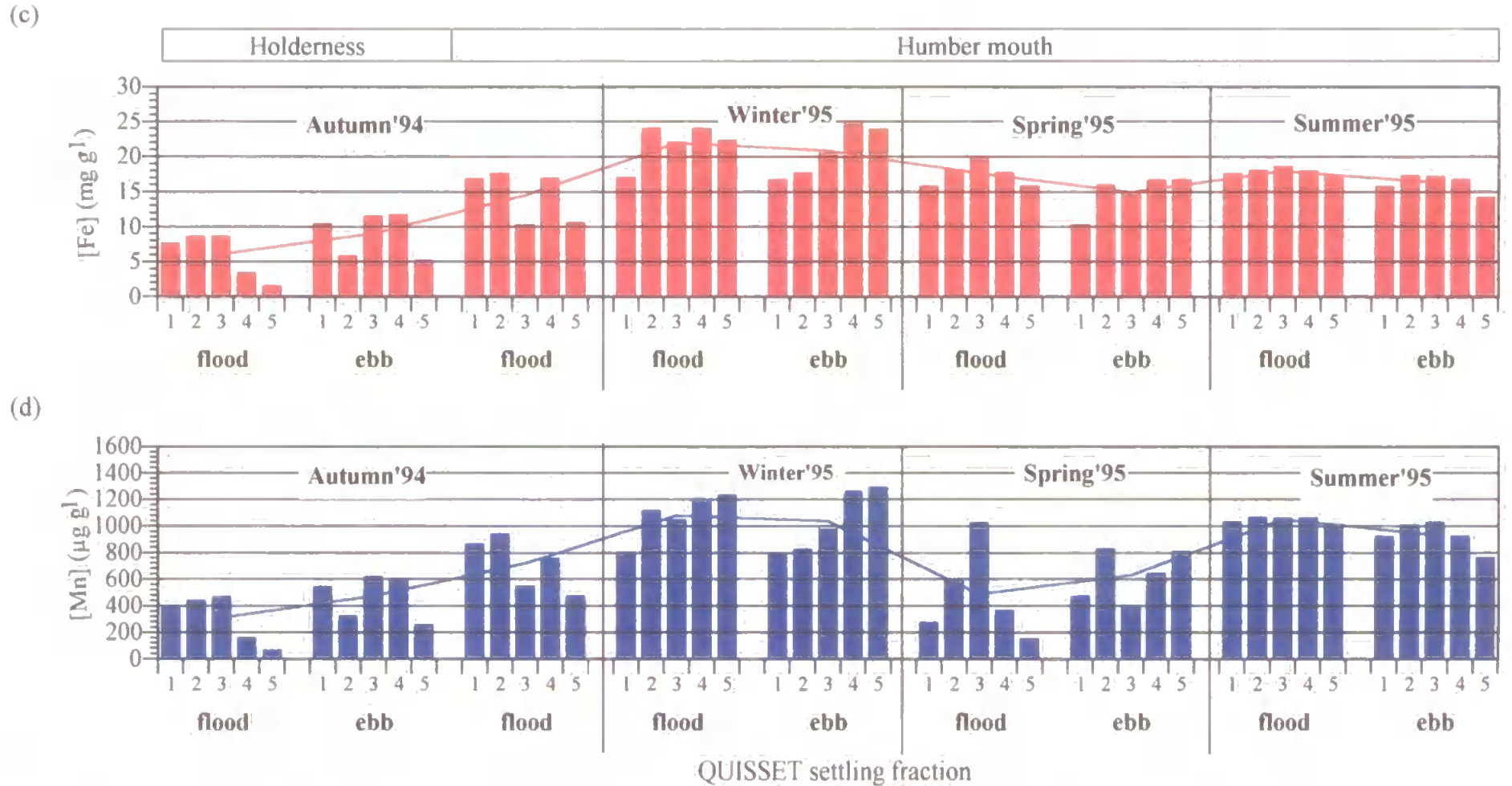


Figure 5.6 continued. Concentrations of (c) Fe_p and (d) Mn_p determined in each of the five sample fractions derived from the deployment of the QUISSSET tubes. The QUISSSET fractions 1-5 were collected at 5, 20, 80, 300 and 300+ minutes, respectively, after the QUISSSET was stood in the vertical position. The lines show the average metal concentration for each QUISSSET experiment.

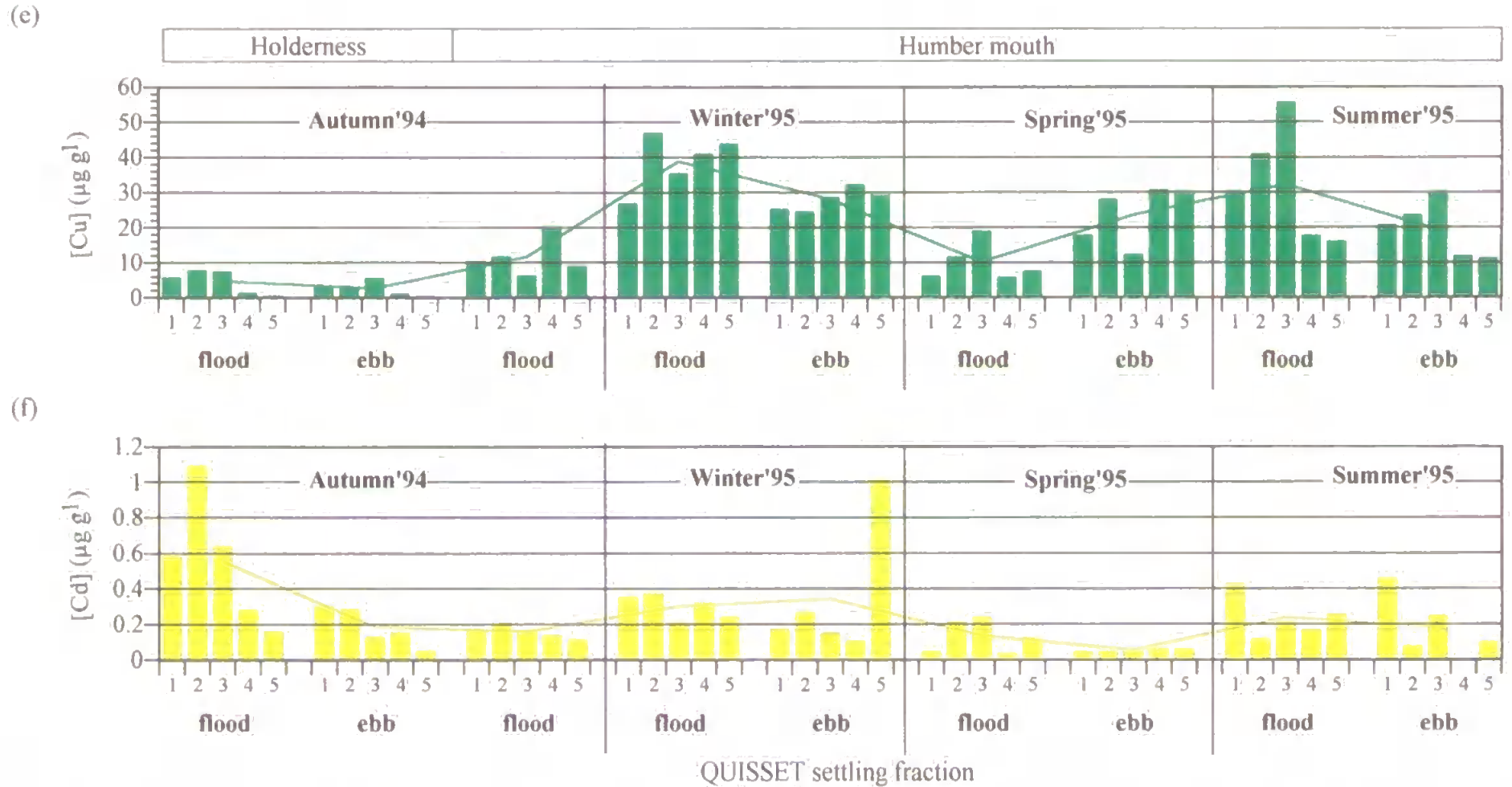


Figure 5.6 continued. Concentrations of (e) Cu_p and (f) Cd_p determined in each of the five sample fractions derived from the deployment of the QUISSSET tubes. The QUISSSET fractions 1-5 were collected at 5, 20, 80, 300 and 300+ minutes, respectively, after the QUISSSET was stood in the vertical position. The lines show the average metal concentration for each QUISSSET experiment.

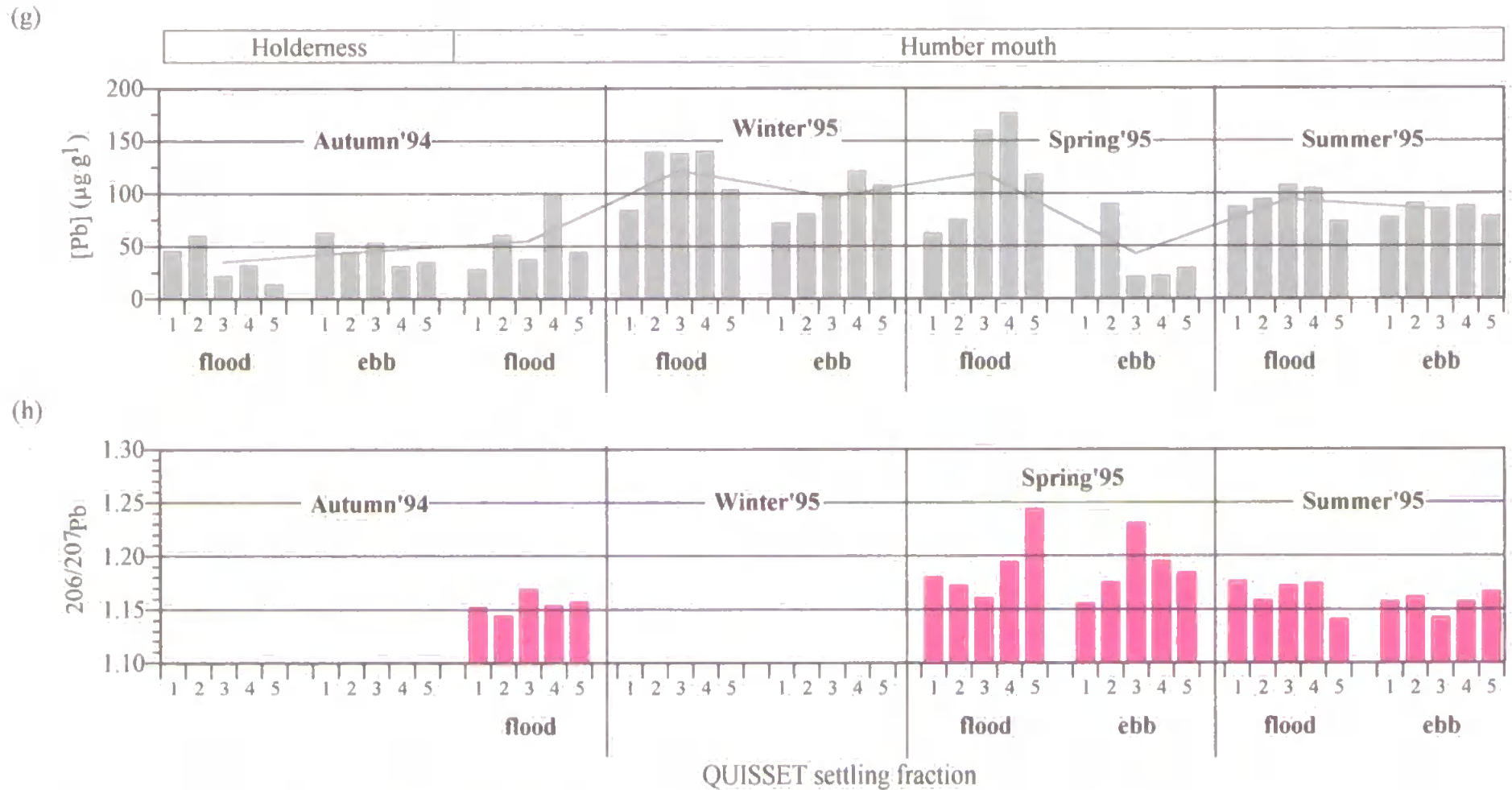


Figure 5.6. continued. Concentrations of (g) Pb_p and (h) $^{206}/^{207}\text{Pb}$ isotopic ratio determined in each of the five sample fractions derived from the deployment of the QUISSET tubes. The QUISSET fractions 1-5 were collected at 5, 20, 80, 300 and 300+ minutes, respectively, after the QUISSET was stood in the vertical position. The lines show the average metal concentration for each QUISSET experiment.

material. The average concentrations of Fe_p , Mn_p and Pb_p were however slightly enhanced during the ebb tide possibly a consequence of entrained estuarine SPM or the resuspension of bed sediments as previously mentioned in section 5.3. In contrast the average concentrations of Cu_p and Cd_p were elevated during the flood tide, a trend highly exaggerated by Cd_p (concentrations $\geq 0.6 \mu\text{g g}^{-1}$ for the heaviest fractions 1-3) possibly indicative of an enhanced marine source. The high Cd_p concentrations could have been due to preferential association with marine derived particles of a more biogenic or organic nature as previously mentioned in Chapter 3 (sections 3.2.3 & 3.4). Indeed during autumn'94 the SPM W_s^{50} of $< 10^{-4} \text{ mm s}^{-1}$ previously suggested a permanently suspended background particle population of marine origin. However the lack of supporting data i.e. chlorophyll a concentrations, %POC etc. restricts any firm conclusions.

During autumn'94 the average concentration of SPM and all particulate trace metals, except Cd, showed a subsequent increase during the flood tide in the mouth of the Humber Estuary and indeed all subsequent flood tides compared to both the Holderness experiments. This is attributed to the importance of the Humber Estuary as a source of anthropogenic trace metals to the receiving nearshore coastal waters. Consideration of the residual currents and tidal movements adjacent to the Holderness coast i.e. tide floods to the south-east might have implied that the flood profiles obtained adjacent to the Holderness coast and in the Humber mouth would be similar, concurrent with the same body of water flooding south-easterly from the Holderness Cliffs and subsequently being swept up past the mouth of the Humber Estuary (enhanced by the north-westerly winds, see Figure 3.3a & b) but this was not found. It seems more likely that the relative proportion of Holderness derived particulate material was greater at the sampling site adjacent to the Holderness Cliffs leading to lower particulate trace metal levels compared to the mouth of the Humber. The analysis of $^{206/207}\text{Pb}$ isotopic ratios was only performed during autumn'94 in the Humber Estuary due to available sample volumes and indicated, in general, no distinct variations in $^{206/207}\text{Pb}$ ratio with particle settling fraction. However the average $^{206/207}\text{Pb}$ of 1.157 indicated an increase in Pb anthropogenic burden *cf.* Holderness Cliff 'end member' material $^{206/207}\text{Pb}$ of 1.200, also serving to illustrate the Humber as an important anthropogenic source of Pb_p to the coastal zone (see Chapter 6). Interestingly, during the flood tide in spring'95 the $^{206/207}\text{Pb}$ isotopic ratio increased notably to values approaching 1.200 and above in the lighter settling fractions 4 and 5.

This trend was accompanied by decreasing SPM, Mn_p, and Cu_p concentrations (Fe_p and Cd_p also decreased but the trend is less obvious) but increasing %POC suggesting the presence of marine derived material, possibly Holderness clay, in the lightest settling fractions. This increase in proportion of marine particles in the Humber mouth during the spring flood tide has previously been implied by the lower W_s⁵⁰ compared to the ebb tide, the large spring tidal range and the presence of chlorophyll a, albeit low.

The trace metal concentrations detected for each QUISSET experiment in the mouth of the Humber Estuary all showed variation with season in addition to particle settling preferences. Generally the highest levels of trace metals were found during winter'95 and lowest in spring'95, except for Pb_p, where both the highest and lowest concentrations were observed in the spring. During winter enhanced SPM concentrations (particularly in the heaviest settling fractions 1-3), W_s⁵⁰, D⁵⁰ and effective densities previously implied a mass dominant estuarine particle source, possibly attributed to the resuspension of bed sediments. Particulate iron and Mn showed increasing concentrations with the lighter settling fractions (more pronounced during the ebb tide) perhaps reflecting an association with more colloidal material or smaller relatively light particles with a larger specific surface area. Indeed the W_s⁵⁰ of all metals studied (refer to section 5.5.2) were slightly smaller than the total SPM (except Cd_p, winter flood tide, refer to Table 5.5) perhaps indicating preferential association with more permanently suspended material i.e. not temporally resuspended large bed particulates.

During summer'95 Fe_p, Mn_p and Pb_p showed uniform distributions amongst the settling fractions during both the flood and ebb tides. The particle settling studies of the previous section suggested a permanently suspended particle population of seawater density. This would imply that each settling fraction would be of a similar composition and hence the uniform distributions of the aforementioned metals. However Cu_p and Cd_p showed some variability in concentration with settling fraction. The distributions of Cu_p displayed the same trend during both the flood and ebb tides and suggested an increasing association with the heavier settling fractions 1-3. This was particularly evident during the flood tide when concentrations increased to 55.8 µg l⁻¹ in fraction 3. The relatively high chlorophyll a concentration of 4.2 µg l⁻¹ during the flood tide previously suggested an increase in proportion of biological particles present in the water column and perhaps

indicates an enhanced association of Cu with biological material (as previously suggested during summer for Cu_p in section 3.3). The chlorophyll a concentrations of individual settling fractions are not known restricting further interpretation of these results. The Cd_p concentrations showed a more variable trend with particle settling fraction but on both the flood and ebb tide did indicate an increase in concentration with the fastest particle settling fraction 1. However the concentrations were similar during both tides (0.43 and 0.46 µg g⁻¹ for the flood and ebb tide respectively) in contrast to the total concentration of chlorophyll a (see Table 5.1) not supporting the above hypothesis as applied to Cu_p. The ^{206/207}Pb isotopic ratios also showed little variation with particle fraction again suggesting that all settling fractions had a similar composition.

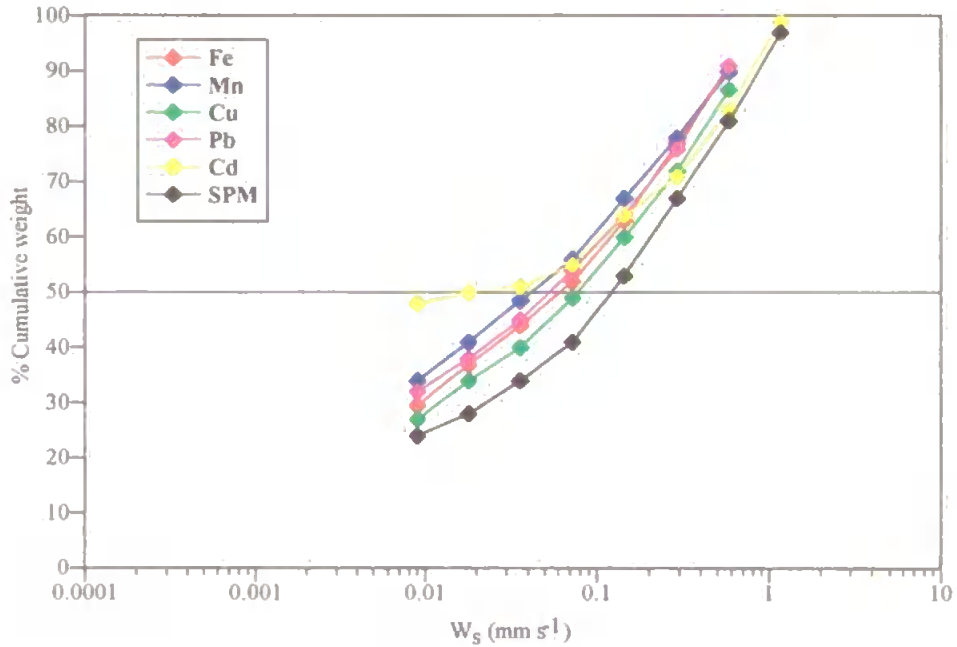
In general, all the trace metals studied show no overall preferential association with any settling fraction. However considering the highly dynamic regime of the Humber coastal zone and seasonally varying contributions from multiple particle sources this is perhaps not surprising. In general, each QUISSET experiment showed the same particulate trace metals trends with particle fraction. For example during the ebb tide in winter all metals studied, except Cd_p, showed increasing concentrations with the lighter settling fractions. This compares to the flood tide during the following spring when all metals exhibited a concentration 'pinnacle' in the median settling fraction 3 (fraction 4 for Pb_p).

5.5.2 Settling velocities of particulate metals

In order to investigate the trace metal settling data further a quantitative approach was adopted where the median settling velocity for each trace metal for each QUISSET experiment was derived essentially in the same way as described in section 5.3 for particulate matter. Two examples of the settling velocity distributions of SPM, Fe, Mn, Cu, Cd and Pb are illustrated in Figure 5.7. In the calculation of % cumulative weight of metal the concentration of trace metal (w/w) is converted to total weight in the fraction by multiplying by the weight of SPM i.e. % cumulative weight of trace metal is a function of SPM. The position of the cumulative weight curves for each metal relative to that of the SPM is an indication of whether the particulate metal is settling faster, slower or the same as the median particulate mass. For example if the metal of interest is preferentially associated with faster settling fractions indicative of resuspended bed

material its settling curve will be placed to the right or below that of the median SPM meaning that the W_s^{50} for the metal will be greater than the W_s^{50} for the SPM. The W_s^{50} determined for each trace metal within each experiment are shown in Table 5.5.

(a)



(b)

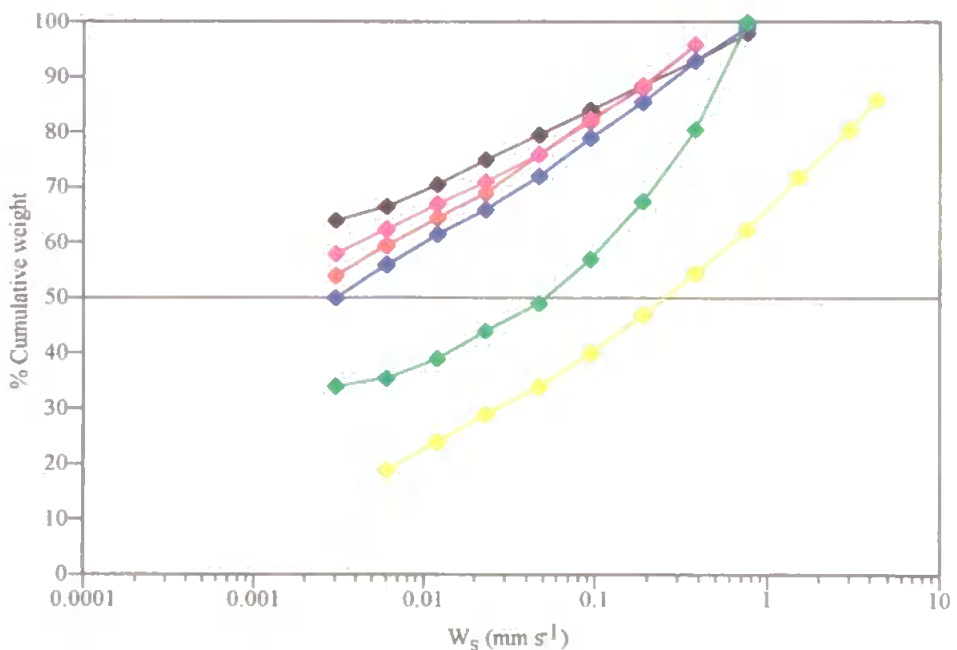


Figure 5.7 The settling velocity distributions for Fe, Mn, Cu, Cd, Pb and SPM for QUISSET settling experiments performed in the mouth of the Humber Estuary during an ebb tide in (a) winter'95 and (b) summer'95. Extrapolation of the curves were performed when necessary to obtain a median settling velocity.

Table 5.5 Median settling velocities for individual trace metals compared to mass SPM.

QUISSET experiment		W_s^{50} (mm s^{-1})					
		SPM	Fe	Mn	Cu	Cd	Pb
Autumn'94	Holderness flood	$<10^{-4}$	0.11	$<10^{-4}$	0.2	$<10^{-4}$	0.023
	Holderness ebb	0.027	0.007	0.062	0.26	0.66	0.13
	Humber flood	0.003	0.022	0.062	$<10^{-4}$	0.078	$<10^{-4}$
Winter'95	Humber flood	0.095	0.084	0.051	0.051	0.11	0.071
	Humber ebb	0.125	0.060	0.042	0.078	0.018	0.054
Spring'95	Humber flood	0.035	0.037	0.105	0.150	0.105	0.014
	Humber ebb	0.170	0.028	0.200	0.028	0.040	0.750
Summer'95	Humber flood	0.0009	0.0016	0.0016	0.090	0.0005	0.0046
	Humber ebb	0.0004	0.0017	0.003	0.050	0.260	0.0008

The W_s^{50} for the trace metals were divided into three classifications in an attempt to group trace metal behaviour according to their W_s^{50} in comparison to that of SPM. This provided a method to investigate whether the settling characteristics, and hence advective transport of contaminants, such as trace metals, could be treated in the same manner as the particulate mass in pollutant dispersal/transport models. The metal classification fell into three categories (Williams, 1995);

- (i) metals which settle faster than the median SPM,
- (ii) metals that settle at approximately the same rate as that of the median SPM,
- (iii) metals that settle slower than the median SPM

The results of the above categorisation are simplified in Table 5.6 and are colour coded to illustrate the individual QUISSET experiment and aid interpretation of the data. The present results indicate that none of the trace metals examined had a dominance in any one classification when comparing their W_s^{50} to that of the mass SPM. However some trends were evident. For example samples taken adjacent to the Holderness coast during autumn'94 showed that all metals studied, except Fe during the ebb tide, exhibited settling rates faster than or equal to the SPM. This suggests that the trace metals were associated with the more dense faster settling fractions of the particle population likely to have originated from either the Humber Estuary or from the resuspension of bed sediments as previously implied in section 5.3.

Table 5.6 Quantitative classification of trace metal W_s^{50} compared to those of the mass SPM where symbols represent particular QUISSET experiments.

Metal	Classification		
	Faster than SPM (i)	Same as SPM (ii)	Slower than SPM (iii)
Fe	□ ■ ■ ■ ■ ●		○ ■ ■ ● ●
Mn	○ ■ ■ ■ ■ ●	□	■ ■
Cu	□ ○ ■ ■ ■ ●		■ ■ ■ ● ●
Cd	○ ■ ■ ■ ■ ■	□ ■	● ●
Pb	□ ○ ■ ■ ■ ●		■ ■ ■ ■

Key: Autumn'94 Holderness flood (□) and ebb (○), Humber mouth flood (■); Winter'95 Humber mouth flood (■) and ebb (●); Spring'95 flood (■) and ebb (●); Summer'95 Humber mouth flood (■) and ebb (●).

Samples taken at the mouth of the Humber Estuary revealed some interesting seasonal trends. During the flood tide in winter'95 all the trace metals studied, except Cd, settled slower than the median SPM. Previous sections have identified the dominance of estuarine particulate matter, possibly a high proportion of resuspended bed material during this season. It is therefore possible that the trace metals preferentially associated with the relatively small lighter particles (compared to resuspended bed sediments), maybe colloidal material, with enhanced specific surface areas and hence lower W_s^{50} compared to the total SPM. However the calculation of the SPM W_s^{50} takes account of the whole particle including the individual minerals e.g. quartz, silicates. The density of quartz for example is 2650 kg m^{-3} (Allen, 1985) suggesting that in situations where estuarine material dominates the particle budget the apparent density and W_s^{50} of the SPM population is likely to be high. However, the trace metal analysis only quantifies surface bound concentrations i.e. Fe and Mn oxyhydroxides (see section 2.2.2) that are likely to be less dense in comparison and hence exhibit lower trace metal W_s^{50} .

The following spring'95 indicates some differences in trace metal settling trends between successive flood and ebb tides. All metals, except Pb, settled faster than the total SPM during the flood whilst the ebb tide portrayed a more mixed picture. The Humber Estuary has previously been established (refer to Chapter 3) as a major anthropogenic source of trace metals. During the flood spring tide contaminated estuarine particulate matter could have become diluted with less dense marine/Holderness particles relatively depleted in trace metal content and hence the lower SPM W_s^{50} in comparison to those of the trace metals. The particles during the ebb

tide were denser than the flood which perhaps suggests a mixture of estuarine particulate matter and resuspended bed sediments which serves to complicate the trace metal settling trends. The following summer revealed an opposite trend to the winter where all metals, except Cd during the flood tide, settled faster than the median SPM. The particle population was dominated by permanently suspended large particles probably of marine/biogenic origin, whereas the trace metals were likely to have originated from the estuary and hence were associated with the faster settling particle fractions and hence exhibited faster W_s^{50} . Autumn settling velocities at the mouth of the Humber presented a mixed picture with Fe, Mn and Cd settling faster than that of the SPM in comparison to Cu and Pb which settled slower than the SPM.

Trace metal settling velocities have received limited attention in the scientific literature. Niedergesäß *et al.* (1987;1994) reported some values for the Elbe Estuary and Williams (1995) similarly for the North Sea and Irish Sea. Trace metal settling velocities from the Elbe and Humber estuaries have been classified as outlined above in order to compare recent trends and are illustrated in Table 5.7.

Table 5.7 Trace metal settling velocity data from the Elbe and Humber estuaries.

Metal	Classification		
	Faster than SPM (i)	Same as SPM (ii)	Slower than SPM (iii)
Fe		□	■ ● ■ ● ○
Mn	○	■ ● ●	■ ● ■ □
Cu	○		
Pb	□ ○		■ ●

Key: Autumn'90 Elbe river flood (■) and ebb (●); Spring'91 Elbe river flood (■) and ebb (●); Winter'92 Humber flood (■) and ebb (●); Autumn'93 Humber flood (□) and ebb (○). Elbe river data extracted from Niedergesäß *et al.* (1994); Additional Humber data extracted from Williams (1995).

The trends in the Humber study of the North Sea (Williams, 1995) show some interesting similarities with the present data. Winter'92 settling velocities for Fe, Mn and Pb in the Humber Estuary during flood and ebb tides (except Mn ebb) were slower than the SPM in agreement with the trace metal data from winter'95 (Table 5.6). Results from autumn'93 in the Humber showed mixed results with Mn, Cu and Pb all settling faster than SPM during the ebb tide (unfortunately QUISSET experiments were not

performed during ebb tide in the mouth of the Humber Estuary in autumn'94) in comparison to the flood tide where Fe, Mn and Pb all behaved differently. Data from the Elbe Estuary (Niedergesäß *et al.*, 1994) showed varying behaviour patterns with Fe and Mn during the flood and ebb tide in autumn'90 both settling slower than the SPM whilst spring values indicated that Fe was still settling slower than the particulate material, but Mn was settling at approximately the same rate.

5.6 Summary

The results presented in this study are the first to examine the concurrent seasonal variations in the settling velocity of SPM, Fe, Mn, Cu, Cd and Pb in the Humber coastal zone. The calculation of trace metal W_s^{50} showed distinct changes with season relative to the SPM for all the metals studied. In winter all metals, except Cd during the flood tide, settled slower than the average SPM. This was attributed to enhanced proportions of estuarine particulate matter, specifically resuspended bed sediments dominating the particle population and hence increasing the particle W_s^{50} . The trace metal behaviour would therefore imply preferential association with the more permanently suspended lighter particles with presumably higher specific surface areas and hence W_s^{50} 's lower than the mass particle population. The following spring'95 ebb tide similarly portrayed a particle population perhaps dominated by heavy resuspended material enhanced by the prevailing spring tide. However trace metal W_s^{50} 's were mixed in behaviour complicating further interpretation. The trace metal W_s^{50} obtained during the flood tide were greater than that of the SPM. The large tidal range would have diluted the amount of estuarine particulate matter with marine SPM of typically lower W_s^{50} (see Table 5.1, autumn W_s^{50} obtained adjacent to the Holderness coast) and trace metal content (refer to Chapter 3). Hence the majority of the metals would have been associated with the estuarine proportion of particles and hence greater W_s^{50} compared to the total SPM. In agreement the following summer showed that all metals, again except Cd during the flood tide, settled faster than the average SPM presumably because the trace metals were associated with the more dense, estuarine derived particle fractions of the permanently suspended population. The results are summarised in further detail in Table 5.8.

Table 5.8 Summary of particle and associated trace metal dynamics in the Humber coastal zone.

Season	Particle characteristics				Trace metal characteristics	
	W_s^{50} (mm s ⁻¹)	Chl a/POC (µg l ⁻¹ /%)	D ⁵⁰ (µm)	$\rho_s - \rho$ (kg m ⁻³)	W_s^{50} (mm s ⁻¹)	Conclusions
Autumn Holderness	ebb >> flood (0.27 >> 10 ⁻⁴)	-	ebb ≅ flood (92 ≅ 83)	ebb > flood (6 > 0)	ebb & flood all metals ≥ SPM (except Fe ebb)	Trace metal source predominantly from the Humber Estuary and therefore preferential association with EPM and/or resuspended bed sediments, hence greater W_s^{50} than the total SPM.
	Entertainment of EPM or resuspension of bed sediments during ebb?		> pure Holderness clay material	Resuspension during ebb tide/evidence of EPM?	10 ⁰ -10 ⁻⁴ mm s ⁻¹ Trace metal transport metal specific.	
Autumn Humber	flood = 0.003 Tidal range = 6.6 m Outflow: 165 m ³ s ⁻¹ Wind: NW	-	flood = 49	flood = 2	mixed response	Background marine SPM with mixed metal settling times complicating interpretation of trace metal sources.
	Background marine SPM, significant dilution of EPM due to spring tide		< Holderness 'end member' material	Low density particulate matter	10 ⁻¹ -10 ⁻⁴ mm s ⁻¹ Trace metal transport metal specific	
Winter Humber	ebb ≅ flood (0.125 ≅ 0.095) Tidal range = 5.0 m Outflow: 425 m ³ s ⁻¹ Wind: NE	POC ebb ≅ flood (12%) Chl a -	ebb < flood (90 < 166) Maximum bottom sediment entrainment on flood or some flocculated Holderness material present?	ebb > flood (35 > 6)	ebb & flood all metals < SPM (except Cd flood)	Metals preferentially associated with permanently suspended particulate matter or dominant EPM source where SPM W_s^{50} includes residual mineral phases e.g. quartz [†] . Trace metal analysis of surface bound species only therefore less dense and lower W_s^{50} .
	Resuspended estuarine bed sediments & small marine SPM component			Flocculated material generally less dense	<4x10 ⁻² mm s ⁻¹ (except Cd ebb) Trace metal short - intermediate range transport	

Table 5.8 continued. Summary of particle and associated trace metal dynamics in the Humber coastal zone.

Season	Particle characteristics				Trace metal characteristics	
	W_s^{50} (mm s ⁻¹)	Chl ^a /POC (µg l ⁻¹ /%)	D ⁵⁰ (µm)	$\rho_s - \rho$ (kg m ⁻³)	W_s^{50} (mm s ⁻¹)	Conclusions
Spring Humber	ebb >> flood (0.170 >> 0.035) Tidal range = 6.6 m Outflow: 345 m ³ s ⁻¹ Wind: S	<u>POC</u> ebb ≅ flood (~ 15) <u>Chl a</u> ebb ≅ flood (~ 0.8)	ebb ≅ flood (52 ≅ 54)	ebb > flood (110 > 20)	<u>ebb</u> mixed response <u>flood</u> all metals > SPM (except Pb) 10 ⁰ -10 ⁻² mm s ⁻¹ Short range transport of trace metals	Ebb tide has a particle population dominated by EPM. Resuspension of bed sediments complicates trace metal patterns Flood tide increase in % of marine SPM, but estuarine source of trace metals therefore greater W_s^{50}
Summer Humber	ebb ≅ flood (0.0004 ≅ 0.0009) Tidal range = 4.9 m Outflow: 70 m ³ s ⁻¹ Wind: NE & SW	<u>POC</u> ebb ≅ flood (~ 17) <u>Chl a</u> ebb < flood (0.8 < 4.2) Increase in % biogenic particles on flood	ebb < flood (74 < 120)	ebb ≅ flood (~ 0)	<u>ebb & flood</u> all metals > SPM (except Cd flood) <10 ⁻³ mm s ⁻¹ (except Cu) Trace metal intermediate range transport	Trace metals associated with more dense particles of the total SPM population but metal W_s^{50} generally low compared to other seasons except for Cu. Trace metals still likely to have an estuarine source.

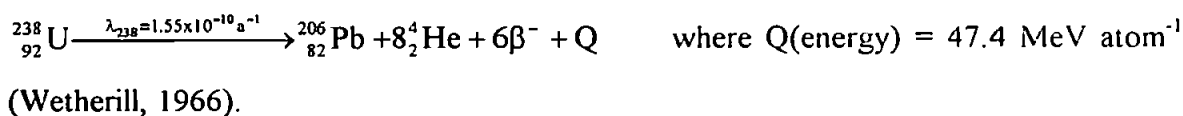
*Chlorophyll a concentration; †Density of quartz = 2650 kg m⁻³ i.e. $\rho_s - \rho = 1625$ kg m⁻³ (Allen, 1985); -Data not available; EPM - estuarine particulate matter.

The complicated trace metal concentration distributions with particle settling fraction (Figure 5.6) were difficult to interpret fully possibly due to the complex nature of multi-source particle populations. However these results do have important implications for the modelling and subsequent prediction of sediment chemistry transport models. They indicate, that in some cases, trace metal contaminant behaviour does not necessarily reflect that of the SPM and changes according to tidal state, prevailing weather, season and location. This work also potentially highlights the difficulties involved when trying to compare a total median particle settling velocity with a partially extracted trace metal settling velocity further suggesting, that when doing work of this nature one should use total trace metal concentration and not an approximate to the easily extractable fraction. However notwithstanding this caveat, spring flood and summer W_s^{50} 's suggested that the trace metals were associated with the smaller proportion of relatively dense particles and hence settled faster than the total SPM i.e. trace metal transport models based on the settling characteristics of the total SPM could overestimate trace metal transport by approximately one order of magnitude. This contrasts to winter conditions where such models could underestimate trace metal transport by a similar order of magnitude.

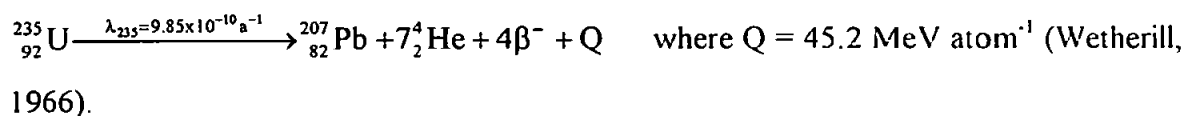
6 Stable lead Isotope Ratios in North Sea Particulates

6.1 Introduction

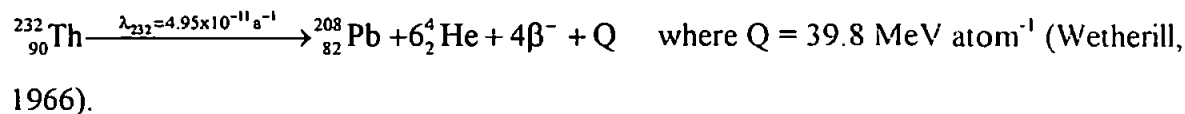
Lead has four naturally occurring isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb), but the element actually has 32 isotopes in all (Bowen, 1988). The other 28 are radioactive and are typically characterised by extremely short half lives e.g. ^{190}Pb , $T_{1/2} = 1.2$ minutes. Of the four stable lead isotopes of interest ^{204}Pb is non-radiogenic while the other three originate from natural radioactive decay of the unstable uranium isotopes. The decay of ^{238}U gives rise to the uranium series and ultimately ends in stable ^{206}Pb :



The decay of ^{235}U gives rise to the actinium series which ends up with stable ^{207}Pb :



The decay of ^{232}Th results in the formation of stable ^{208}Pb and can be written as:



The abundance of the three radiogenic isotopes have each been increasing at known independent rates throughout Earth's history relative to that of non-radiogenic ^{204}Pb . The present day composition of so called 'modern lead' lies within the area bounded by $^{206}\text{Pb}/^{204}\text{Pb} = 18.6-19.0$ and $^{207}\text{Pb}/^{204}\text{Pb} = 15.6-15.7$ which results in a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.20 ± 0.015 (Kersten *et al.*, 1992).

Lead is widely distributed throughout the Earth and occurs not only as the radiogenic daughter of U and Th but also forms its own minerals from which U and Th are largely excluded e.g. galena (PbS) (Faure, 1986). Indeed the determination of the Earth's age between 4.55-4.57 Ga is based on the 'primordial lead' isotopic composition in U- and Th-free mineral phases in meteorites (Pb in troilite of the iron meteorite Canyon Diablo) assuming that the earth and meteorites formed at the same time from an isotopically homogeneous solar nebula (Faure, 1986). Nier (1938) was the first to discover large variations in the isotopic composition of 'common' lead from different origins ('common lead' is that found in ores/minerals whose U/Pb and Th/Pb ratios are so low that its isotopic composition does not change appreciably with time). This discovery later led to the Holmes-Houtermans Model of Pb evolution in the Earth (Faure, 1986). This model accounts for the isotopic composition of any given sample of common Pb in terms of a single-stage history. It assumes that radiogenic Pb is produced by decay of U and Th in the source regions and that the resulting Pb (primordial plus radiogenic) is then separated from its parents and incorporated into ore deposits as galena. The isotopic composition of Pb in galena does not change because that mineral contains no U or Th. The isotopic composition between 'old' Pb derived from an ore deposit and modern Pb in recent sediments weathered from young sedimentary or igneous rocks thus will differ to an extent that increases with the geological age of the ore formation (Kersten *et al.*, 1992). Isotopic fractionation of modern Pb by present day biogeochemical processes e.g. weathering, accumulation by phytoplankton etc. does not lead to an enrichment or depletion of any of the Pb isotopes because of the extremely low U and Th decay rates and the relatively low mass differences between the Pb isotopes (Chow *et al.*, 1975). Lead emitted into the environment retains the isotopic composition of the ore from which it was derived. Therefore, there is the potential to distinguish sources of Pb pollution (Chow *et al.*, 1975; Elbaz-Poulichet *et al.*, 1986; Sturges & Barrie, 1987; Sturges & Barrie, 1989a & 1989b; Maring & Duce, 1990; Hopper *et al.*, 1991; Kersten

et al., 1992; Veron *et al.*, 1992; Rosman *et al.*, 1993; Sturges *et al.*, 1993; Williams *et al.*, 1994; Monna *et al.*, 1995; Moor *et al.*, 1996; von Blanckenburg *et al.*, 1996) and to evaluate the degree of anthropogenic contamination (Hamilton & Clifton, 1979; Patterson & Settle, 1987; Gobeil *et al.*, 1995; Grousset *et al.*, 1995; Williams, 1995; Farmer *et al.*, 1996) by simple mixing models of end members as documented in the literature cited for various environmental mediums e.g. marine particulates, seawater, atmospheric aerosols, soils etc.

However it should be kept in mind that a number of geological/geochemical and anthropogenic processes can add or remove Pb and U so perturbing the 'natural' isotopic signal leading to 'anomalous' Pb signatures (see Faure, 1986 for further details).

6.2 Variation of Stable Lead Isotopes due to Mixing

Lead isotopic compositions are often represented through ratios of a radiogenic isotope to the non-radiogenic isotope (^{204}Pb) whose abundance does not change with time (Doe & Stacy, 1974). The Pb isotopic composition for sediments and SPM of the western North Sea are plotted in Figure 6.1. Also shown are isotopic ratios of 'end member' sources and for reference, modern crustal Pb ratios (Kersten *et al.*, 1992), the isotopic standard reference material NIST 981 (Hirata, 1996) and primordial Pb based on the Pb ratios in troilite of the iron meteorite Canyon Diablo (Chen & Wasserburg, 1983). The primary source of Pb found in the environment over the past 10 years is mainly derived from the alkyl Pb compounds added to petrol as antiknock agents (Elbaz-Poulichet *et al.*, 1986). Today the U.K does not contain any workable deposits of lead ore and all Pb is imported (Hamilton & Clifton, 1979). The major source of lead ore and bullion to the UK and the rest of northern Europe is of Pre-Cambrian age from Australia (Mt. Isa and Broken Hill mines) and Canada (British Columbia orefield). The isotopic composition of both of these sources of Pb are very similar ($^{206/207}\text{Pb}=1.037$ and 1.064 for Australian and Canadian respectively, Chow *et al.* (1975)) but totally different from any other type of Pb found within the UK and northern Europe i.e. less radiogenic than modern crustal

Pb and local ores and hence its identification from a knowledge of the isotopic signature of the sample under question.

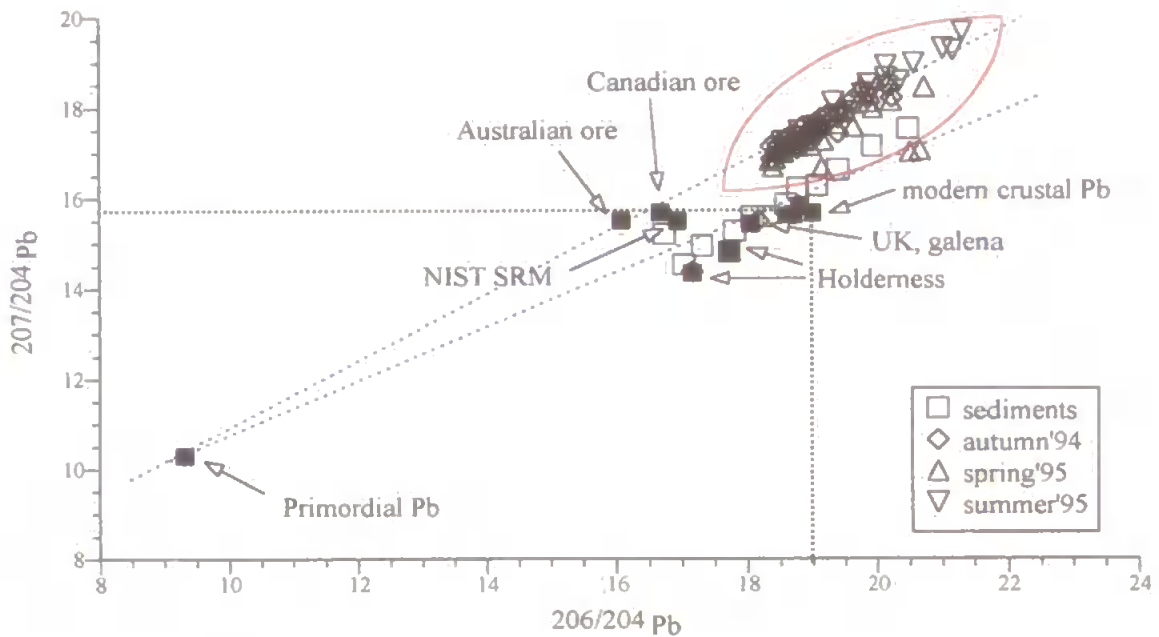


Figure 6.1 Isotope ratios of lead from SPM samples in the western North Sea taken in autumn'94, spring'95 and summer'95, also shown are bed sediment ratios (from winter'92 and autumn'94) and a number of key ratios (■) as labelled.

The Pb isotopic results from the western North Sea (Figure 6.1) firstly show that all the SPM samples are clustered together (indicated by the ellipse) and do not exhibit any discernible differences in signatures between successive seasons. However the Pb isotopic ratios are greater than average crustal Pb and imported Pb ores i.e. alkyl Pb used in petrol, suggesting enrichment of U. Such anomalous Pb ratios are not uncommon (Faure, 1986) and are often the result of the mixing of Pb from several systems having different U/Pb and Th/Pb ratios i.e. deviation from the assumptions made in the Holmes-Houterman model on the single-stage history of Pb evolution. The underlying sediment samples are generally less radiogenic than the SPM samples and show ratios similar to those of typical crustal Pb and UK Pb ores. These results are in good agreement with previously published Pb isotopic ratios of SPM and sediment samples in the North Sea by Williams (1995). The increase of radiogenic Pb in the SPM samples compared to the bottom sediment samples is perhaps indicative of atmospheric deposition of Pb from

sources enriched in U, where either the flux is recent (and therefore not reflected in sedimented material) or the SPM is permanently suspended (refer to Chapter 5).

Assuming that the Pb isotopic ratios of primordial Pb indicated do represent the least radiogenic Pb minerals on Earth and that these were formed at the same time as Earth itself then generally modern sediments, Holderness cliff boulder clay material and UK galena minerals Pb isotopic ratios lie close to a line joining primordial Pb with typical crustal Pb, in agreement with Williams (1995). This also assumes that isotopic ratios are additive and respond in an approximately linear way within the isotopic range studied. In comparison it would appear that SPM Pb signatures fall closer to a line joining primordial Pb with Pb ores used in petrol, albeit that the SPM isotopic ratios are more radiogenic i.e. augmented by U enriched sources. Williams (1995) reported an exceptionally high $^{206/204}\text{Pb}$ ratio of 30.75, suggesting ^{238}U enrichment, from an apatite processing plant, Albright and Wilson, who are permitted to discharge 3.6 tonnes of Pb per year into the Irish Sea. There are numerous UK industrial plants discharging into the western North Sea (see Table 6.1 for the main industrial sources of Pb). Unfortunately the isotopic ratios of each input have not been characterised which hinders further explanation of the radiogenic Pb ratios found in the SPM of the western North Sea, but it is conceivable that these anthropogenic inputs add substantially to the Pb burden of the receiving waters and possibly the increase in isotopic ratios as observed.

Further work examining the isotopic ratios of effluent discharges and atmospheric aerosols is required in the area to give a fuller explanation and rationalisation of the Pb isotopic ratios found before specific sources can be pinpointed and apportioned.

In the majority of environmental applications of Pb isotopes often the $^{206/207}\text{Pb}$ isotope is quoted for samples and sources of Pb. However a change observed in this ratio could be due to changes in the abundance of either ^{206}Pb or ^{207}Pb , as both are radiogenic isotopes. Williams (1995) calculated the % abundance of each Pb isotope from the following equation (Equation 6.1) and subsequently expressed the $^{206/207}\text{Pb}$ isotope as a function of individual isotope abundance to investigate possible relationships;

$$\% \text{ abundance of isotope } i = \frac{\frac{i}{206}}{\frac{204}{206} + \frac{207}{206} + \frac{208}{206} + 1} \times 100 \quad 6.1$$

where $i = 204, 206, 207$ or 208 .

Table 6.1 List of the industrial sources of Pb discharging into rivers, estuaries and the nearshore coast of the western North Sea. (Greenpeace, 1992)

Company	N ^o pipes	Receiving body of water	Permitted Pb discharge (t a ⁻¹)
Courtaulds Fibres Ltd	1	River Humber	5.47
SCM Chemicals Ltd	1	River Humber	12.4
Tioxide Europe Ltd	2	River Humber	52
Doverstrand Ltd	1	River Humber	0.46
Porvair Plc	1	Tidal River Great Ouse	0 ^a
Croda Chemicals Ltd	1	River Don	0.24
SUB-TOTAL			71
British Steel Plc: Teeside Works	4	Tees Bay	365
ICI Chemicals & Polymers Ltd: Billingham Works	major	River Tees	0 ^b
BASF Plc	2	River Tees Estuary	0 ^a
Tees Storage Company Ltd	1	River Tees Estuary	0 ^a
SUB-TOTAL			365
Rohm & Haas (UK) Ltd	1	River Tyne	0 ^a
Cooksons Industrial Materials Ltd	1	River Tyne	0 ^a (146 estimate)
SUB-TOTAL			146
TOTAL			582

^aNRA monitoring identified discharge of Pb without consent: ^bNRA monitoring identified discharge of Pb, company has 'deemed consents' which allows a company to discharge a wide variety of chemicals without having to meet limits on the amounts or concentrations of these chemicals (Greenpeace, 1992).

The % abundance of each Pb isotope for the SPM and sediment samples were computed for the western North Sea data and are shown in Figure 6.2. The % abundance of ²⁰⁶Pb, and ²⁰⁷Pb displayed linear relationships with ^{206/207}Pb at 99.9% confidence limits ($r=0.85$ & 0.88 respectively, where $n=90$) but showed opposite gradients i.e. with increasing

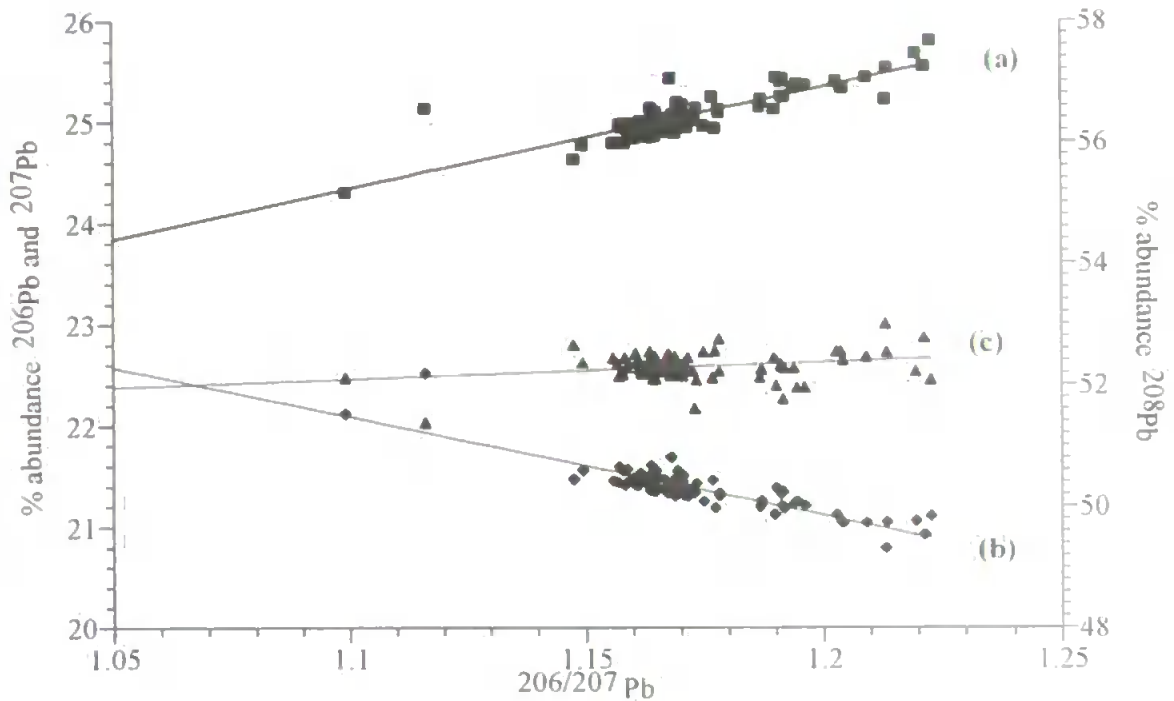


Figure 6.2 Variation of the isotopic abundance of Pb with the $^{206/207}\text{Pb}$ isotopic ratio (a) ^{206}Pb : $y=10.0x + 13.3$, $r=0.85$; (b) ^{207}Pb : $y=-9.8x + 32.8$, $r=0.88$ and (c) ^{208}Pb : $y=2.7x + 49.0$, $r=0.24$.

$^{206/207}\text{Pb}$ ratio observed increasing % abundance of ^{206}Pb but decreasing % abundance of ^{207}Pb . However this relationship is clearly not on a 1:1 basis i.e. an increase in 1% ^{206}Pb does not correspond to a 1% decrease in ^{207}Pb or more simply different slopes, m_i . A linear trend is represented by the general equation for a straight line;

$$y_i = m_i x + C_i \quad 6.2$$

where m =gradient of the line for isotope i and C =intercept on y axis for isotope i .

This data compares favourably with that reported by Williams (1995) and is summarised in Table 6.2. However in comparison recent results indicate that the % abundances of ^{208}Pb and non-radiogenic ^{204}Pb (data not shown in Figure 6.1) also show, to a lesser extent, significant linear correlations with $^{206/207}\text{Pb}$ at the 95% confidence levels ($r=0.24$ and 0.35 respectively) but both exhibit small opposing gradients (m) of 2.7 and -3.1 respectively. This indicates that the % abundances of ^{206}Pb and ^{207}Pb are the dominant controlling factors in the value of $^{206/207}\text{Pb}$ isotopic ratios.

Table 6.2 Comparison of m_i and C_i for the linear expressions relating % abundance of ^{206}Pb and ^{207}Pb as a function of $^{206/207}\text{Pb}$.

Location	m_{206}	C_{206}	m_{207}	C_{207}
western North Sea data	10	13.3	-9.8	32.8
North Sea & Irish sea data ^a	9.9	13.4	-10.4	33.4

^aWilliams (1995)

Using the derived linear equations (Figure 6.2a & b) and the measured $^{206/207}\text{Pb}$ ratios of individual SPM or sediment samples, the % abundance of ^{206}Pb and ^{207}Pb can be computed. Figure 6.2 basically represents a mixing of natural and anthropogenic sources of Pb in the western North Sea ($^{206/207}\text{Pb}=1.05$, representing a 50:50 mix of Australian and Canadian Pb ores added to petrol and $^{206/207}\text{Pb}=1.23$ representing the uncontaminated Holderness cliff material)¹. Thus the ^{206}Pb and ^{207}Pb isotopes mix conservatively over the linear range investigated, but slight differences in line gradients suggest that they will not behave conservatively during the mixing of natural and contaminated Pb (Williams, 1995).

6.3 Seasonal Distributions of Lead Isotope Ratios in the Humber Plume

The $^{206/207}\text{Pb}$ isotopic ratios of SPM for the Humber Plume in autumn '94, spring '95 and summer '95 are presented in Figure 6.3. The $^{206/207}\text{Pb}$ isotopic ratios are contoured and compared with isohalines. During autumn '94 the lowest ratios of 1.164-1.170 emanate from the Humber Estuary and generally move anticlockwise with the residual circulation staying close to the coastline. This process is helped by the dominate north-westerly winds (see Table 6.3 & Figure 3.3a & b). The salinity structure demonstrates a similar pattern but correlation statistics do not reveal any significant relationships between $^{206/207}\text{Pb}$ and salinity. This is not surprising considering that salinity is a conservative tracer, whilst particulate material is generally very reactive. The distribution of $^{206/207}\text{Pb}$ ratios do indicate lower ratios in the vicinity of the Plume region, identified by the salinity

¹ The majority of $^{206/207}\text{Pb}$ ratios emanated from an intensive study of the Humber Plume area. The main particle source to this area (Wilmot & Collins, 1981; McCave, 1987) is from the erosion of the Holderness Cliffs and hence its use as an appropriate end member for uncontaminated $^{206/207}\text{Pb}$ isotopic ratios.

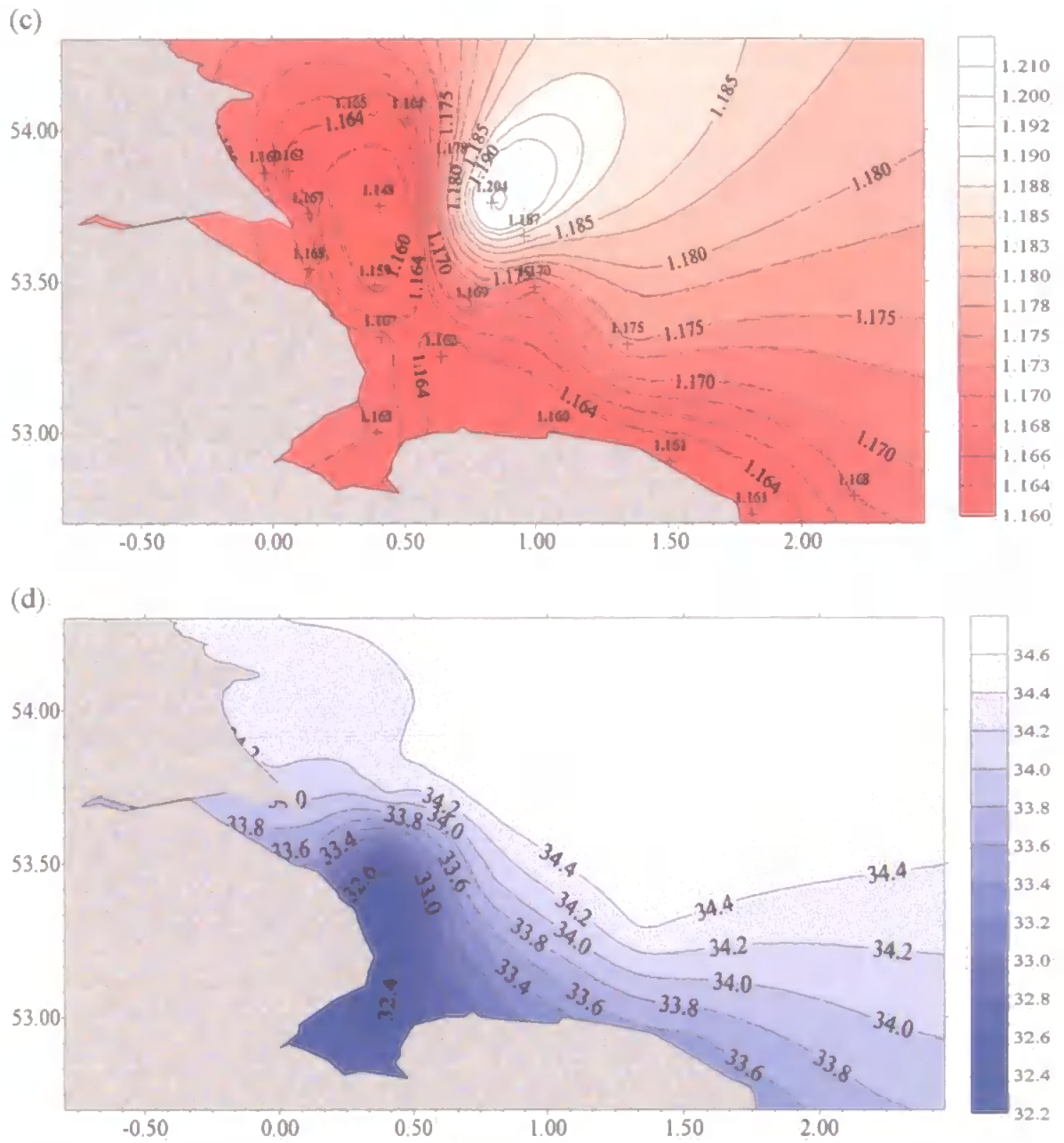


Figure 6.3 continued. Contour plots of (c) $^{206/207}\text{Pb}$ (crosses show sampling locations and ratio) and (d) salinity in the Humber coastal zone during spring '95.

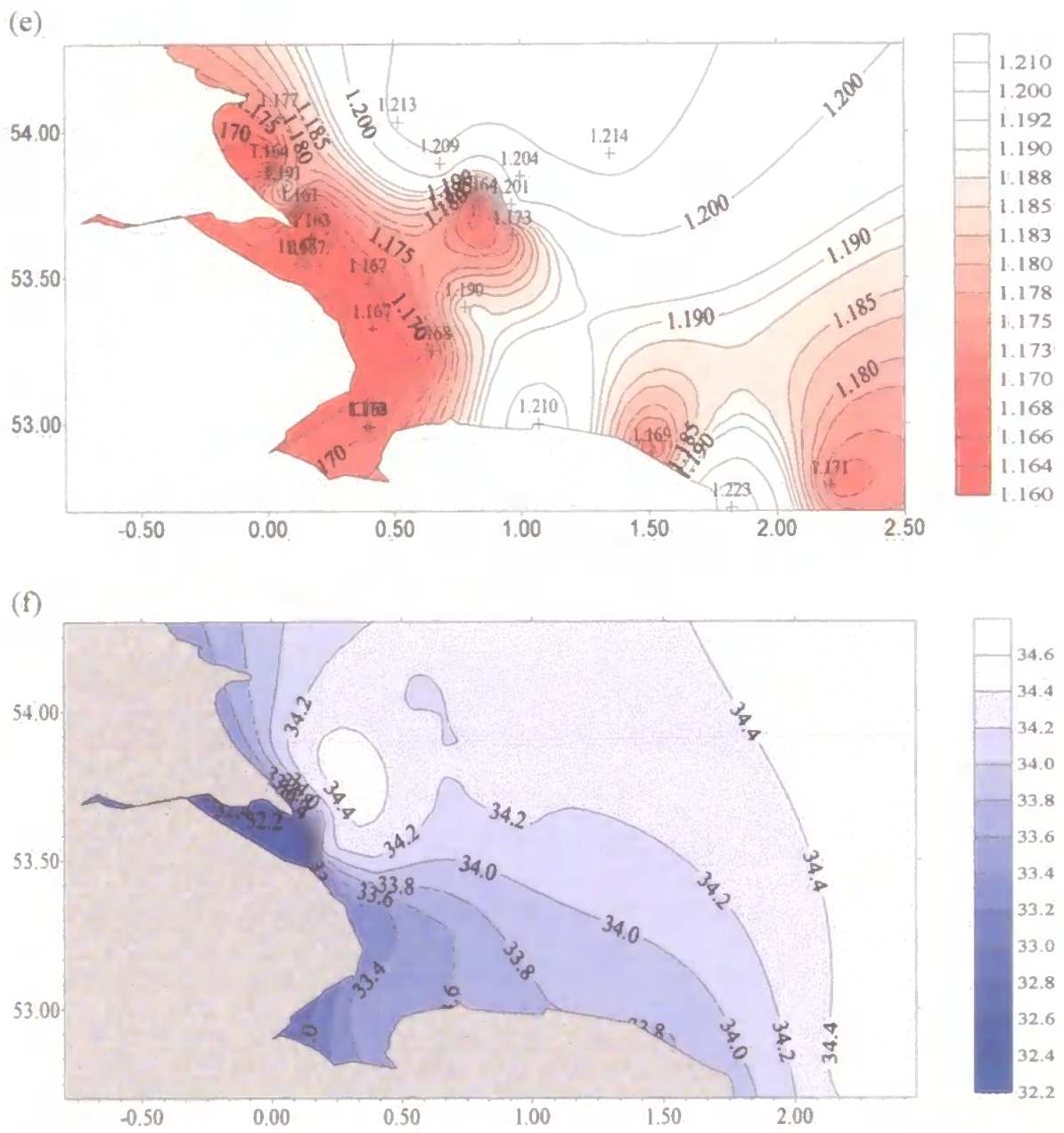


Figure 6.3 continued. Contour plots of (e) $^{206/207}\text{Pb}$ (crosses show sampling locations and ratio) and (f) salinity in the Humber coastal zone during summer '95.

structure, with increasing ratios seawards. This presumably reflects dilution of contaminated estuarine SPM of low $^{206/207}\text{Pb}$ isotopic ratio with marine SPM of higher isotopic ratios of the order 1.20 i.e. similar to that of Holderness clay material.

Table 6.3 Summary of $^{206/207}\text{Pb}$ isotopic ratios and physical parameters in the Humber coastal zone.

	Season		
	Autumn'94	Spring'95	Summer'95
N ^o SPM samples	14	21	25
Residual Flow ^a (m ³ s ⁻¹)	165	345	70
Prevailing wind direction ^b	NW	S to E	mixed
Average wind speed, knots ^b	15	15-20	-
$^{206/207}\text{Pb}$ SPM ratio			
minimum	1.164 ± 0.009	1.148 ± 0.010	1.161 ± 0.011
maximum	1.192 ± 0.006	1.204 ± 0.008	1.223 ± 0.011
Salinity regression, r	0.26	0.46 ^c	0.26

^aResidual flow at the mouth of the Humber Estuary estimated using a 2-D, depth averaged, hydrodynamic model (Wood, 1993); ^bWind data obtained from the BODC via the Meteorological Office (see Chapter 3, Figure 3.3); ^cSignificant positive regression ($P < 0.05$).

In spring'95 elevated residual outflows from the Humber Estuary revealed a Plume of lower salinity waters (see Figure 6.3d) flowing in a south-easterly direction. Comparison of the 34 isohaline between autumn'94 and spring'95 reveal the broader extent of the Plume. The dominate winds gusting from south to east (see Table 6.3, Figure 3.3e & f) helping to push the Plume north around Spurn Head and up the Holderness coast. This is reflected in the distribution of $^{206/207}\text{Pb}$ isotopic ratios (see Figure 6.3c). The 1.170 contour line extends much further into the coastal waters during the spring period pushing back the marine SPM of higher $^{206/207}\text{Pb}$ ratios in the order of 1.20. Lower isotopic ratios of 1.160 dominate the near coastal environment and correlation with salinity reveals a significant positive relationship ($r=0.46$ for $n=19$, $P < 0.05$, see Table 6.3) suggesting that under periods of elevated flow regimes estuarine SPM swamps the nearshore waters, carrying anthropogenically modified SPM characterised by lower $^{206/207}\text{Pb}$ isotopic ratios. The extent of the Plume under these conditions is obviously dependent on prevailing wind direction, strength and duration.

The following summer shows a contrasting picture both in salinity and $^{206/207}\text{Pb}$ distributions (see Figure 6.3e & f). Estuarine outflows have diminished to $70 \text{ m}^3\text{s}^{-1}$ resulting in intense surface salinity stratification near the mouth of the estuary. However comparison of the 34 isohaline between autumn'94 and summer'95 show similar distributions from the estuary mouth to the Norfolk coast. Lead isotopic distributions also show large gradients just east of the mouth of the Humber Estuary. Generally the $^{206/207}\text{Pb}$ isotope 'Plume' is restricted in extent. This is shown by the 1.170 contour that, in comparison to autumn'94, does not flow south east in the direction of flow of the residual currents, but remains reasonably close clustered around the mouth of the Humber Estuary. This data suggests that, despite the salinity structure, estuarine outflows are not strong enough to carry particulate material far offshore. This results in large variations in the $^{206/207}\text{Pb}$ isotopic ratios due east of the mouth of the Humber Estuary as the degree of mixing between estuarine SPM (low in $^{206/207}\text{Pb}$ ratios) and marine SPM (with increased ratios) is reduced i.e. a decrease in estuarine outflow translates to a reduction in the amount of energy available in the system to mix the two particle populations.

6.4 Lead Isotope Ratios in the Mouth of the Humber Estuary

The temporal changes in $^{206/207}\text{Pb}$ isotopic ratio at the mouth of the Humber Estuary were investigated for each season in an attempt to aid interpretation of the observed Plume distributions. The results are summarised in Table 6.4. Autumn and spring surveys exhibited large tidal ranges of 6.6 m which result in lower average salinities with a larger degree of variation when compared to summer conditions i.e. approaching neap tidal range of 4.5 m. Residual outflows from the mouth of the Humber Estuary increased from $165 \text{ m}^3\text{s}^{-1}$ in autumn'94 to $345 \text{ m}^3\text{s}^{-1}$ in the following spring. The average $^{206/207}\text{Pb}$ isotopic levels ranged from 1.165 in autumn'94 and summer'95 to 1.176 in spring'95 but are not statistically different implying little variation in the average $^{206/207}\text{Pb}$ isotopic ratios throughout the year at the mouth of the Humber Estuary. Figure 6.4 shows a rise in isotopic ratios with increasing salinity for autumn, spring and summer surveys and the subsequent increase in anthropogenic character as fresher water is advected past the

anchor station in the mouth of the Humber Estuary into the nearshore coastal waters of the Plume. During the summer small variations in Pb isotopic ratios are reflected by lower salinity variance.

Table 6.4 Master variables and the mean \pm standard deviation of $[\text{Pb}]_p$ and $^{206/207}\text{Pb}$ isotopic ratios for the Humber mouth anchor stations.

	Season		
	Autumn'94	Spring'95	Summer'95
N ^a SPM samples	14	18	14
Tidal Range ^a , (m)	6.6	6.6	4.9
Salinity	31.10 \pm 2.09	30.79 \pm 2.71	32.59 \pm 1.16
[SPM], mg l ⁻¹	292 \pm 304	310 \pm 282	60 \pm 47
Residual Flow ^b , m ³ s ⁻¹	165	345	70
Average $^{206/207}\text{Pb}$	1.165 \pm 0.010	1.176 \pm 0.015	1.165 \pm 0.007
Average $[\text{Pb}]_p$, $\mu\text{g g}^{-1}$	81 \pm 19	130 \pm 85	80 \pm 31

^aTidal range at Spurn Head; ^bWood (1993).

If $^{206/207}\text{Pb}$ isotopic ratios are plotted as a function of salinity for each anchor station in autumn, spring and summer the following equations approximate the linear relationships obtained;

Autumn'94: $y = 0.0035x + 1.06, r=0.71^a$ 6.3

Spring'95: $y = 0.0036x + 1.06, r=0.65^a$ 6.4

Summer'95: $y = 0.0036x + 1.05, r=0.61^a$ 6.5

^aSignificant for $P < 0.05$.

The three relationships are remarkably similar and indicate that irrespective of time of the year the Humber Estuary is a significant source of anthropogenic Pb. The extent to which this is reflected in the Plume and nearshore coastal waters (Figure 6.3) is therefore a function of the estuarine outflow, tidal regime and prevailing wind strength and direction.

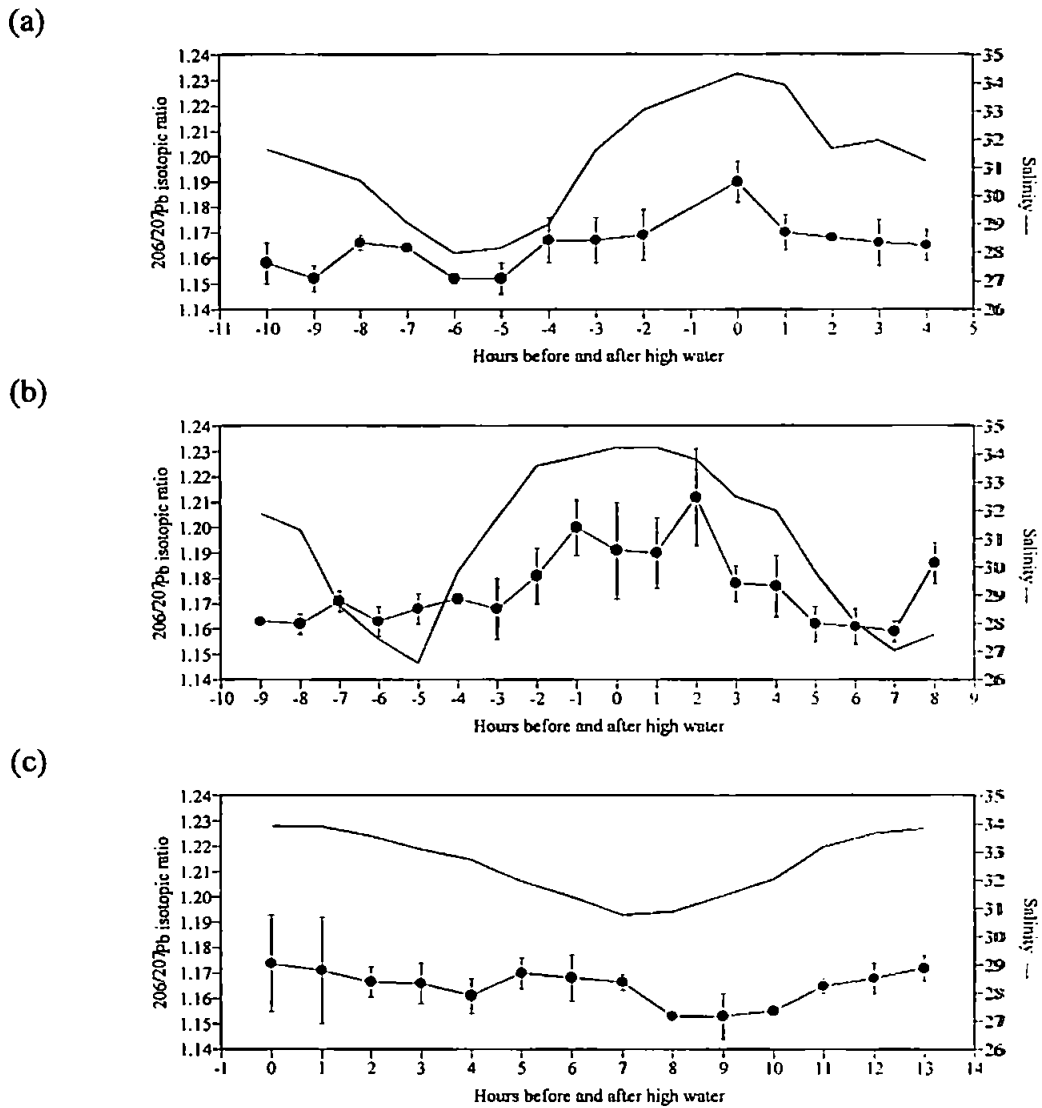


Figure 6.4 Variation in the $^{206}/^{207}\text{Pb}$ isotopic ratio and salinity at the mouth of the Humber Estuary (HW5, refer to Figure 2.3) during (a) autumn'94, (b) spring'95 and (c) summer'95.

6.5 Applications of Lead Isotope Studies

6.5.1 The Humber Plume

In an attempt to predict the % anthropogenic Pb in SPM samples of the Humber Plume a simple two component particle mixing model can be derived if the following assumptions are made;

- 1) conservative and additive mixing of anthropogenic and natural Pb,
- 2) there are principally only two Pb sources in the Humber Plume characterised by distinctively different $^{206/207}\text{Pb}$ isotopic ratios:

a) Anthropogenic Pb = Pb derived from alkyl Pb additives in petrol

$$^{206/207}\text{Pb} = 1.055$$

(50:50 mix of Australian and Canadian ores, see section 6.2)

b) Natural Pb = Pb derived from erosion of Holderness Clay

$$^{206/207}\text{Pb} = 1.234$$

then the $^{206/207}\text{Pb}$ isotopic ratio of the SPM sample is;

$$^{206/207}\text{Pb} = x_1 1.055 + x_2 1.234 \quad 6.6$$

where; x_1 = fraction of anthropogenic Pb and x_2 = fraction of natural Pb, but for mass balance;

$$x_1 + x_2 = 1 \quad 6.7$$

therefore substituting equation 6.7 into equation 6.6;

$$^{206/207}\text{Pb} = x_1 1.055 + (1 - x_1) 1.234 \quad 6.8$$

For example $^{206/207}\text{Pb}$ isotopic ratios of SPM from the mouth of the Humber Estuary ranged between 1.152-1.190 during autumn'94 which equates to % anthropogenic Pb of between 46% and 25% respectively. This is in good agreement with results from Williams (1995) who reported between 20-40% anthropogenic Pb for SPM samples in the North Sea during winter periods. The mean, minimum and maximum amounts of anthropogenic Pb have been calculated for the mouth of the Humber Estuary and Plume waters for each season and are summarised in Figure 6.5.

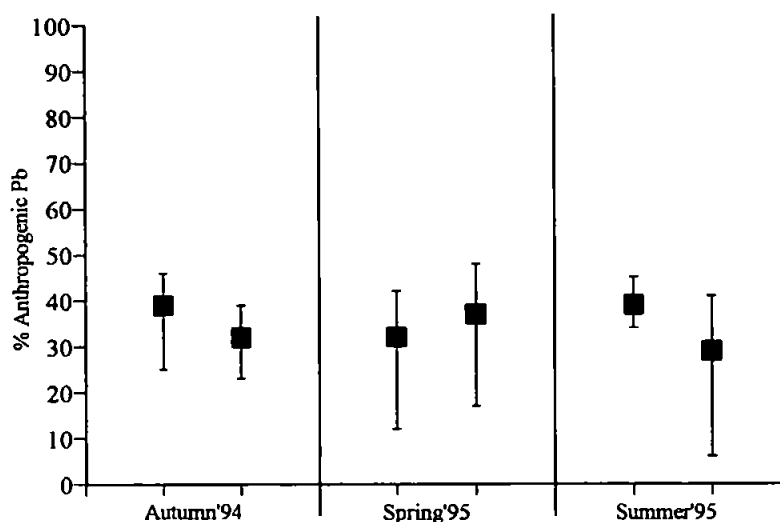


Figure 6.5. The mean, minimum and maximum derived % anthropogenic Pb in SPM of the Humber Estuary (■) and Plume waters (■) for each season.

The anthropogenic component of Humber Estuary material ranged from an average of 39% in autumn and summer to 32% in the spring. The latter decrease may have resulted from an increase in estuarine outflow diluting the anthropogenic signal, but remains within the range found in autumn and winter. The Humber Plume SPM showed slightly lower average anthropogenic contributions of approximately 30% in the autumn and summer periods and a slightly higher percentage of 37% in the spring, when compared to estuarine SPM the values are well within the large experimental variations observed.

Figure 6.6 shows the $^{206/207}\text{Pb}$ isotopic ratios of bed sediments from winter '92. This data, although not concurrent with recent SPM samples, does show some low $^{206/207}\text{Pb}$ ratios e.g. just east of the Silver Pit, a bathymetric 'deep', a low isotopic $^{206/207}\text{Pb}$ ratio of 1.116 was observed. The Silver Pit was used as a sewage dump site for numerous years which could have increased the anthropogenic Pb loading of the sediments. The mean $^{206/207}\text{Pb}$ ratio for Humber Plume bed sediments of 1.155 ± 0.022 equates to 44% anthropogenic Pb. This indicates that during periods of increased wave/current flows an increase in the resuspension of bed sediments could provide a source relatively high in anthropogenically derived Pb to the overlying water column.

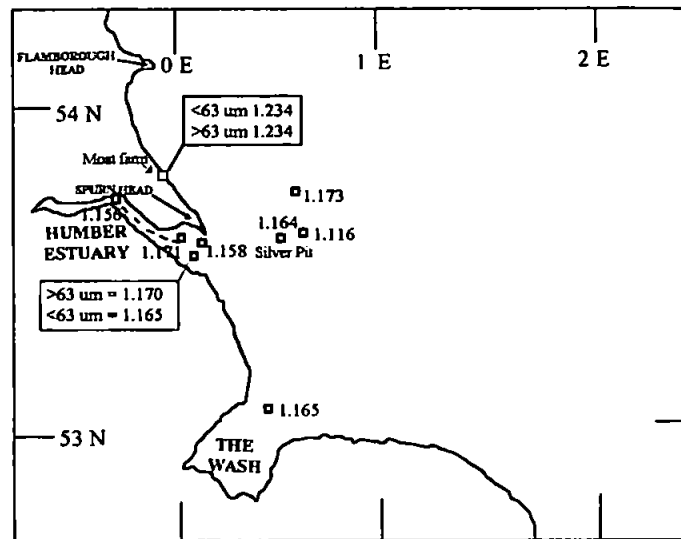


Figure 6.6 $^{206/207}\text{Pb}$ isotopic ratios in bed sediments of the Humber Plume (□) and Holderness cliff material (□) during winter'92.

Kersten *et al.* (1992) reported significant variations in the $^{206/207}\text{Pb}$ isotopic ratios during wind-directed aerosol sampling in the south-eastern North Sea and reported ratios of 1.140 when the wind direction was between 045° and 180° i.e. NE to S. The low isotopic ratios found in the Humber Plume and subsequent high anthropogenic load of Pb found in SPM samples during spring when winds were dominantly blowing from E to S could therefore be augmented by the deposition of atmospheric aerosols with low $^{206/207}\text{Pb}$ ratios.

6.5.2 Lead isotope ratios in estuaries and plumes

While the Pb in atmospheric aerosols is predominantly of anthropogenic origin (Kersten *et al.*, 1992), particulate matter in surface waters, as shown, will also contain a contribution of natural Pb derived from the erosion of the drainage area which in the case of the Humber Plume is dominated by the erosion of the Holderness Cliffs. Table 6.5 summarises the range of the isotope ratios found at present in the SPM and sediments of the major estuaries draining into the western North Sea and associated Plumes. The lowest $^{206/207}\text{Pb}$ ratio was found in the SPM of the Thames, followed by the Plumes of the Tees and Tyne. The former ratio can be attributed to extensive urban runoff from the city of London and its environs. Whilst the low ratios found near the

Table 6.5 Comparison of $^{206/207}\text{Pb}$ isotopic ratios from the major estuaries and associated Plumes of the western North sea, offshore SPM from the Doggerbank and pre-industrial sediments.

Location	Sediments	SPM		
		autumn'94	spring'95	summer'95
Humber				
Estuary	1.158 ± 0.006^a 1.165 ± 0.012^b	1.165 ± 0.010	1.176 ± 0.015	1.165 ± 0.007
Plume	1.155 ± 0.022^a	1.177 ± 0.011	1.168 ± 0.011	1.179 ± 0.027
Tees				
Plume, south	1.169 ± 0.009^c	1.149 ± 0.014	1.169 ± 0.001	1.162 ± 0.014
Plume, north	1.157 ± 0.007^c	1.157 ± 0.006	1.165 ± 0.003	1.203 ± 0.009
Tyne				
Plume	1.161 ± 0.002^c	1.167 ± 0.002	1.159 ± 0.015	-
Tweed				
Plume	-	1.171 ± 0.001	1.171 ± 0.006	-
Thames				
Estuary	-		1.134 ± 0.006^d	
Plume	-		1.166 ± 0.019^d	
Doggerbank			1.183 ± 0.013^d	
Pre-Industrial			1.211 ± 0.006^d	
Holderness		1.234 ± 0.015^a		
Cliff		1.196 ± 0.012^c		

^aWinter'92; ^bAutumn'94; ^cSpring'95; ^dWinter'89, Data from Kersten *et al.* (1992).

discharge of the Tees and Tyne are likely due to the large discharges from the numerous industrial works as detailed in Table 6.1. The general increase in $^{206/207}\text{Pb}$ ratios seawards as evident from intensive studies of the Humber Plume area and data from the Thames Estuary (1.134), Plume (1.166) and further offshore at the Doggerbank (1.183) implies a higher percentage of modern Pb by mixing with uncontaminated SPM eroded from Holocene sediments of either the Holderness Cliffs (Humber coastal zone) or sediments of the North Sea bed (Thames coastal region). The isotope ratios of the Tees and Tyne show changes with season but do not show any common trends except the progressive increase in isotopic ratio from autumn'94 to the following summer for the north Tees. This is attributable to the increase in SPM originating from natural sources,

presumably as estuarine outflow from the Tees decreases. However, it is also evident that not all seasonal trends can be explained by simple two component mixing processes.

6.6 Summary

Lead isotope systematics can be used to estimate sources and the relative proportion of anthropogenically derived Pb. However the isotopic composition of contaminant Pb may still be a complex mixture of various ore signatures. The isotopic gradients in Europe between the provenance of the alkyl Pb used in fuel and natural Pb are more pronounced than regions under North American influence offering a favourable opportunity to trace anthropogenic Pb in the environment. However the lack of $^{206/207}\text{Pb}$ isotopic ratios quantifying the numerous industries ultimately discharging Pb into the estuaries of the western North Sea restricts source apportionment. This study represents the first of its kind to examine distributional trends of $^{206/207}\text{Pb}$ isotopic ratios with season. It shows that, for the Humber coastal zone, the Humber Estuary is a significant source of anthropogenic Pb to the coastal zone all the year, but the extent to which this permeates into further offshore marine waters is a complex function of tidal regime, estuarine outflow and prevailing wind direction. A simple two component mixing model of anthropogenic and natural Pb in the Humber coastal zone can be used to predict the percentage of contaminant Pb in particulate material and shows good agreement with previous work in this area (Williams, 1995). Differences between average Plume and estuary values in spring'95 suggest other sources of contaminated Pb and evidence from Chapter 3 and the literature (Kersten *et al.*, 1992) suggests continental atmospheric aerosol deposition, although resuspension of contaminated bed sediments could also provide a transient source.

Traditionally Pb isotope studies have been extensively used by geological scientists but rarely by marine geochemists. The use of the $^{206/207}\text{Pb}$ isotopic ratio clearly provides a valuable tool to help understand the mixing and transport of Pb in the environment (Williams *et al.*, 1994). However the decline in the use of Pb as an additive in petrol will limit the future use of this method to distinguish between sources.

7 Conclusions and Further Work

7.1 The Objectives and Achievements of this Study

The data presented in this study have provided new insights into the important factors that influence the biogeochemical pathways and their consequences for seasonal variability in the distributions of particulate Fe, Mn, Cu, Cd and Pb in the coastal waters of the western North Sea. The initial aims of this study as outlined in section 1.3 have been achieved and are summarised as follows;

- 1) An extensive seasonal particulate trace metal database (Fe, Mn, Cu, Cd & Pb) in the western North Sea has been reported that is the most comprehensive for any nearshore coastal region. Maximum concentrations of SPM and the particle reactive metals Fe, Pb, and to some extent Mn, were shown at the mouths of the Humber, Tees and Tyne estuaries. Concentrations generally decreased from winter to summer. The subsequent spreading of resultant anthropogenically modified plumes of SPM and associated metals was shown to be highly influenced by freshwater discharge, spring/neap tidal cycle, prevailing wind conditions and biogeochemical processes. The large effect of the wind strength and direction on the shape of the Humber Plume was corroborated by simulated particulate trace metal models of the Humber coastal zone (Allen, pers comm). The concentrations of Fe_p and Mn_p were strongly correlated in all seasons indicating their similar sources and biogeochemical cycles. The Cu_p signal was variable in comparison owing to enhanced concentrations in offshore regions during the summer. This was attributed to organic and/or biogenic particle interactions that were patchy in nature and would therefore be very difficult to

simulate accurately in model predictions. Particulate Cd showed enhanced concentrations in offshore regions, notably adjacent to the Tweed Estuary during the spring and summer. The distribution data and positive correlation found with concentration of chlorophyll a during spring suggested enhanced biogenic particulate interactions.

- 2) An intensive seasonal sub set of the data from the Humber coastal zone was examined in depth and revealed distinct seasonal cycles of Cu_p and Pb_p . Both metals displayed minimum average concentrations during autumn but maximum values during summer and spring for Cu_p and Pb_p respectively. In contrast, Cd_p distributions, unlike the whole coastal zone, did not display any clear discernible trends with season. However the resulting distributions in all trace metals studied were largely due to (a) their contrasting reactivities towards anthropogenically modified lithogenic and biogenic particles, (b) the relative contributions of different particle populations to the total particulate load in the water column at different times of the year, and (c) the prevailing meteorological conditions. The general lack of any statistical relationships between Cu_p , Cd_p and Pb_p with salinity, concentration of SPM, Fe_p and Mn_p in the Humber coastal zone did not suggest that the estuary was the mass dominating source to the Plume region. This further inferred (a) the highly unconservative nature of particulate material and (b) the relative influence of other trace metal sources to the region i.e. resuspended bed sediment, eroded Holderness clay material, biogenic particles, diffuse atmospheric inputs (for Pb_p) etc. For example during winter the higher concentrations of Pb_p offshore in the Humber coastal zone in combination with winds originating from continental Europe inferred the relative significance of the atmosphere as a Pb_p source. However the significant inter correlation's observed between Pb_p and Fe_p/Mn_p generally indicated the strong association of Pb_p with the hydrous Fe and Mn oxide coatings of particles originating from the Humber Estuary.

The first comprehensive investigation into the seasonal variation of Cu, Cd and Pb settling velocities (by the use of QUISSET's) in the Humber coastal zone was also carried out. The lowest W_s^{50} of all three metals was of the order $\leq 10^{-4}$ mm s^{-1} indicative of trace metals associated with background concentration of particles in permanent suspension (Jago *et al.*, 1993). The largest W_s^{50} ranged between 0.26-0.75

mm s⁻¹ in the order Pb>Cd>Cu. In relation to the W_s^{50} of the total SPM clear seasonal trends were evident. In general during winter all metals settled slower than the SPM irrespective of tidal state, a trend that was reversed in the following summer. Such behaviour has important implications for trace metal transport models such as ECOS (Estuarine and coastal ocean simulator) (Harris, pers comm) which at present do not take account of such variations. The use of settling tubes in the mouth of the Humber Estuary enabled the settling characteristics of estuarine particulate matter and associated trace metals to be calculated. Data from the flood and ebb tides during winter and spring indicated that Cu, Cd and Pb would deposit to the bottom sediments in 0.5-6 days (calculations based on a water depth of 20 m) i.e. the Humber Plume region was acting as a particulate trace metal sink. However Pb_p and Cd_p (based on the flood W_s^{50} only) settling characteristics during summer alternatively implied that it would take between 50-460 days to settle to the bed and would hence undergo more long range transport with the residual circulation.

- 3) The temporal water sampling at anchor stations in the Humber coastal zone showed the reduction in the propagation of the freshwater signal and average dissolved and particulate trace metals with distance away from the estuary mouth. This was due to dilution of estuarine enriched particles and waters with relatively depleted marine/Holderness sources. Anomalies in this trend were attributed to relative differences in the spring/neap tidal cycle during sampling. The tidally-averaged salinity at the mouth of the Humber Estuary varied with seasonal changes in the input of freshwater. Whilst the salinity variance was subsequently related to the tidal range. Similarly the tidally averaged SPM concentration was linearly related to the tidal range, the relative differences in which explained the inter-annual contrast between seasons sampled during the NSP and LOIS surveys. Generally the temporal variations in concentration of particulate and dissolved Cu and Cd can be explained on the basis of freshwater input into the Humber Estuary. However deviations from this trend by Cd_p , particularly during spring and summer suggested enhanced particulate biogenic interactions. In contrast, the tidal variations in dissolved and particulate Pb were unrelated to salinity and changes in concentration of SPM. Fe_p and Mn_p and thus difficult to explain. The simultaneous sampling of dissolved and particulate Cu, Cd and Pb at the mouth of the Humber Estuary was used in combination with modelled

estimates of the residual volume outflow of water to calculate the fluvial discharge from the Humber to the western North Sea. This data represents the first seasonal quantification of Cu, Cd and Pb fluxes across this estuarine-coastal interface during the period autumn'94 to summer'95. The results showed that the total trace metal fluxes displayed significant seasonal variations. The total fluxes of Cu, Cd and Pb increased from autumn to maximum levels in spring and decreased to minimum fluxes in the following summer. Estimates of the integrated annual average flux of Cu, Cd and Pb were of the order of 153, 4.29 and 504 kg day⁻¹ respectively. When compared with the annual estimates of Cu, Cd and Pb inputs derived from NRA data (riverine, sewage and industrial sources) for 1992 estuarine retention of approximately 25% and 56% for Cu and Cd respectively was calculated. However more Pb was exported from the Humber Estuary to the North Sea than could be explained by the documented input sources indicating alternative sources, e.g. contaminated fluvial bed sediments (Millward & Glegg, 1997). The variability in both particulate and dissolved fluxes of Cu, Cd and Pb were generally explained by variations in the volume outflow of water from the mouth of the Humber. However the relative influence of the tidal range on metal flux was also highlighted i.e. the correlation of metal flux vs. water outflow improved when data taken during extreme tidal amplitudes of 6.6 m (autumn'94 and spring'95) was excluded from the calculation. Extrapolation of the linear relationships between the fluxes of particulate Cu, Cd and Pb with residual water outflow suggested negligible particulate trace metal transport across the estuarine-coastal interface at residual outflows <80-100 m³s⁻¹ i.e. typical summer flow conditions. This may, in part, explain the lack of correlation found between particulate Cu, Cd and Pb vs. salinity in the Humber coastal zone during summer'95. The percentage of the metal transported in the particulate phase also varied both with metal and season. Copper transport was dominated (73-80%) by the particulate phase during autumn, winter and spring but by the dissolved phase (66%) in summer. This was in contrast to the behaviour of Cd and Pb. Cadmium demonstrated a gradual decrease in particulate flux dominance from autumn (70%) through to summer (10%) whilst Pb displayed little variation with season indicating that between 94-100% of the total flux was transported in the particulate phase.

4) A number of studies were undertaken to investigate the particle reactivities and subsequent effect on the seasonal distributions of Mn, Cd and Cs in the western North Sea. It was unfortunate that radioisotopes of Cu and Pb were not available during the present study to compliment and complete the data set. Nevertheless these studies included;

a) an assessment of the seasonal partitioning behaviour of Mn, Cd and Cs onto different particle types in the western North Sea. Particles were differentiated by their spatial location and settling velocity but generally revealed the following order in particle affinity or reactivity: $Mn > Cd \geq Cs$. Spatially sampled particles from the mouth of the Humber Estuary were more reactive towards ^{54}Mn and ^{137}Cs than those from other nearshore coastal environments sampled, although no clear spatial differences were apparent for ^{109}Cd . This was attributed to the high adsorption capacity of fresh active Fe/Mn oxyhydroxide surfaces of primary hydrogenous particles (Chester & Hughes, 1967) originating from the Humber. However significant seasonal variations in the uptake of ^{54}Mn and ^{109}Cd from solution a) complicated the relative assessment of particle reactivity and b) inferred their possible coupling to biogenic particles when the water column was not dominated by estuarine particulate matter. Radiochemical experiments performed on predominantly lithogenic particles in the mouth of the Humber Estuary also revealed interesting differences in trace metal reactivity with season, tidal state, and settling velocity. The uptake of dissolved ^{54}Mn and ^{109}Cd was subsequently found to be a linear function of the number of self maintaining catalytic Mn_p adsorption sites. The uptake of ^{137}Cs was similarly a function of the number of specific adsorption sites but the nature of these were not established. Although from experimental studies it was evident that the number of ^{137}Cs adsorption sites on the particles in the water column, unlike those accommodating ^{54}Mn and ^{109}Cd , did not change with season, particle settling velocity or tidal state.

c) the first investigations in the Humber coastal zone into the possible biological mediation or uptake of ^{54}Mn , ^{109}Cd and ^{137}Cs . The uptake of dissolved ^{54}Mn ,

^{109}Cd and ^{137}Cs by phytoplankton was negligible during maximum production in spring and indeed was less than or equal to uptake onto lithogenic particles. However substantial increases in K_D values i.e. particle adsorption relative to the killed control for ^{54}Mn and ^{109}Cd during summer indicated some active biological cycling but one not directly related to photosynthetic activity. Comparison with phytoplankton total carbon biomass revealed significant increases of diatoms coincident with enhanced uptake again inferring some biological cycling of ^{54}Mn and ^{109}Cd . Dissolved metal speciation calculations using MINEQL and total dissolved metal concentrations obtained in the Humber coastal zone during summer suggested that the enhanced uptake of ^{54}Mn was due to alga uptake. In comparison, the increase in K_D 's obtained for ^{109}Cd were attributable to enhanced complexation of Cd_d with particulate phase phytochelatin produced by coastal marine diatoms. However these hypotheses remain speculative and need to be fully resolved by further experiments with more comprehensive biological supporting parameters i.e. DOC/POC characterisation and concentrations, microbial activity/biomass etc.

- 5) The isotopic ratios of Pb in nearshore sediments and SPM of the Humber coastal zone have been used to assess the % anthropogenic contribution to the observed concentrations. This study represents the first concurrent seasonal distribution of $^{206/207}\text{Pb}$ in the Humber coastal zone. The seasonal similarity in the linear relationships apparent between the $^{206/207}\text{Pb}$ ratio and salinity in the Humber mouth confirmed that (a) the estuary was a source (albeit not mass dominating) of anthropogenic Pb_p to the nearshore coastal region and (b) that the proportion of anthropogenic contamination could be predicted. Calculations assuming a two component particle end member model suggested that between 30-40% of the extracted Pb_p originated from anthropogenic sources. The subsequent propagation of the signal in the Plume was found to be a complex function of tidal regime, prevailing hydrodynamics and meteorological conditions. This was similarly concluded from the stable metal distribution data in chapter 3. The $^{206/207}\text{Pb}$ isotopic ratios showed little variation between particles differentiated by their settling characteristics indicating that all particles originating from a common source have a similar isotopic composition irrespective of particle density.

6) This study has identified some key seasonal processes which have profound effects on the trace metal behaviour and resulting distributions in the western North Sea. It has also determined essential partition coefficients and trace metal settling velocities which will assist in the refinement of conceptual trace metal transport models in coastal zones. It is foreseen that the extensive seasonal particulate trace metal database in combination with the computed estuarine flux data will also be used extensively in the future for the parameterisation and subsequent validation of trace metal transport models that are currently under development and further refinement for the Humber coastal zones e.g. ECOS Humber Plume model as part of the LOIS national study.

The following model summaries for winter and summer (Figure 7.1a & b respectively) show the contrast in trace metal input, output and reactivity and highlight the areas which require further investigation in order to fully quantify the import, relative importance of trace metal processes occurring within and export from the Humber coastal zone/Plume region. The fundamental difference between winter and summer is the composition, origin and reactivity of the SPM. For instance, during winter the water column in the Humber Plume is dominated by estuarine particulate matter (SPM and temporally resuspended bed sediments) and associated trace metals (Cu, Cd and Pb) that rapidly settle to the bed and do not undergo long range transport. In comparison during summer, a much reduced estuarine flux of particles combined with biological production produces a water column with relatively more particulate organic material that has contrasting trace metal reactivities i.e. enhanced affinity for Cu and Cd relative to estuarine particles. The median settling velocities of the trace metals indicates the deposition of Cu_p in Plume sediments but potential export of Cd_p and Pb_p to the coastal zone.

Winter
Dominant SPM sources: Estuarine particulate matter & resuspended bed sediments

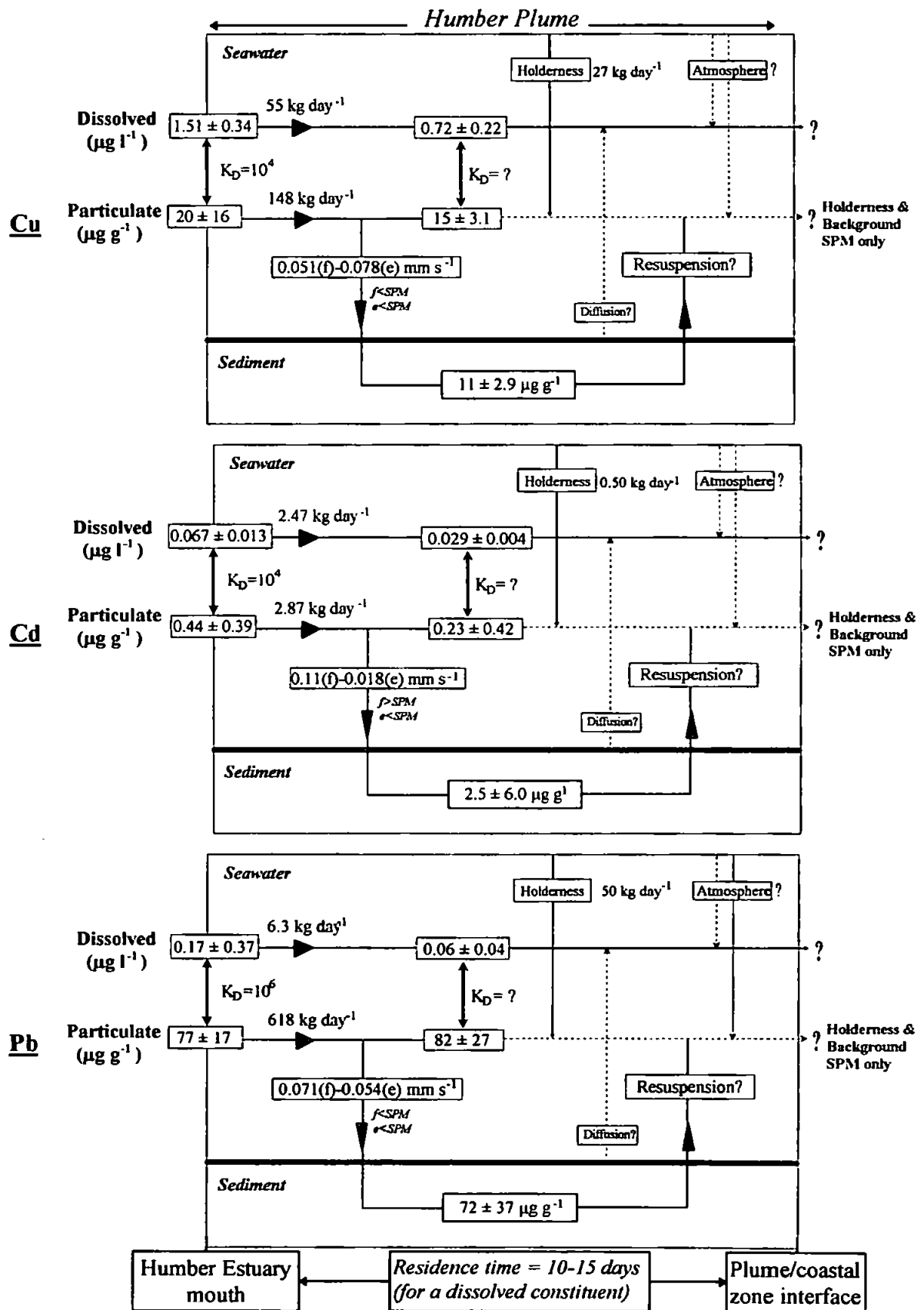


Figure 7.1a Pathways and pools of Cu, Cd and Pb in the Humber Plume during winter'95, where 'e' and 'f' denote ebb and flood tides respectively.

Summer

Dominant SPM sources: Estuarine particulate matter, biogenic particles & background/Holderness material

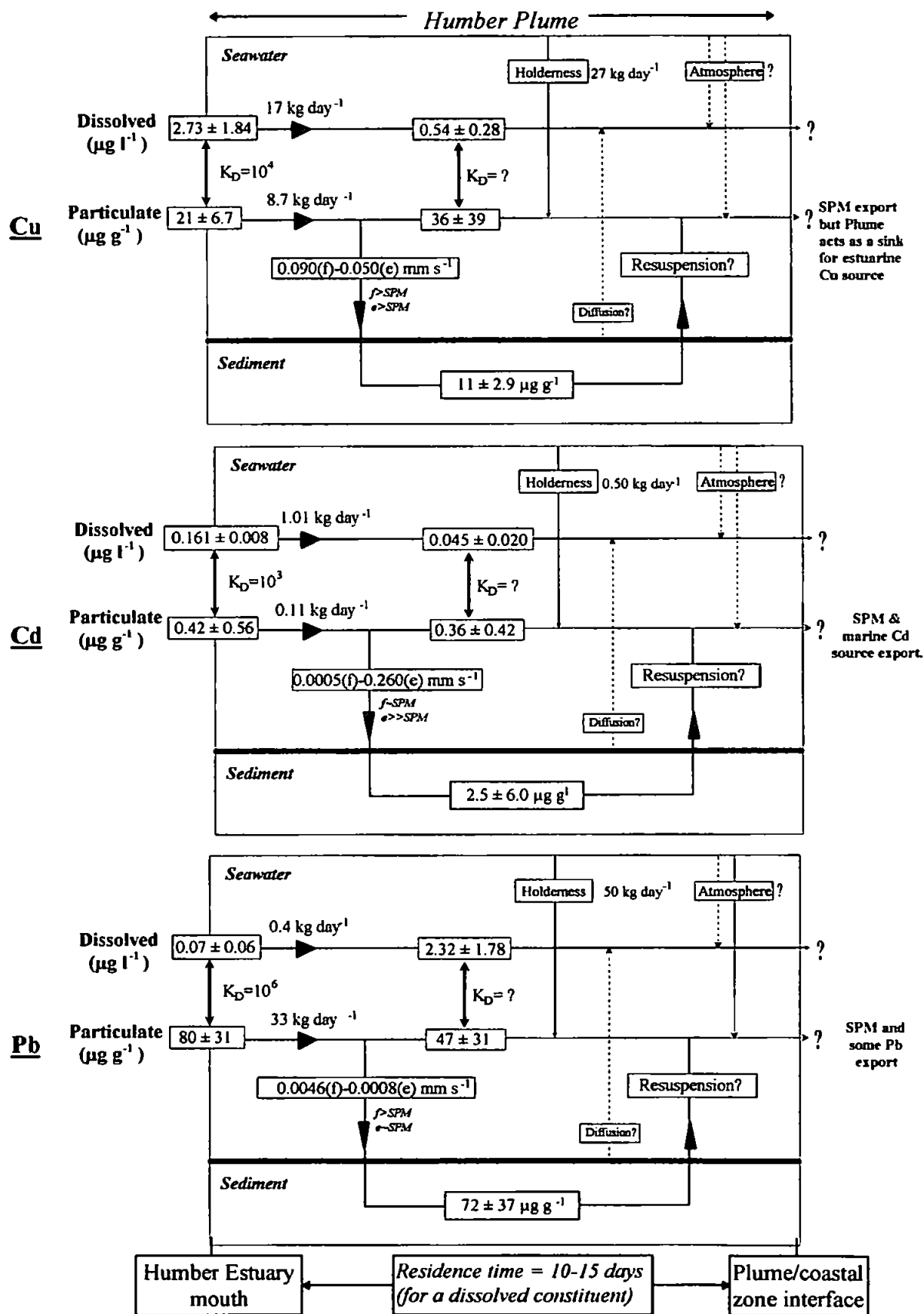


Figure 7.1b Pathways and pools of Cu, Cd and Pb in the Humber Plume during summerr'95, where 'e' and 'f' denote ebb and flood tides respectively.

7.2 Further Studies

1) The quantification of;

- a) atmospheric wet and dry trace metal deposition rates, including characteristic metal particulate concentrations (w/w),
- b) porewater dissolved trace metal fluxes,
- c) sediment resuspension rates and
- d) coastal water inputs of dissolved and particulate trace metals

into the Humber coastal zone in order to quantify all the sources of metals and subsequently provide a comprehensive model of trace metal particle-water dynamics with predictive capabilities.

2) Sequential extraction of SPM and bed particles to assess the solid state speciation of trace metals in the Humber coastal zone e.g. degree of particulate organic Cu and Cd associations.

3) All future sampling trace metal campaigns carried out adjacent to estuary mouths should recognise and study the affects of the flood and neap tidal cycles on resultant chemical fluxes and distributions in coastal zones.

4) The biological mediation of trace metals should be extensively investigated. Results from the present study have indicated the enhanced biological uptake of ^{54}Mn and ^{109}Cd with increasing diatom biomass suggesting the possible role of phytoplankton in the recycling of trace metals. The role of free living and particle attached microbes and bacteria in particulate and dissolved trace metal cycling should also be carefully investigated to establish the relevant biochemical pathways in marine systems.

5) The use of radiochemical analogues has proved a quick, relatively contamination free and useful technique in examining the behaviour of Mn, Cd and Cs in marine

environments. However only a limited number of metals and preliminary experiments were undertaken in this study and further work should be carried out (a) with other trace metals and (b) in the extensive coastal zone and on pure particle end members to test particle mixing models.

- 6) This study has generally focused on the particulate phase and to some extent the dissolved phase. However particle size is arbitrarily defined by the nominal filter pore sizes. Recent developments in cross flow ultrafiltration techniques provide a means to collect and assess the importance of the reservoir of colloidal trace metals and their relative reactivity. Further studies should also include such determinations and may aid in unravelling the complexity of trace metal cycling in dynamic coastal regimes.
- 7) The quantification of Pb isotopic ratios of effluent discharges and atmospheric aerosols is required in the western North Sea to gain a better understanding and rationalisation of the Pb isotopic ratios found before specific sources can be identified.

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and Ecosystem Ecology; Biodiversity and Conservation; Biomonitoring; Ecological Modelling; and Human Ecology.

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Ana Maria Rodrigues

South America

In 1996, the 7th International Conference on Environmetrics took place for the first time in South America, Sao Paulo, Brazil, from 22 to 26 July. The aim of the Conference was to promote communication among people involved in quantitative analysis of environmental phenomena and stimulate the co-operation between basic and applied science specialists, so that they could face the challenge of finding appropriate solutions for environmental problems.

Another event that happened in 1996, was the National Symposium on Oceanography that was held at the Oceanographic Institute of the Sao Paulo University. Approximately 400 papers were displayed as posters. Besides, we have the pleasure of receiving some

eminent scientists, either from Europe or USA, as invited lecturers. They were:

Prof. Keith Dyer, University of Plymouth, UK.
Prof. P Tuley, Southampton University, UK;
Dr. Phil Woodworth, Proudman Oceanography Lab., UK;
Dr. David Caron, Woods Hole Oceanographic Institute, USA;
Dr Donald Olson, Resenstiel School of Marine and Atmospheric Sciences, USA;
Dr Pablo Glonoso, Proudman Oceanography Lab., UK.
Prof. J C Fauaugeres, University Bordeaux 1, France,
Dr. Manfred Ehrhardt, Kiel University, Germany;
Dr. Steven Bay, Southern California Coastal Water Research Center, USA.

These scientists, in addition to their plenary lectures also gave mini-courses on their main specialities. During the Congress, we also had a fortnight course named "Ecotoxicological Evaluation of Marine Sediments" given by Marian Nipper from the National Institute of Water and Atmospheric Research in New Zealand.

Hilda de S L Mesquita

Charlie Boyden Memorial Small Grants Scheme and Travel Grants

Trace Metals in Bermuda Inshore Waters

J.L. Dixon, Department of Environmental Sciences, University of Plymouth, Drake Circus, Plymouth PL4 8AA, UK.

INTRODUCTION

Bermuda

Bermuda is a small subtropical island in the Sargasso sea located approximately 1000 km off the east coast of the United States. It consists of a series of interconnected islands of aeolian limestone overlying a volcanic seamount (Jickells & Knapp, 1984) which extends some 4000m to the sea floor. The shallow Bermuda platform holds the waters of the coral reefs and lagoons, the islands and several small harbours and bays formed by the land masses. The latter are termed the Bermuda Inshore Waters (Moms *et al.*, 1977). Bermuda has no heavy industry or rivers, but supports a dense population of 60,000. Its major industries are tourism (600,000 tourists annually) and international business. Recent years have seen continued increases in population growth and land development which has ultimately increased public awareness and concern over the deleterious effect of man's activities on the pristine inshore waters of Bermuda.

The principal routes by which marine pollutants are introduced to Bermuda inshore waters include urban run-off, atmospheric deposition, in-situ leaching of contaminants from local sources, small scale industrial plants e.g. Bermuda Electric Light Company (BELCO) and raw sewage outfalls. The aims of this work were to sample a number of potentially contaminated sites including Pembroke Canal, Mills Creek (which receives inputs from Pembroke Canal through a sluice gate), Hungry Bay sewage outfall (principally containing sewage from the city of Hamilton) and the water adjacent to the scrap metal dumpsite located in Castle Harbour (Figure 1) to determine the degree of metal

contamination. These results were used in conjunction with numerous ecotoxicological studies to ascertain whether any deleterious effects were being observed on marine life but are not the subject of this report.

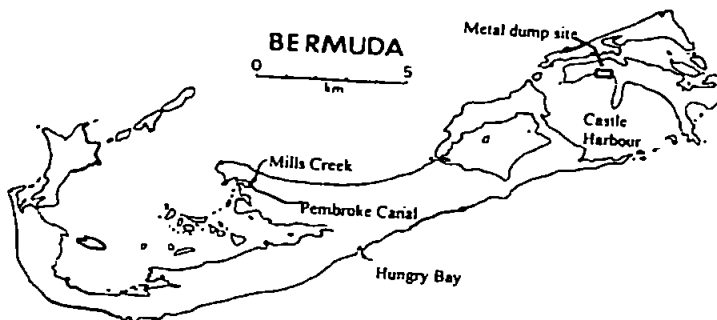


Figure 1. Map of Bermuda showing sampling stations

SAMPLING AND ANALYTICAL METHODS

Water and surface sediment samples were collected at Pembroke Canal, Mills Creek, Hungry Bay and Castle Harbour (Figure 1). The particulate bound and dissolved trace metals Mn, Pb, Ni, Cu, V, concentration of suspended particulate matter (SPM) and % total organic carbon (TOC) were determined at each of the sampling sites. The low SPM concentrations found in the nearshore areas of Bermuda in combination with time constraints of the course restricted the analysis of trace metals to the water column 'dissolved' phase and particulate bound sediment species.

Seawater samples were obtained using 5 litre, pre-washed, acid cleaned Niskin bottles deployed by hand. The bottles were sent down open and closed with a messenger approximately 2 m from the seabed. Sampling sites were rarely greater than 15 m deep and only one depth was sampled at each location. Samples for trace metal analysis were subsequently collected in 500 ml, pre-acid cleaned low density polyethylene bottles (LDPE) and transported back to the laboratory for immediate filtration.

The filtrate was acidified to c pH 2 by the addition of nitric acid (ULTREX) in order to stabilise metal ions, minimise microbial action and help prevent adsorption onto container walls (Milward & Turner, 1995). Dissolved metals were extracted using a mixed complexant (2% v/v) of Ammonium Pyrrolidinedithiocarbamate and Diethylammonium Diethyldithiocarbamate (APDC/DDDC) prepared in 3.5% NaCl, filtered and cleaned with chloroform. The dissolved metals Mn, Pb, Ni, Cu and V were analysed by graphite furnace atomic absorption spectrometry (AAS) (Perkin Elmer 1100B Deuterium Background Correction) by straight-line calibration. A detection limit of three times the standard deviation of the procedural blanks has been applied to all the data.

Sediment samples were collected using a shipek grab which collects a mixed surface sample. Care was taken when subsampling into pre-acid cleaned LDPE containers to avoid sediment in direct contact with the metal sides of the grab. Samples were collected with a plastic spatula (pre-cleaned and stored in plastic bags). Sediment samples were transported back to the laboratory where they were freeze dried for 3-4 days. The salt 'crust' was carefully removed before approximately 0.2 g of sediment was transferred to a pre-weighed crucible for total organic carbon determination by loss on ignition (Mook & Hoskin, 1982). Approximately 0.4 g of the freeze dried sediment were transferred to a pre-acid cleaned teflon digestion bomb and approximately 4 ml of ultra pure nitric acid (ULTREX) added. The bombs were heated in an oven at 110°C for 24 hours. The sediment samples were then allowed to cool and made to volume (20 ml) with Milli-Q water. Procedural blanks were also prepared by the above method without the addition of sediment. The accuracy of the sediment extraction was assessed by the recovery of trace metals from the certified reference material MESS-1 and showed between 60 - 85% recovery, metal dependant. Analysis was performed by flame AAS (instrument as above), direct calibration using Perkin Elmer mixed standard solutions.

RESULTS AND DISCUSSION

Pembroke Canal and Mills Creek

The data is presented from the landward site sampled upstream in the canal (PC4) to the outer reaches of Mills Creek (MC4). Dissolved lead concentrations range from 0.1-8.7 nmol l⁻¹ and show decreasing concentration down the canal with a rapid increase at the head of Mills Creek (MC1). The behaviour of particulate lead mirrors the dissolved distribution often showing a ten fold increase in the canal compared to some points in the Creek. The chemistry of lead is known to be dominated by its affinity with the particulate phase (Balls, 1985, James *et al.*, 1993, Statham *et al.*, 1993, Tappin *et al.*, 1995) but under low concentrations of suspended particulate matter such as those exhibited in Mills Creek (approx. 1.0 mg l⁻¹) the aqueous phase Pb(II) shows strong complexation to hydroxide and carbonate anions (Turner *et al.*, 1981). Consideration of the limestone geology of Bermuda would suggest the formation and dominance of the carbonate species. Copper distributions largely show a similar pattern of behaviour exhibiting typical dissolved concentrations between 2-330 nmol l⁻¹ and particulate levels from 9-4200 µg g⁻¹. Particulate lead and copper levels demonstrate comparable figures to those found by Lyons *et al.*, (1982). Manganese again shows similar broad trends to the aforementioned metals. The remarkable feature dominant is the presence of high dissolved manganese near the head of Mills Creek (MC2). Consideration of the redox chemistry of manganese suggests diffusion of the dissolved Mn(II) species from the underlying anoxic sediments to the overlying water column. The slow oxidation kinetics, low SPM concentrations and hence no auto catalytic adsorption mechanism onto pre-existing surfaces of precipitated Fe/Mn oxyhydroxides could account for the observed persistence of reduced manganese in the water column for this site. Nickel essentially shows the broad features observed by the previous metals but demonstrates a greater variation in concentration throughout Mills Creek. Examination of Vanadium concentrations yield levels of particulate metal in excess of 20 mg g⁻¹ in the Pembroke Canal running through the BELCO plant. Vanadium and Nickel are known constituents of oil and the strong inter-correlation of particulate vanadium and nickel (R²=0.99, Table 1) indicates their association. Peaks in concentrations of dissolved nickel and vanadium at site MC3 are a result of bottom sediment contamination during water sampling. Inter-metal correlations (Table 1) reveal the particle affiliation of particulate lead, manganese and vanadium. It also highlights a strong association between particulate copper and lead. Similar correlations are apparent between dissolved Cu, Pb and Ni as highlighted.

Table 1. Values of R² for significant (P<0.05) linear relationships between trace metals, SPM and TOC

	TOC	Pb _p	Mn _p	Ni _p	V _p	Pb _d	Ni _d
Mn _p	0.54	0.31					
Ni _p	0.42		0.31				
Cu _p		0.80					
V _p	0.37		0.28	0.99			
SPM		0.71	0.73		0.72		
Ni _d						0.45	
Cu _d						0.94	0.43

Castle Harbour

Sampling site CH1 is immediately adjacent to the scrap metal dumpsite (comprising mainly motor vehicles) with subsequent samples following a transect into the harbour. A plume of elevated trace metal water is shown notably for dissolved manganese, nickel and copper. This pattern is exaggerated in sediment distributions where all metals show at least a doubling of concentrations at the site closest to the dump compared to further into the harbour.

Hungry Bay

Sites close to the sewage outfall reveal little trends in trace metal distributions. Noticeable exceptions include a decrease in particulate vanadium from HB2 to HB3. It is difficult to rationalise the persistence of dissolved Mn in the oxic water column and the high values were attributed to contamination on the boat from Manganese (II) Hydroxide. Generally values of both dissolved and particulate metals reflect those found in the control site.

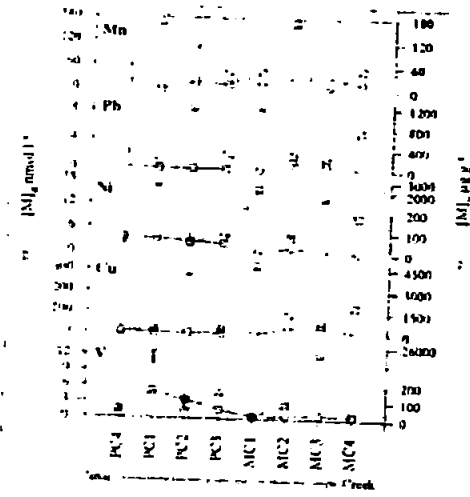


Figure 2. Trace metal distributions in Pampetro's Canal and Mills Creek.

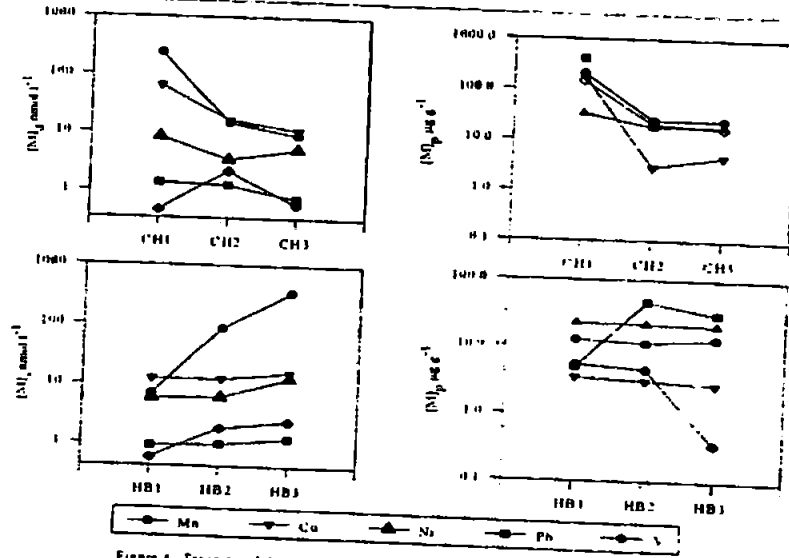


Figure 4. Trace metal distributions in Castle Harbour (CH) and Hunga Bay (HB).

Table 2. Percentage TOC and concentration of SPM in Pembroke Canal and Mills Creek

	PC4	PC1	PC2	PC3	MC1	MC2	MC3	MC4	Control
% TOC	15	64	29	33	40	26	27	31	3
SPM (mg l ⁻¹)					0.78	1.07	17.5	1.21	1.43

Table 3. Percentage TOC and concentration of SPM in Hungry Bay and Castle Harbour.

	HB11	HB2	HB3	CH1	CH2	CH3	Control
% TOC	3	3	5	36	7	3	3
SPM (mg l ⁻¹)	0.28	0.39	0.30	25.2	1.44	2.53	1.43

CONCLUSIONS

Results suggest that there is substantial evidence of anthropogenic metal contamination in both Pembroke Canal and Mills Creek relative to offshore control sites. The canal receives a significant number of inputs including groundwater seepage, landfill run-off and industrial wastes which are probable sources. Of worthy remark are the exceptional concentrations of particulate vanadium which in some instances account for in excess of 2% of the total particulate matter. It is likely that oil contamination is responsible for the vanadium and nickel values especially at site PC1 which was within BELCO's perimeter and before the oil skimmer, designed to retard oil contamination further downstream out of the plant. Significant boating activity and the location of a boatyard in Mills Creek account for the elevated particulate and dissolved copper concentrations, known constituents of marine paints. The most notable other source into the Creek is obviously through the sluice gate allowing passage of Canal contaminants into the marine system. The region of interface between the Canal and Creek is likely to be a zone of complex chemical interactions, arising principally due to the increase in salinity and general change in matrix composition. A further point location of particular sediment metal contamination is not surprisingly immediately adjacent to the scrap metal dump site in Castle Harbour, an obvious source, where all metals analysed exhibited elevated concentrations. These values are generally restricted to this site only and are not observed further offshore with the exception of dissolved vanadium a likely product of oil seepage from dumped cars. Dissolved metal levels in Castle Harbour rarely exceeded those found at the control in the two sites further away from the dump. Care was exercised when considering the enhanced water column levels at CH1 due again to the incorporation of bottom sediment into the rinsin bottle. Hungry Bay sewage outfall demonstrated no apparent trends in trace metal concentrations and typical levels found do not suggest significant anthropogenic contamination in either the dissolved or particulate phase. However it is important to bear in mind that the sewage pipe does not constantly discharge waste and it was not certain whether it was discharging during sampling and hence caution advised when interpreting the data.

Acknowledgements - This work was carried out as part of the Summer School Program 'Hazardous Assessment of Marine Contaminants (16 June - 6 July 1996)' at the Bermuda Biological Station for Research, Inc. Sample collection and analysis was carried out by a number of course participants including Miss Sharon Johnson (University College of Wilmington, North Carolina, U.S.A), Miss Jennifer Mohammed (Rosentiel School of Marine and Atmospheric Science, University of Miami, U.S.A) and Mr Arben Memo (Central European University, Budapest, Hungary). Special thanks also goes to Mr Doug Connelly (BBSR) for his time, assistance and patience throughout the course. A small grant was awarded by ECSA to contribute towards the travel expenses.

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News from the Estuarine Research Federation

The recent ERF newsletter (volume 23, number 1, winter 1997) contains much information, particularly two large articles. The first is about the responses of Tampa Bay and Sarasota Bay seagrass meadows to nitrogen load reductions. This case study contains lessons for seagrass meadows worldwide especially as a response to better wastewater and sewage effluent control and fertilizer reductions. The response by politicians to estuarine changes in this case is particularly of interest.

The second large article concerns NOAA's National Estuarine Eutrophication Survey and gives selected results for the mid-Atlantic, south (US) Atlantic and Gulf of Mexico regions. An extensive matrix contains the trends in Chlorophyll *a*, anoxia (duration, frequency and spatial coverage) and SAV (spatial coverage of submerged aquatic vegetation) since 1970. For further information contact Suzanne Bricker on E-mail sbricker@seamail.nos.noaa.gov

The newsletter contains news from NOAA and USEPA and the ERF component societies but the most notable announcement is the ERF 14th International Conference to be held at Providence, Rhode Island from 12-16 October 1997. The theme is *The State of Our Estuaries* and the symposium aims to assess this for estuaries and their resources worldwide. Thematic sessions include using science, freshwater flow, consequences of habitat change, estuarine fishes (science and management), nutrient driven eutrophication, dissolved oxygen in temperate estuaries,

recovering bays and estuaries, and geographic signatures. There are special sessions on most other topics of estuarine science and management. Contact: ERF 97, PO Box 6887, Providence, RI 02940, USA. Fax: +401 455 4004

The Newsletter announces a new electronic newsletter for aquatic sciences *HydroWire*, an online weekly newsletter for aquatic scientists, is now on WWW at <http://www.hydrowire.org>. It is sponsored by AGU-Ocean Sciences, The American Society for Limnology and Oceanography, the Oceanography Society, and the ERF.

ECSA members wishing to join ERF should contact the ECSA membership Secretary Peter Head (inside cover)

Book and Report Reviews

OCEANOGRAPHY: AN ILLUSTRATED GUIDE

C.P. Summerhayes & S.A. Thorpe 1996
Manson Publ., London, 352pp
HB ISBN 1-864545-38-3 £48.00
also in SB ISBN 1-874545-37-5 £29.50

This volume was published to mark the establishment in the UK of the Southampton Oceanography Centre (SOC), a coming together at one site of a NERC Research Laboratory, its research vessels section including the vessels themselves and University Oceanography Department. This volume opens with a forward by Robert Ballard, discoverer of the wreck of the Titanic and explorer of deep ocean vent systems. In it he highlights the youthfulness of the science of oceanography, its importance to our

Special topic focus - the biogenic interactions of particulate cadmium in the western north sea

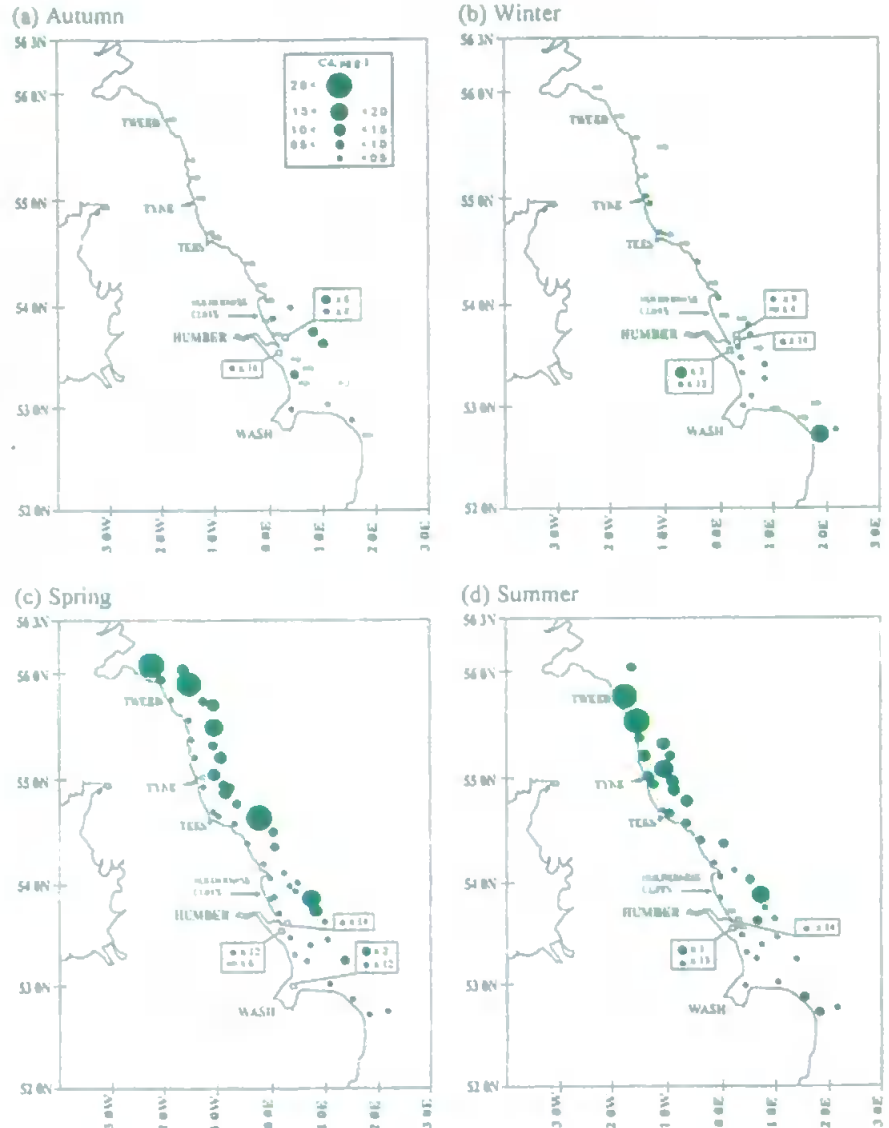
One of the objectives of the RACS coastal surveys of the western North Sea was to investigate the seasonal behaviour of particulate trace metals. Here we describe the seasonal distribution of particulate cadmium (Cd) between 52° - 56° N. These data, combined with phytoplankton incubation studies, have shown a 3-10 fold increase in Cd partition coefficients (K_D) under summer conditions. This suggests that the use of a single K_D value in modelling trace metal particle-water interactions can underestimate particulate metal concentrations and hence the flux in the nearshore coast.

The partition of a metal between the particulate and dissolved phases is defined by the conditional partition coefficient

$$K_D = \frac{P}{C}$$

where P is the particulate (w/w) and C the dissolved phase (w/v) concentration respectively. K_D 's are essential in the modelling of trace metal cycling and transport in estuarine and nearshore coastal zones. However K_D 's are sensitive to particle type and therefore change with season. The accurate estimation of K_D and subsequent changes with season are imperative in the development of geochemical models.

The concentration of particulate Cd varied from 0.01-2.25 $\mu\text{g g}^{-1}$ (mass of metal per dry weight mass of suspended sediment). Highest concentrations were evident offshore in the northern part of the survey area during spring and summer 1995. Average particulate Cd levels showed a strong seasonal trend with concentrations increasing from winter through spring to summer (0.28, 0.45 and 0.53 $\mu\text{g g}^{-1}$ respectively). This is consistent with the affinity of Cd for biogenic particles, relative to lithogenic material. It is interesting to note that particulate Cd concentrations in the northern part of the coastal track were very low and often below detectable limits during autumn 1994 and winter 1995, coincident with low chlorophyll a concentrations. Indeed linear regression analysis of particulate Cd vs. chlorophyll a concentrations yielded a significant positive relationship ($r^2=0.52$,



Distribution of particulate Cd ($\mu\text{g g}^{-1}$) in the water column of the western North Sea coastal zone during (a) autumn 1994, (b) winter 1995, (c) spring 1995 and (d) summer 1995. (\square) indicates the concentrations found during tidal stations at hourly observations.

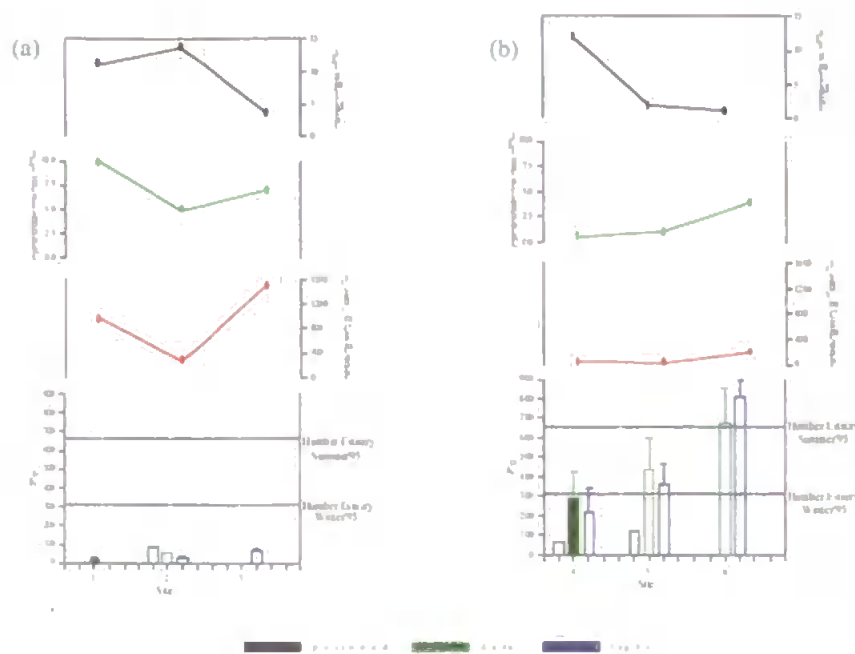
$P < 0.05$) during spring 1995. However this correlation did not hold during the summer period when the highest particulate Cd concentrations ($> 2.0 \mu\text{g g}^{-1}$) were found adjacent to the Tweed Estuary. This may have been due to the preferential association of Cd with particulate organic material and detritus originating from the Tweed.

In order to investigate the apparent biological interactions of Cd, a series of experiments were performed in conjunction with measurements of primary production, phytoplankton biomass and species identification in the spring and summer surveys (see below). The

Cruise	Date	Position		Water depth (m)	Temp ($^{\circ}\text{C}$)	Salinity (ppt)	Total Biomass (μgCl^{-1})	Figure ref. no.
		Lat	Long					
CHI18B/95	02/04/95	53.075N	0.987E	5.5	6.14	33.54	5.8 (60)	1
	03/04/95	53.255N	0.657E	4.9	6.28	33.12	2.5 (8)	2
	04/04/95	53.655N	0.962E	4.6	6.43	34.48	8.8 (42)	3
CHI19C/95	02/07/95	53.420N	0.772E	3.6	13.29	33.88	9.0 (20)	4
	10/07/95	53.728N	0.657E	4.2	12.21	34.17	18.8 (44)	5
	11/07/95	53.000N	0.393E	4.3	16.84	33.61	93.1 (88)	6

uptake of dissolved ^{109}Cd during spring conditions (opposite) gave values (K_D 's < 100) that are small compared to typical values found for predominantly lithogenic material sampled in the mouth of the Humber. This suggests little active biological mediation of Cd during spring despite reasonably high primary productivity and chlorophyll a concentrations. However the uptake of ^{109}Cd during the following summer generally showed an increase in the derived K_D 's of one order of magnitude, independent of incubation conditions. Despite the observed relative increases, the K_D 's were similar in magnitude to those obtained for Humber material in summer 1995. One could therefore reason that simple passive adsorptive processes could account for the observed uptake. However, comparison of typical SPM concentrations (60 mg l^{-1}) found in the mouth of the Humber during summer 1995 to the incubation sites ($1\text{--}10 \text{ mg l}^{-1}$), suggests different surface processes or reactions. A difference between poisoned and unpoisoned samples was generally evident, indicating an active uptake process not directly related to photosynthesis since there was no statistical difference between ^{109}Cd uptake under light and dark incubation conditions. It is therefore suggested that the increase in observed K_D 's during summer 1995, when production and chlorophyll a concentrations were low, was possibly due to enhanced association with phytodetritus or with extracellular polysaccharide-like products exuded by phytoplankton or bacteria.

However trace metal uptake may also depend on the relative biomass and species of phytoplankton present. Despite lower rates of primary productivity, total phytoplankton carbon was substantially greater during experiments at sites 5 and 6 in summer 1995 compared to all other incubation locations. This was coincident with the higher ^{109}Cd K_D values obtained for unpoisoned samples during summer 1995. Indeed regression analysis of light and dark derived K_D 's for ^{109}Cd vs. total phytoplankton carbon yielded significant positive relationships ($r^2=0.97$ and 0.92 for light and dark incubations respectively, $P<0.05$), again inferring the enhanced affinity of Cd for biogenic particles. The dominant species present by mass during



The uptake of dissolved ^{109}Cd expressed as K_D 's for samples poisoned and incubated under light and dark conditions with corresponding concentrations of SPM, chlorophyll a and primary production rates for each experiment during (a) spring 1995 and (b) summer 1995. For site locations see Table. Samples were poisoned with mercuric chloride.

the summer were the diatoms *Rhizosolenia alata*, *R. delicatula* and *Leptocylindrus danicus*. Considering the number of diatoms present in these two experiments it is not surprising that significant linear relationships ($r^2=0.96$ and 0.92 for light and dark incubations respectively, $P<0.05$) were found between the ^{109}Cd K_D 's and the total biomass of diatoms present. The coastal marine diatom *Thalassiosira weissflogii* is known to rapidly produce phytochelatin after exposure to Cd free ion concentrations as low as 12 pM . It is believed that production of this metal-binding peptide is a general metal detoxification system, although Cd has also been found to be an effective inducer of phytochelatin synthase. Typical total dissolved Cd concentrations found during summer 1995 were 0.40 nM . The free Cd^{2+} concentration was obtained indirectly by a computer modelling program (MINEQL) that calculates the concentration of dissolved trace metal species i.e. CdCl_2 , CdSO_4 etc. from known equilibrium constants for complexation reactions at defined temperatures and pH. This yielded typical free ion concentrations of the order 12 pM . It is therefore possible that the increased K_D 's for ^{109}Cd observed in summer 1995 at sites 5 and 6 were due to enhanced complexation of dissolved Cd with phytochelatin produced and exuded by coastal marine diatoms abundant in the water column at these sites.

These experiments have demonstrated significant seasonal variability in the K_D 's for Cd in coastal waters related to, and probably consequent upon, the seasonal cycle of biological production and decay. The formation of biogenic particles associated with phytoplankton blooms is therefore an important factor in controlling both the concentration and speciation of the dissolved Cd phase and hence its toxicity in the water column. Furthermore the use of a single K_D for Cd, i.e. typical of the lithogenic particulates that dominate the Humber coastal zone during winter months, could lead to significant underestimates of particulate Cd concentrations, and thus erroneous estimates of the flux of dissolved and particulate Cd to the southern North Sea, especially during spring and summer months.

Joanna Dixon and Alan Morris, CCMS, Plymouth Marine Laboratory,
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