

1995

Particulate Trace Metals in British Coastal Waters

Williams, Mark Richard

<http://hdl.handle.net/10026.1/1934>

<http://dx.doi.org/10.24382/1353>

University of Plymouth

All content in PEARL is protected by copyright law. Author manuscripts are made available in accordance with publisher policies. Please cite only the published version using the details provided on the item record or document. In the absence of an open licence (e.g. Creative Commons), permissions for further reuse of content should be sought from the publisher or author.

Particulate Trace Metals
in
British Coastal Waters

by

Mark Richard Williams B. Sc. (Hons) M.Sc.

A thesis submitted to the University of Plymouth
in partial fulfilment for the degree of

Doctor of Philosophy

Department of Environmental Sciences

University of Plymouth

Drake Circus

Plymouth

PL4-8AA

In collaboration with:

Plymouth Marine Laboratory, Plymouth
British Maritime Technology, Southampton

Submitted October 1995

LIBRARY STORE

REFERENCE ONLY

| | |
|------------------------|-----------------|
| UNIVERSITY OF PLYMOUTH | |
| Item No. | 9002779856 |
| Date | 2 SEP 1996 S |
| Class No. | T 551.4601 W IL |
| Cont. No. | X 703339825 |
| LIBRARY SERVICES | |

90 0277985 6



Particulate Trace Metals in British Coastal Waters

Mark Richard Williams

Abstract

Key processes affecting the transport of particulate trace metals in the coastal waters of the Irish and North Seas have been examined. Sample collection and experimentation was carried out on board *R.R.S. Challenger* in January 1992 (Irish Sea) and in December 1992 and November 1993 (North Sea). Particulate samples were digested in 1M HCl and the concentrations of Ca, Cd, Co, Cu, Fe, Mn, Pb and Zn were determined, together with the $^{206}/^{207}\text{Pb}$ isotopic ratio. In the North Eastern Irish Sea the concentrations of suspended particulate trace metals were affected significantly by tidal processes, such that ebb tides transport particles of higher trace metal concentrations from the nearshore, while flood tides transport metal-depleted particles from offshore. This tidally-induced transport was confirmed by complementary $^{206}/^{207}\text{Pb}$ analyses, which showed the value of this technique in particle tracing.

In the North Sea suspended particulate trace metal concentrations were higher adjacent to industrialised estuaries and high Pb concentrations were found in the Tyne/Tees region (in the range 200 - 340 $\mu\text{g g}^{-1}$), in combination with low $^{206}/^{207}\text{Pb}$ suggesting an anthropogenic origin. Estimated fluxes of trace metals from the Humber Estuary to the North Sea were relatively small compared to the PARCOM inputs to the estuary. There was little evidence of interannual variability in these fluxes compared to those obtained in December 1988. Samples of end-members of the Humber Plume particle mixing series (estuary and cliffs) were used in radiochemical uptake studies, which indicated a response time of about 1 day for ^{109}Cd , ^{137}Cs and ^{65}Zn to reach a new equilibrium. When the end-members were mixed together in various proportions they showed the uptake of ^{109}Cd and ^{54}Mn behaved non-additively. Settling of suspended particulate trace metals in the plume region was examined in unique experiments involving stable and radioisotopes. It was shown that trace metals were preferentially associated with different settling fractions. Lead was associated with slow settling particles whereas Cu was associated with particles settling more rapidly. The results presented in this dissertation allowed the development of a conceptual model for fine sediment transport for trace metals, which could be interfaced with established hydrodynamic models.

Contents

| | |
|---|-------------|
| COPYRIGHT | i |
| ABSTRACT | iii |
| CONTENTS | iv |
| ACKNOWLEDGEMENTS | vii |
| DECLARATIONS | viii |
| | |
| CHAPTER 1 - INTRODUCTION | 1 |
| 1.1. BRITISH COASTAL WATERS. | 2 |
| 1.2. NORTH EASTERN IRISH SEA. | 3 |
| 1.2.1. <i>Physical Parameters of the Irish Sea.</i> | 4 |
| 1.2.2. <i>Freshwater Inputs into the Irish Sea.</i> | 5 |
| 1.2.3. <i>Anthropogenic Inputs into the Irish Sea.</i> | 8 |
| 1.3. NORTH SEA. | 8 |
| 1.3.1. <i>Physical Parameters of the North Sea.</i> | 8 |
| 1.3.2. <i>Freshwater Inputs to the North Sea.</i> | 9 |
| 1.3.3. <i>Anthropogenic Inputs.</i> | 14 |
| 1.4. FACTORS AFFECTING THE TRANSPORT OF PARTICULATE TRACE METALS..... | 15 |
| 1.4.1. <i>Particle-Water Interactions.</i> | 15 |
| 1.4.2. <i>Benthic Processes.</i> | 17 |
| 1.4.3. <i>Particle Tracing Techniques: ^{206/207}Pb isotopic ratio.</i> | 21 |
| 1.4.4. <i>Modelling Approaches to Sediment Transport.</i> | 22 |
| 1.5. <i>Aims of the Study.</i> | 24 |
| | |
| CHAPTER 2 - SAMPLING AND METHODOLOGY | 25 |
| 2.1. SAMPLE COLLECTION..... | 26 |
| 2.1.1. <i>Overview of Sampling Strategy.</i> | 26 |
| 2.1.2. <i>Suspended Particulate Matter.</i> | 28 |
| 2.1.3. <i>Sampling of Sediments.</i> | 29 |
| 2.1.4. <i>Sampling using Settling Velocity Tubes.</i> | 30 |
| 2.1.5. <i>Additional Samples.</i> | 32 |
| 2.1.6. <i>Particle Sizing.</i> | 33 |
| 2.2. PARTITION EXPERIMENTS..... | 34 |
| 2.2.1. <i>Experimental Procedure.</i> | 34 |
| 2.2.2. <i>Five day K_D Values.</i> | 34 |
| 2.2.3. <i>Kinetic Experiment.</i> | 35 |
| 2.2.4. <i>Settling Fraction K_D Values.</i> | 35 |
| 2.2.5. <i>Mixing Experiments.</i> | 36 |

| | |
|---|------------|
| 2.3. SAMPLE TREATMENT AND ANALYSIS..... | 36 |
| 2.3.1. <i>Selection of Digest for Determining Particulate Trace Metals in Particles.</i> | 36 |
| 2.3.2. <i>Treatment of Particulate Samples.</i> | 40 |
| 2.3.3. <i>Treatment of Sediment Samples.</i> | 42 |
| 2.4. INSTRUMENTATION..... | 44 |
| 2.4.1. <i>Flame Atomic Absorption Spectroscopy (Flame AAS).</i> | 44 |
| 2.4.2. <i>Graphite Furnace Atomic Absorption Spectroscopy (GFAAS).</i> | 45 |
| 2.4.3. <i>Inductively Coupled Plasma Mass Spectrometry (ICP-MS).</i> | 48 |
| 2.5. QUALITY ASSURANCE..... | 48 |
| 2.6. CONCLUSION. | 51 |
| CHAPTER 3 - TRACE METALS IN BRITISH COASTAL WATERS..... | 52 |
| 3.1. INTRODUCTION. | 53 |
| 3.2. TRACE METALS IN THE NORTH EASTERN IRISH SEA..... | 53 |
| 3.2.1. <i>Trace Metals in Bed Sediments.</i> | 53 |
| 3.2.2. <i>Sediment Cores.</i> | 58 |
| 3.2.2.1. <i>Description of the Sediment Cores.</i> | 58 |
| 3.2.2.2. <i>Dissolved and Particulate Trace Metals in Sediment Cores.</i> | 59 |
| 3.2.3. <i>Trace Metals in Suspended Particulate Matter.</i> | 67 |
| 3.2.3.1. <i>Variation of Particulate Trace Metal Concentrations at Site Y over a Tidal Cycle.</i> | 68 |
| 3.2.3.2. <i>Tidal Variation of Particulate Metals at Site Z.</i> | 73 |
| 3.3. TRACE METALS IN THE LOIS COASTAL ZONE - NORTH SEA..... | 76 |
| 3.3.1. <i>Spatial Variation of Surface Sediments in the LOIS Coastal Zone.</i> | 76 |
| 3.3.2. <i>Description of a Sediment Core from the Humber Mouth.</i> | 77 |
| 3.3.3. <i>Spatial Variation of Suspended Particulate Matter in the LOIS Coastal Zone.</i> | 82 |
| 3.3.3. <i>Tidal Variation of Particulate Trace Metals at the Humber Mouth.</i> | 90 |
| 3.4. CONCLUSION. | 95 |
| CHAPTER 4 - STABLE LEAD ISOTOPES..... | 97 |
| 4.1. INTRODUCTION. | 98 |
| 4.2. VARIATION IN STABLE Pb ISOTOPIC RATIO'S DUE TO MIXING. | 99 |
| 4.3. APPLICATION OF Pb ISOTOPE STUDIES. | 102 |
| 4.4. CONCLUSION. | 104 |
| CHAPTER 5 - PARTICLE SETTLING EXPERIMENTS..... | 105 |
| 5.1. INTRODUCTION. | 106 |
| 5.2. SAMPLE COLLECTION. | 108 |
| 5.3. ESTIMATION OF SETTLING VELOCITY..... | 109 |
| 5.4. PARTICLE SIZES AND DENSITIES. | 114 |
| 5.5. TRACE METAL ANALYSIS OF SETTLING FRACTIONS..... | 119 |
| 5.5.1. <i>Chemical Composition of the Settling Fractions.</i> | 120 |
| 5.5.2. <i>Qualitative Assessment of the Settling Behaviour of Particulate Metals.</i> | 125 |

| | |
|--|------------|
| 5.5.3. <i>Settling Velocities of Particulate Metals</i> | 128 |
| 5.6. CONCLUSIONS..... | 131 |
| CHAPTER 6 - RADIOCHEMICAL EXPERIMENTS..... | 134 |
| 6.1. INTRODUCTION..... | 135 |
| 6.2. KINETIC EXPERIMENTS..... | 137 |
| 6.2.1. <i>Introduction</i> | 137 |
| 6.2.2. <i>Trace Metal Uptake onto Suspended Particulate Matter</i> | 140 |
| 6.2.2.1. <i>Irish Sea</i> | 140 |
| 6.2.2.2. <i>North Sea</i> | 142 |
| 6.3. PARTITIONING OF TRACE METALS WITH MARINE PARTICLES OVER FIVE DAYS..... | 147 |
| 6.4. PARTICLE MIXING EXPERIMENTS..... | 149 |
| 6.5. UPTAKE OF TRACE METALS BY PARTICLES WITH DIFFERENT SETTLING VELOCITIES..... | 154 |
| 6.6. CONCLUSION..... | 157 |
| CHAPTER 7 - CONCLUSIONS: APPLICATION OF THE RESULTS FOR MODELLING THE LONG RANGE TRANSPORT OF PARTICULATE TRACE METALS..... | 158 |
| 7.1. THE OBJECTIVES AND ACHIEVEMENTS OF THIS STUDY..... | 159 |
| 7.2. IMPLICATIONS FOR MODELLING LONG RANGE TRANSPORT OF PARTICULATE TRACE METALS..... | 162 |
| 7.3. FURTHER STUDIES..... | 169 |
| References..... | 171 |
| Appendix A - Instrumental Conditions | |
| Appendix B - SVT Trace Metal Concentrations | |
| Appendix C - Published Work | |

Acknowledgements.

The completion of this study has involved the help of numerous people whom the author wishes to acknowledge. Dr. G.E. Millward has been a friend and the director of studies for this work. He has selflessly provided the scientific guidance, support, encouragement and at times the discipline needed for the completion of this work. Grateful thanks are also due to the following:

Dr. Alan Morris of Plymouth Marine Laboratory (supervisor), has shown keen interest in my progress and has been instrumental, often behind the scenes, in many of the scientific opportunities provided to me throughout my study.

Dr. Steve Hill (supervisor) has provided much support and analytical help throughout this study.

Dr. Sarah Jones and Dr. Colin Jago from the University of Wales, Bangor, for useful discussions and help regarding the use and loan of Settling Velocity Tubes.

Mr Bob Clifton from Plymouth Marine Laboratory, has willingly given his time and experience to help with the work performed using radioisotopes.

Mrs Trish Frickers from Plymouth Marine Laboratory, who provided invaluable assistance in the use of ICP-MS, during the analysis of stable Pb isotopes.

Dr. Sarah Colley from Institute of Oceanographic Sciences, Deacon Laboratory, for the loan of equipment used for the extraction of sediment porewaters.

Dr. Andrew Turner and Mr Keith Sayers for the collection and provision of shorebased samples from the River Tweed and River Ouse prior to cruise CH99/92.

Miss Tonia Sands for help with experiments during the *R.R.S. Challenger* cruise CH108A/93.

Colleagues of British Maritime Technology, Southampton, in particular Mr Andrew Tyler for his support.

The scientists and crew aboard the *R.R.S. Challenger* cruises CH88A/92, CH99/92 and CH108A/93, without whom this study would not be possible.

The members of the Coffee Club, who are friends and colleagues, and have provided in a various ways, both socially and academically, help and support during this study.

Declarations.

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award. Financial support for this study was provided primarily by the Natural Environment Research Council (CASE award No GT4/91/AAPS44), additional financial assistance was provided by Plymouth Marine Laboratory and British Maritime Technology. The assistance of all those involved is duly and gratefully acknowledged. However, the thesis remains the sole work of the author.

A programme of advanced study was undertaken which included guided reading in topics relating to marine chemistry. Instruction and training was given in a range of analytical methodologies applicable to investigations of the chemistry of marine particles, including flame atomic absorption spectroscopy, inductively coupled mass spectrometry, and radiochemistry.

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.

Williams, M.R., Millward, G.E., Hill, S. and Morris, A.W., 1993. $^{206}/^{207}\text{Pb}$ isotopic ratios applied to particulate transport processes - North Eastern Irish Sea. *Netherlands Journal of Aquatic Ecology*, **28**, 353 - 358.

Millward, G.E., Williams, M.R. and Clifton, R.J., 1993. Particle sources and trace element reactivity in the Humber Plume. *Netherlands Journal of Aquatic Ecology*, **28**, 359 - 364.

Conferences and Presentations.

- Dec. 1991 Marine Chemistry Discussion Group -Southampton, attendance
- Apr. 1992 Mineralogy Society, Burlington house, London, attendance.
- Sep. 1992 ECSA-22, University of Plymouth, attendance and assistance with administration.
- Nov. 1992 The Royal Society Meeting on the North Sea, London.
- Mar 1993 CONAPEG, University of Plymouth. Departmental oral presentation.
- Apr. 1993 ICP-MS NERC Steering Group Meeting, Plymouth, Oral paper presented - $^{206}/^{207}\text{Pb}$ Isotopic Ratios Applied to Particulate Transport Processes - North Eastern Irish Sea.
- Apr. 1993 ECSA local Meeting on the Solway Firth, Cumbrian, and Galloway Coasts, Penrith, attendance.
- May 1993 Marine Chemistry Mini-Conference, Torquay. Oral paper presented - The application of Pb stable isotopes in elucidating geochemical processes.
- Aug. 1993 ECSA-23, University of Groningen, Groningen, The Netherlands. Oral paper presented - $^{206}/^{207}\text{Pb}$ Isotopic Ratios applied to Particulate Transport Processes - North Eastern Irish Sea. Written paper submitted to conference proceedings. Co-author on additional paper.
- Sep. 1993 Chemical Sedimentology, Cardiff. Oral paper presented - The behaviour and Transport of Lead in Morecambe Bay Using $^{206}/^{207}\text{Pb}$ Isotopic Ratio as a Pollution Source Indicator.
- Sep. 1993 IES Conference, Warren Springs, Stevenage. Oral paper presented - $^{206}/^{207}\text{Pb}$ Isotopic Ratios applied to Particulate Transport Processes - North Eastern Irish Sea.
- Sep. 1994 ECSA-24, Universidade de Aveiro, Portugal. Oral paper presented - The Mixing and Transport of Particle Associated Metals in the Humber - Wash Coastal Zone, UK.

Courses and External Contacts.

- Mar. 1993 Meeting at the Lead Development Association to discuss lead usage in the U.K. past and present, London.
- Aug. 1993 SERC Graduate School, Dyffm House, Cardiff.
- Oct. 1993 University of Plymouth. Introduction to Scanning Electron Microscopy.
- Apr. 1994. Collaborative fieldwork, Department of Chemistry, Universidade de Aveiro, Portugal.

Regular meetings and discussions were held with colleagues at PML to obtain advice and assistance.

Meetings were held with Dr. Sarah Jones at University of Wales, Bangor relating to work using their Settling Velocity Tubes.

Signed..... 

Date..... 28/5/96

Particulate Trace Metals
in
British Coastal Waters

by

Mark Richard Williams B.Sc. (Hons), M.Sc.

Chapter 1 - Introduction.

Chapter 1 - Introduction.

1.1. British Coastal Waters.

Until relatively recently the coastal waters around the British Isles have been considered a convenient receptacle for anthropogenic waste but attention is now focusing more closely on these waters (Greenpeace, 1992). Over the past seven years the North Sea Project (NSTF, 1993; Charnock *et al*, 1994) and more recently parts of the Land Ocean Interaction Study Project (LOIS) have focused on the coastal region. Of particular interest is the behaviour of trace metals some of which are toxic and show a wide range of reactivities with suspended particles and sediments. The coastal areas which receive the largest industrial discharges of trace metals are the regions between east Anglia and the Scottish border, and the north eastern Irish Sea (Figure 1.1.). These regions form part of the North Sea and Irish Sea respectively.

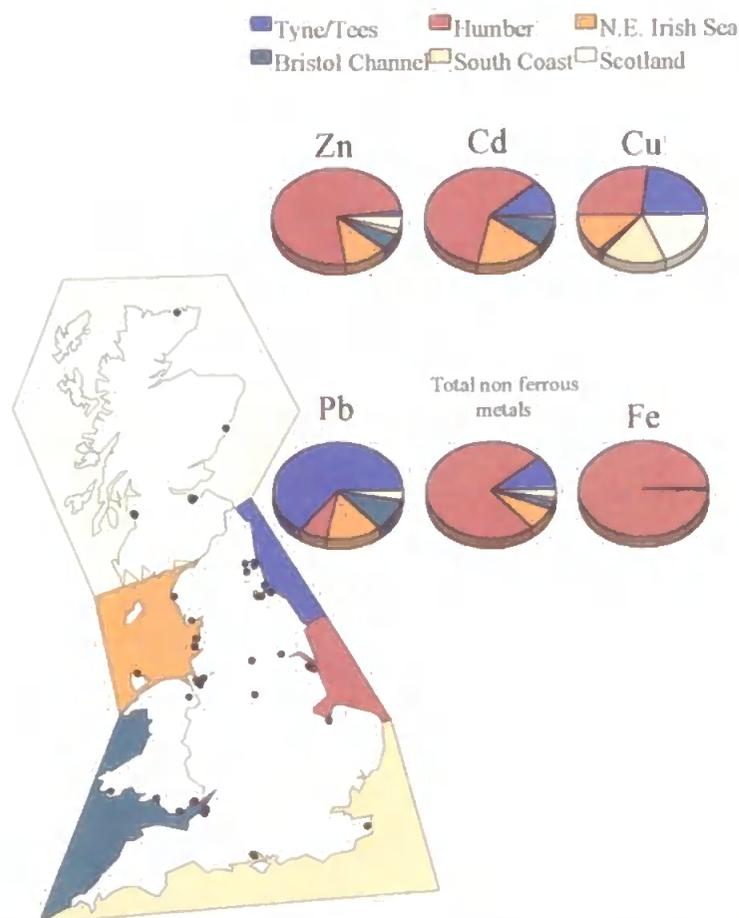


Figure 1.1. Distribution of trace metals discharged from the top fifty metal discharging industries (●) into coastal waters and estuaries of Britain (Greenpeace, 1992).

These two semi-enclosed shallow seas are quite different in character. The North Sea is approximately a magnitude larger in area than the Irish Sea and also receives approximately a magnitude more riverine inputs (Table 1.1.). The North Sea is bordered by eight European countries each of which contributes politically to the usage of the North Sea, whereas the Irish Sea is bordered by Britain and Ireland only. Both seas are important shipping routes and have significant fisheries.

Table 1.1. Comparison of parameters from the Irish Sea and the North Sea.

| | | Irish Sea | North Sea | |
|-------------------|-------------|-----------------------|------------------------|------------------------------------|
| | Area | 51 000 ^a | 575 000 ^a | km ² |
| Water Input | River | 769 ^a | 7 000 ^a | m ³ s ⁻¹ |
| | Rain | ~280 ^b | ~7 800 ^b | m ³ s ⁻¹ |
| | Oceanic | ~850 000 ^d | 1 000 000 ^c | m ³ s ⁻¹ |
| Particulate Input | Oceanic | 6.2 ^e | 10 ^f | x10 ⁶ t a ⁻¹ |
| | Channel | - | 26 ^f | x10 ⁶ t a ⁻¹ |
| | Rivers | 0.3 ^g | 5 ^f | x10 ⁶ t a ⁻¹ |
| | other | 0.3 ^g | 17 ^f | x10 ⁶ t a ⁻¹ |
| Living Resources | Fish | 60 500 ^a | 2 494 000 ^a | t (landed) |
| | Crustaceans | 10 600 ^a | 40 200 ^a | t (landed) |
| | Molluscs | 15 600 ^a | 128 900 ^a | t (landed) |
| | Mariculture | 6 600 ^a | 379 200 ^a | t |

a. The Irish Sea Study Group (1990a). b. estimated from rainfall data. c North Sea Task Force (1993). d Howarth pers. comm., e estimated from oceanic water flux and [SPM] of 0.32 mg l⁻¹, f. Eisma and Irion (1988). g. PARCOM (1991)

1.2. North Eastern Irish Sea.

The Irish Sea receives seawater inputs from the Atlantic Ocean through St. Georges Channel and the North Channel. This area is recipient to a variety of inputs, which includes dumping, industrial discharges and estuarine sources (Foster, 1984; McCartney

et al, 1992). The coastline contains a number of highly industrial regions, with large industrialised, urban developments on the Mersey and Solway Firth (Figure 2.1.).

1.2.1. Physical Parameters of the Irish Sea.

The Irish Sea is divided into a shallow eastern area which is characterised by a typical water depth of 30m and a western side which is composed of a deep north-south trough of 80 - 275m. Two major embayments exist in the eastern Irish Sea - Cardigan Bay and the area referred to as the north eastern Irish Sea which lies to the east of the Isle of Man (Figure 1.2.).

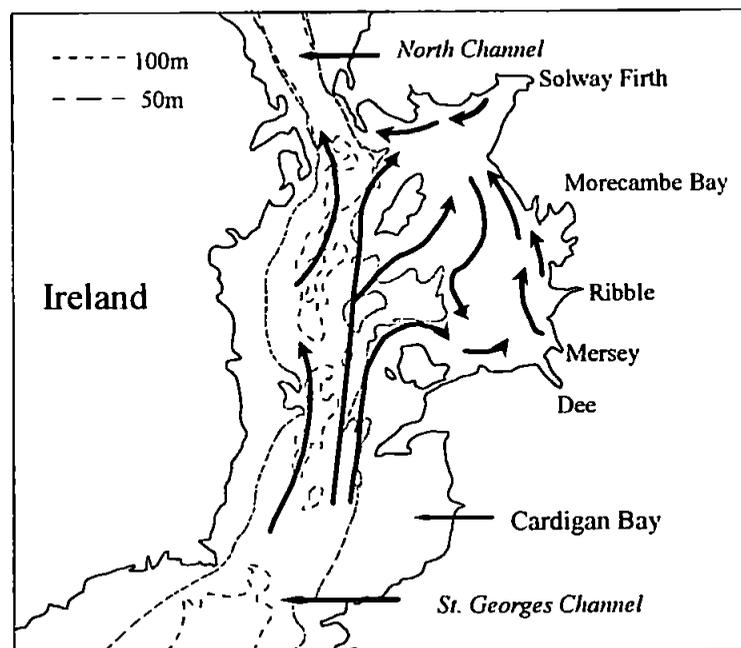


Figure 1.2. Generalised diagram of the near surface water residual currents in the Irish Sea (Ramster and Hill, 1969).

Considerable variation in current patterns exist within this area. The currents are induced by wind, tides and seasonal changes (Belderson and Stride, 1969; Ramster and Hill, 1969; Foster, 1984; Kershaw *et al*, 1992; Davies and Jones, 1992) resulting in highly variable current patterns for the area. Tidal processes strongly influence motion in the Irish Sea with a typical tidal range of 8m, which produce tidal currents in excess of 0.5 m s^{-1} over much of the area. Wind stress plays a less significant role due to the small fetch in most

directions, but if persistent strong winds prevail in either a south westerly or north westerly direction, strong wind induced currents can pass into the Irish Sea through St. Georges and the North Channels respectively, but normally the wind dominates from the south east (Taylor and Parker, 1993). However, during an average year the residual currents produce a northward flow (Figure 1.2.) exiting via the North Channel into the area of the Firth of Clyde (Kershaw *et al*, 1992).

1.2.2. Freshwater Inputs into the Irish Sea.

The rivers discharging into the north eastern region of the Irish Sea are the major contributors of freshwater (Table 1.2.) into the Irish Sea. The freshwater appears to flow along the coastline with water movement causing a 'carving' off of the flow into lower saline gyres (Plate 1.1.). Sharp salinity gradients appeared to only occur during the spring ebb tide (Plate 1.2.), which contains freshwater originating from the south of the region i.e. Liverpool Bay. However, stratification was not observed during the neap ebb tide which suggests that the tidal excursion during the more dynamic spring tide draws water from Liverpool Bay along the coastline but the less energetic neap tide is not sufficiently energetic to draw the fresher water as far north.

Table 1.2. Freshwater Inputs into the Irish Sea (The Irish Sea Study Group, 1990b).

| Region | Rivers | Annual Mean Flow m ³ s ⁻¹ |
|----------------|-----------------------------|--|
| Cardigan Bay | Teifi, Dyfi and others | 81 |
| North Wales | Conwy, Clwyd, Dee | 63 |
| Mersey Estuary | Mersey, Weaver and others | 69 |
| Ribble Estuary | Ribble and others | 39 |
| Morecambe Bay | Lune and others | 65 |
| Cumbria | Derwent and others | 30 |
| Solway Firth | Eden, Esk, Annan and others | 103 |
| Galloway | Water of Luce and others | 150 |
| Ireland | Boyne, Liffey and others | 169 |
| Total | | 769 |

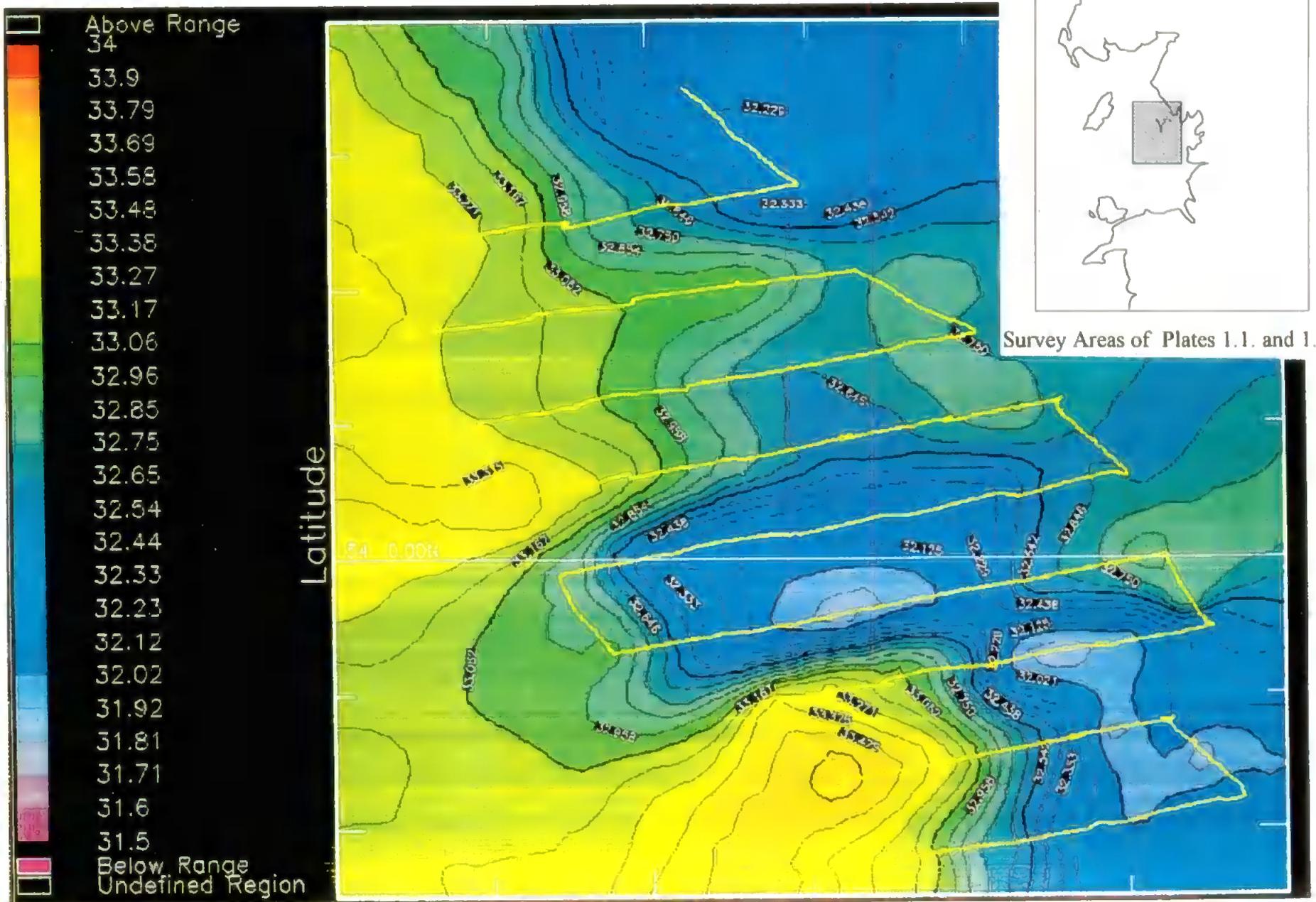


Plate 1.1. Salinity distribution in the area of Morecambe Bay (see insert) as obtained during CH88/92 (not tidally corrected).

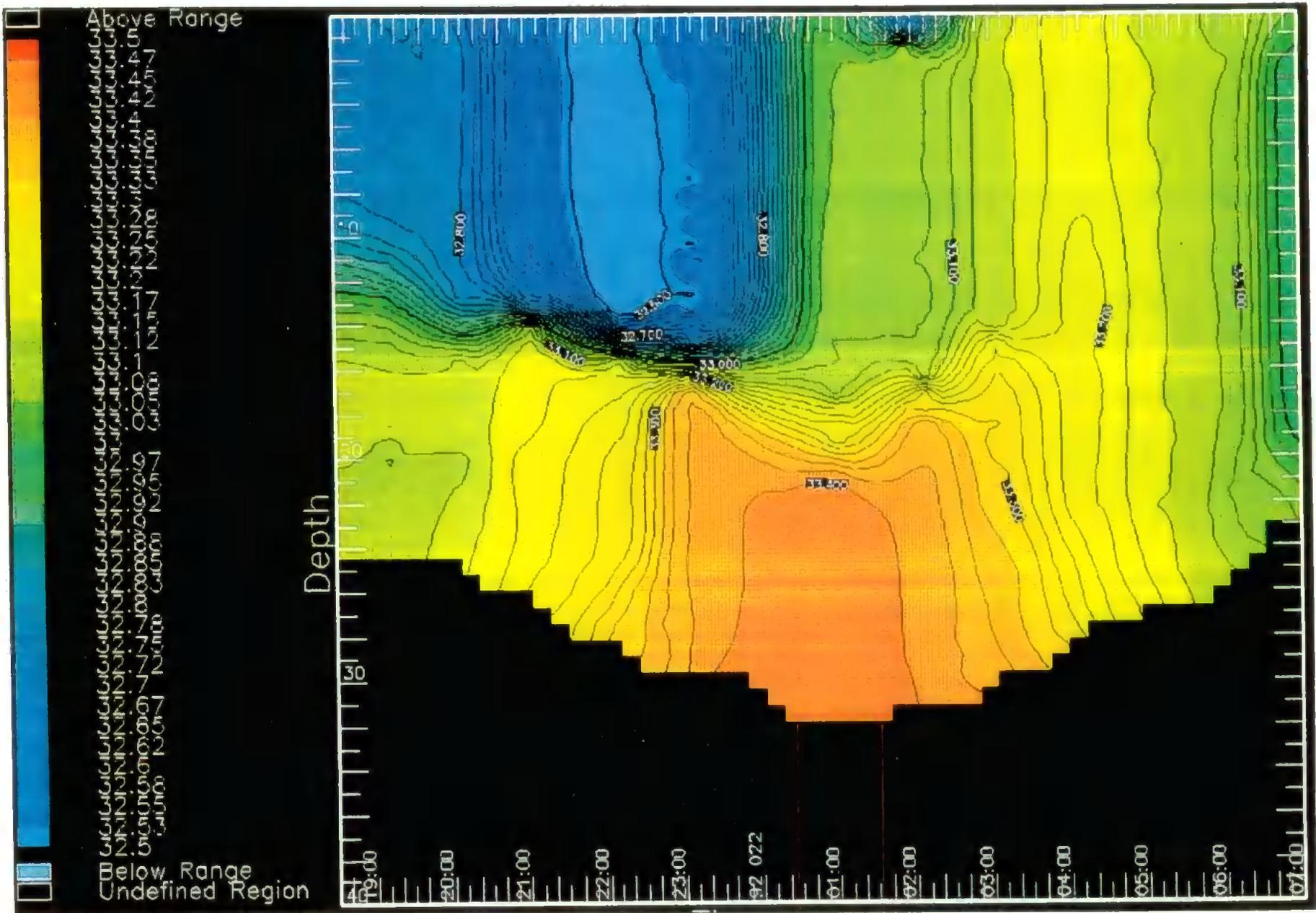


Plate 1.2. Anchor station salinity profile obtained during CH88/92 at Site Y (see Plate 1.1. insert) for a spring tide (not tidally corrected).

1.2.3. Anthropogenic Inputs into the Irish Sea.

The Irish Sea receives a full spectrum of anthropogenic inputs (MAFF, 1993). The sewage and industrial waste dump sites situated in Liverpool Bay receives 1.5×10^6 t a⁻¹ of sewage from North West Water plc annually (MAFF, 1992) and the dredge spoils site receives 3×10^6 t a⁻¹ from the Mersey Estuary and its approaches (MAFF, 1991). Inputs of trace metals into the north eastern Irish Sea (Cd : 24 t a⁻¹, Cu : 74 t a⁻¹, Zn : 554 t a⁻¹ and Pb : 44 t a⁻¹) have been estimated by PARCOM (1991) and comprise of direct industrial and sewage discharges, in addition to riverine inputs. The dominant input is via riverine sources for much of the area, the exception is for the Cumbrian coastline where direct industrial inputs have dominated. The two main industrial sources of trace metals along the Cumbrian coastline are the phosphate rock processing plant at Whitehaven and the nuclear reprocessing plant at Sellafield.

Table 1.3. Typical particulate trace metal concentrations in the Irish Sea.

| Metal | Particulate Trace Metal Concentrations | |
|-------|--|---|
| | Sediment $\mu\text{g g}^{-1}$ | SPM $\mu\text{g g}^{-1}$ |
| Cd | <0.2 - 1.7 ^a | 0.43 - 1.3 ^b ; 0.16 ^c ; 0.22 ^e |
| Pb | 29 - 570 ^a | 19 - 100 ^b |
| Cu | 11 - 130 ^a | 8 - 85 ^b ; 24 ^c ; 16 ^e |
| Zn | 81 - 490 ^a | 140 - 980 ^b ; 295 ^c ; 210 ^e |
| Mn | 470 ^d | 240 - 1400 ^b ; |
| Fe | 18 000 ^d | |

a. Law *et al*, 1989; b. Laslett, 1995; c. Norton *et al*, 1984; d. Malcom *et al*, 1990; e. Jones and Jefferies, 1983.

1.3. North Sea.

1.3.1. Physical Parameters of the North Sea.

The North Sea is connected to the Atlantic Ocean via the English Channel in the south and has a free exchange in the north. Water entering through these areas form an anti-clockwise circulation pattern initially moving down the east coast of Britain and then up

past the entrance to the Baltic Sea and northward along the Norwegian coast (Figure 1.3.). The residual currents are principally wind driven and tidal and density effects are less significant. The central region of the North Sea in the shallow area of the Dogger Bank has weak and variable currents. High sediment trace metal concentrations have been measured in this area, whether these are the result of particulate pollutant transport to this location is still unresolved (Chapman, 1992).

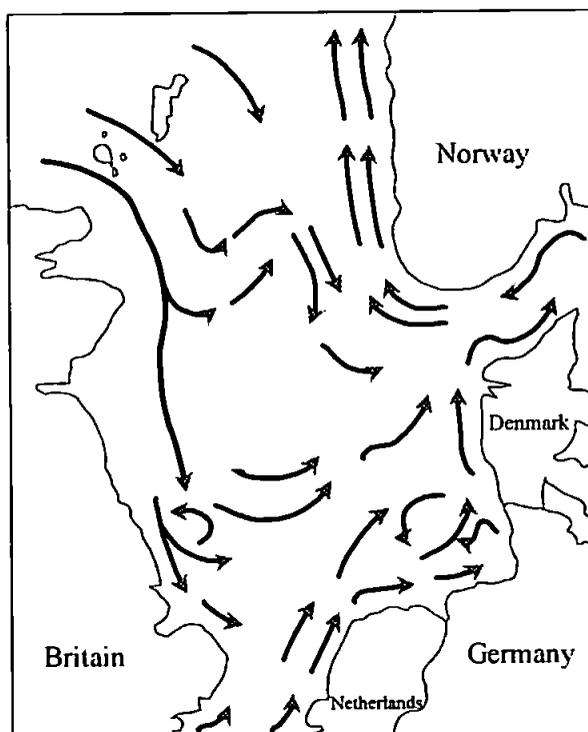


Figure 1.3. Generalisation of the current patterns in the North Sea (Holligan *et al*, 1989).

1.3.2. Freshwater Inputs to the North Sea.

The dominant freshwater inputs into the North Sea are from the continental estuaries draining northern Europe and British estuaries (Humber and Thames), Table 1.4. Of particular significance for this study is the Humber Estuary whose large flowrate and shallow macrotidal character results in a well mixed plume region.

The catchment area of the Humber Estuary (Table 1.4.) is the largest of all British estuaries with a catchment area covering 20% of England. The daily flowrate of the Humber Estuary can reach $1550 \text{ m}^3 \text{ s}^{-1}$ during spate conditions, and has been estimated to carry the effluent of 20% of the population of England (The Humber Advisory Group, 1979). The Humber Estuary is one of the major estuaries on the north east coast of Britain

and an importance influence on the LOIS RACS (Land Ocean Interaction Study - River and Coastal Study) study area (Plate 1.3.). The River Ouse and Trent are the two main freshwater sources into the Humber Estuary. The Trent catchment is industrialised and predominately glacial clays, Triassic marls, and some limestone and sandstone (Institute of Hydrology, 1988). The catchment of the Ouse is mainly rural (except the Aire and Don which contain reservoirs and are heavily industrialised) and is predominantly carboniferous limestone, grits and coal measures with some sands, sandstone, clays, and marls. Headwaters originate mainly from moorland areas (Institute of Hydrology, 1988). Coastal erosion has a significant effect along the Holderness cliffs. In the region of 10^6 t a^{-1} of eroded boulder clay from the Holderness cliffs enters into the coastal water adjacent to the Humber Estuary compared with a flux of 10^5 t a^{-1} from riverine sources (Figure 1.5.). This eroded material consists of 70% fine ($<63\mu\text{m}$) material (McCave, 1987). Of major significance is the question: how much of this relatively pristine eroded boulder clay enters into the Humber Estuary and mixes with anthropogenically altered fluvial particles? The influence of this process has on the SPM in coastal waters is shown in Plate 1.4. The anti-clockwise circulation in the North Sea keeps the suspended particle load close to the east coast contributing to the Humber plume. McCave suggested that about 1.3×10^5 t a^{-1} of particulate material accumulates in the lower estuary. A study of the texture of sediment from the south bank of the lower estuary (Barr *et al*, 1990) showed large areas of clay material, which may suggest the Holderness cliff as an origin. However, seabed drifter studies (O'Connor, 1987) have shown that $<10\%$ of the Holderness material enters the estuary and Zwolsman (1994) estimated about 20% of fluvial particles were retained by the estuary; using these suggestions, the likely composition of sediment in the lower estuary would contain five times more Holderness particles than fluvial particles.

Table 1.4. Mean flowrate data for the main rivers flowing into the North Sea.

| Rivers | Mean Flowrate ($\text{m}^3 \text{s}^{-1}$) | Catchment (km^2) | Sediment Flux ($\times 10^4 \text{ t a}^{-1}$)* | River | Mean Flowrate ($\text{m}^3 \text{s}^{-1}$) | Catchment (km^2) | Sediment Flux ($\times 10^4 \text{ t a}^{-1}$)* |
|--------|--|-----------------------------|---|---------|--|-----------------------------|---|
| Tweed | 41‡ | 4390 | 4.2 | Thames | 82 | 27000 | 17.2 |
| Tyne | 33‡ | 2418 | 2.6 | Scheldt | 100 | 21580 | 14.4 |
| Wear | 12‡ | 1008 | 1.3 | Weser | 326 | 44304 | 25.3 |
| Tees | 12‡ | 1460 | 1.8 | Elbe | 726 | 148500 | 64.9 |
| Humber | 284† | 18112 | 12.6 | +Rhine | 1897 | 200000 | 81.8 |

†Oct, 1993, ‡Nov, 1993. *Derived from $y = 60x^{0.78}$ (Willmot and Collins, 1981) where y = sediment flux (t a^{-1}) and x is the catchment area (km^2). † ‡ Data supplied by NRA, † Ruchay, 1995, Remaining data taken from Turner, 1990

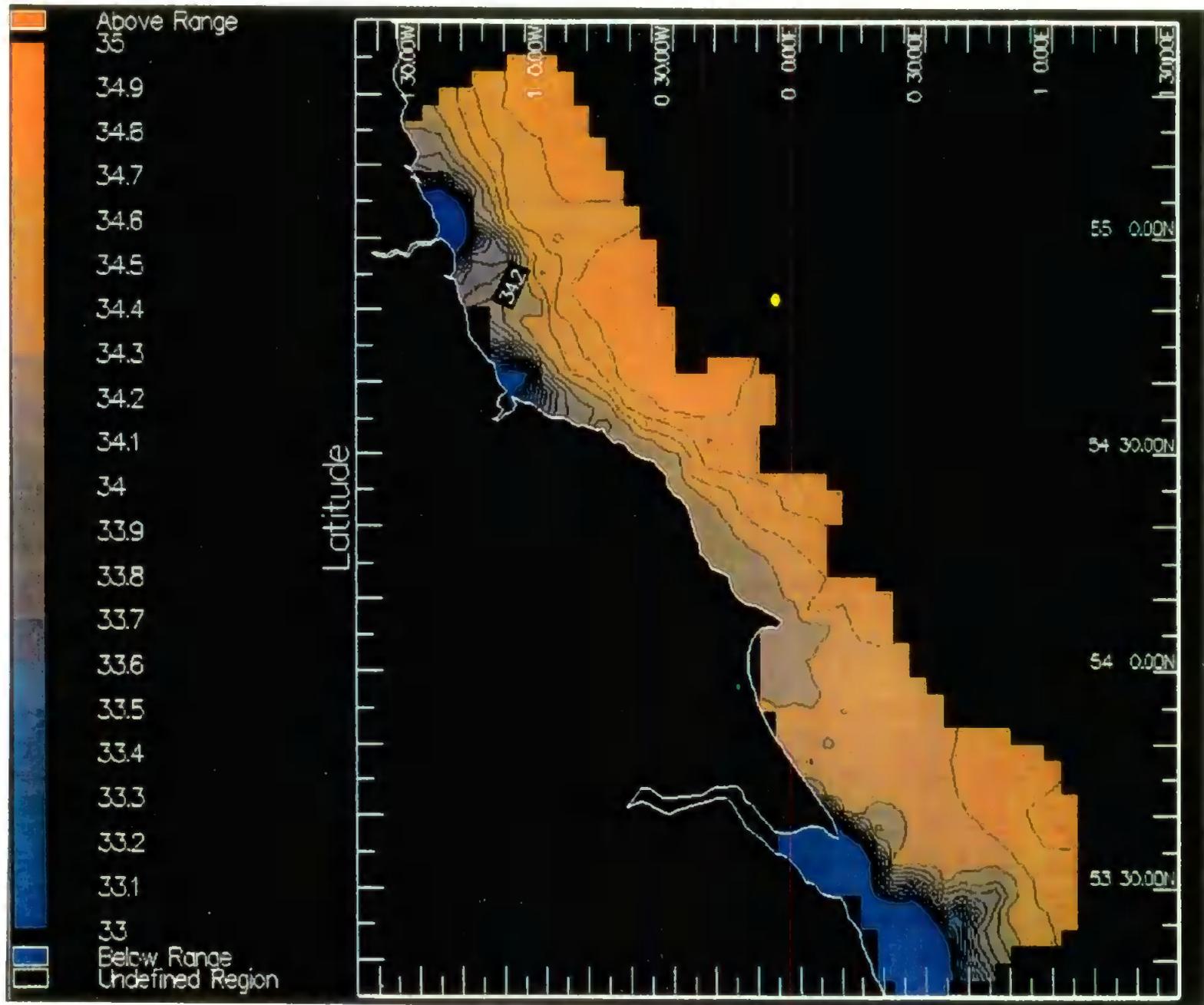


Plate 1.3. Salinity plot of the east coast of England during cruise CH108/93, showing the outflow of freshwater from the Humber, Tees and Tyne (not tidally corrected).

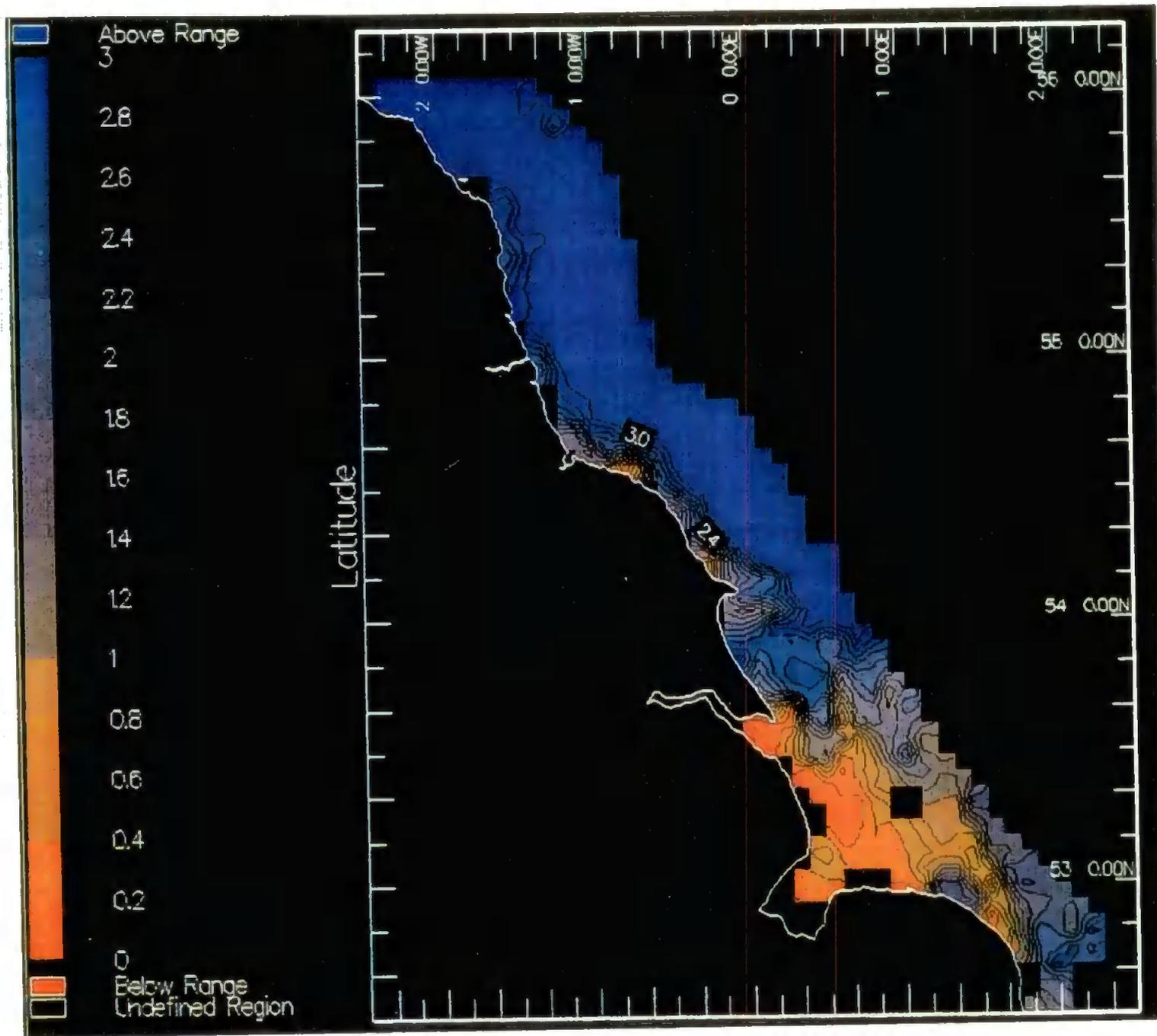


Plate 1.4. Transmittance plot of the east coast of England during cruise CH108/93, showing the Humber plume (not tidally corrected).

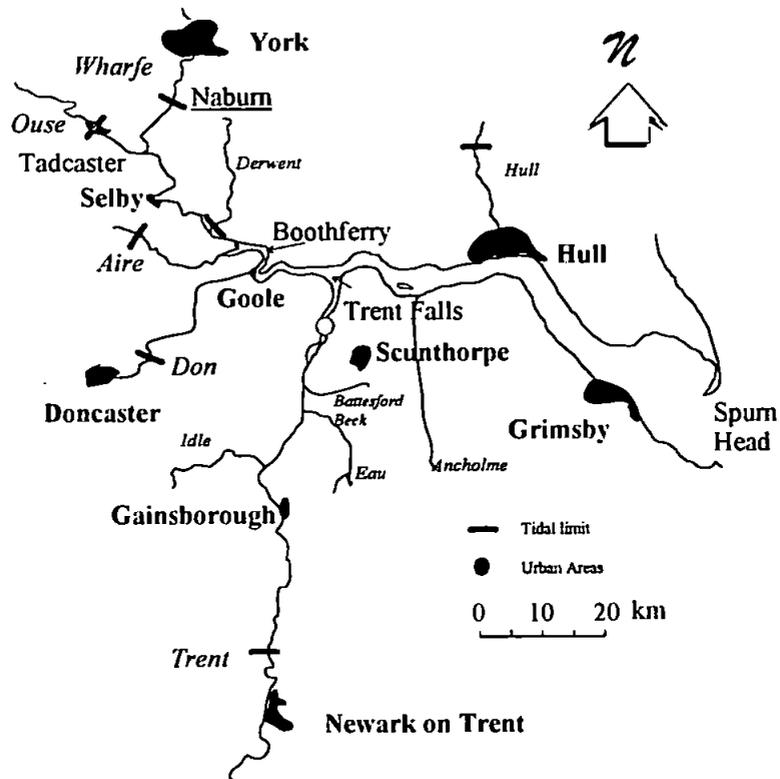


Figure 1.4. Main freshwater inputs into the Humber Estuary.

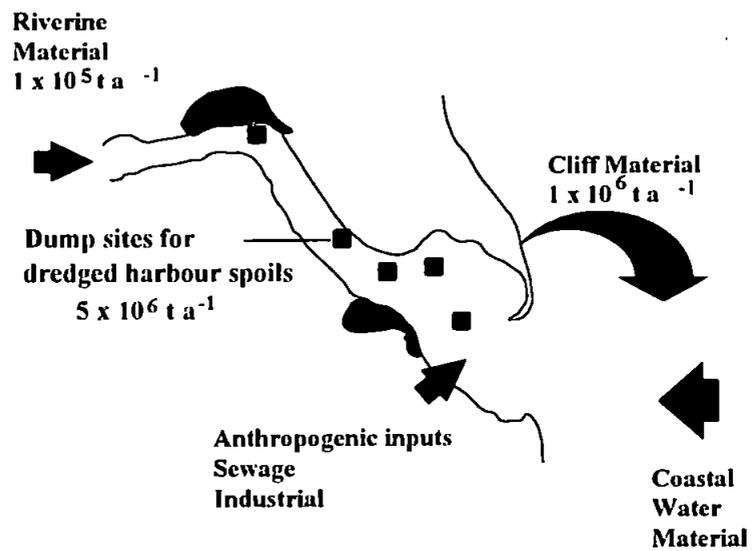


Figure 1.5. Inputs of particulate matter into the Humber Estuary.

1.3.3. Anthropogenic Inputs.

The North Sea is bordered by some of the most industrialised countries in the world and consequently receives considerable input of trace metals from a variety of sources and has a greater flux (PARCOM, 1991) of trace metals (Cd 95 - 66 t a⁻¹, Pb 1200 t a⁻¹, Cu 1500 t a⁻¹ and Zn 7700 t a⁻¹) into its waters compared with the Irish Sea. However, the flux of trace metals into the North Sea give typical particulate trace metal concentrations similar to those found in the Irish Sea (compare Table 1.3. and 1.5.).

Table 1.5. Typical particulate trace metal concentrations in the North Sea.

| Metal | Particulate Trace Metal Concentrations | |
|-------|--|---|
| | Sediment µg g ⁻¹ | SPM µg g ⁻¹ |
| Cd | <2 ^a ; 0.47 ^b | 0.1 - 1.4 ^c ; 0.35 ^d ; 0.3 - 17.1 ^e |
| Pb | 90 ^a ; 141 ^b | 16 - 88 ^c ; 57 ^d ; 50 - 6000 ^e |
| Cu | 23 ^a ; 34 ^b | 18 - 43 ^c ; 14 ^d ; 22 - 519 ^e ; 231 ^f |
| Zn | 190 ^b | 73 - 1100 ^c ; 82 - 3960 ^e ; 1158 ^f |
| Mn | 1141 ^b | 180 - 1900 ^c ; 414 ^d ; 212 - 2750 ^e |
| Fe | 37 800 ^b | 23 200 ^d ; 9 800 - 46 400 ^e |
| Co | 18 ^b | |

a. Murray *et al*, 1980; b. Irion and Müller, 1990; c. Laslett, 1995. d. Kersten *et al*, 1991b; e. Nolting and Eisma, 1988. f Jones and Jefferies, 1983.

Comparison of modern with pre-industrial North Sea sediment by Irion and Müller (1990) showed that Pb exhibited the largest enrichment (2.8) followed by Cd (1.8), Zn (1.6) and Cu (1.6) for North Sea sediments, of the remaining metals examined they concluded that only weak or no enrichment had occurred. Of particular interest to this dissertation are the estuaries of the north east coast of England and in particular the Humber Estuary which makes a significant contribution to the flux of particulate trace metals to the adjacent coastal waters (Turner *et al*, 1991). Some earlier work of Taylor (1979) suggested that the dominant influence in this area was its geology and not industrial input. Less than ten years ago Morris (1988) concluded that 'very little information is available on natural and contaminant constituents' in the Humber and highlighted contamination by As, Cu and possibly Hg. Elevated levels of dissolved Cu and Pb were observed by Balls (1985) in the coastal waters adjacent to the Humber and the Tyne-Tees area, and the Humber Estuary

was identified as a particular source of dissolved Cd. Humber sediments have been shown to be enriched in As, Pb, Cu and Zn (Grant and Middleton, 1990) resulting from selected industrial inputs, in particular the TiO₂ processing. The sediments may reflect historic industrial inputs and act as a reservoir for pollutant metals (Kitts *et al*, 1994).

1.4. Factors Affecting the Transport of Particulate Trace Metals.

Since one of the main considerations of this study is the long range transport of particulate metals it is appropriate to provide an introduction to some of the considerations required when addressing this issue. Further information has been also provided within each chapter as it was considered to be either more appropriate or beneficial to be closer to the results.

1.4.1. Particle-Water Interactions.

An understanding of the interaction of dissolved trace metals with indigenous marine particles is a significant factor in any attempt to model the long range transport of particulate trace metals in coastal waters.

Many complex factors affect the geochemical behaviour of trace metals with marine particles, which include -

- dissolved metal speciation: dissolved trace metals can associate with a variety of ligands; each complex can behave in a different manner.
- particle surface properties: which includes organic and ferromanganese coatings, and the degree of particle flocculation.
- particle residence time: which determines the exposure time of the dissolved trace metal with the particle surface and hence kinetic effects, and includes movement of the particles by settling and resuspension.

One of the most comprehensive studies of dissolved trace metals speciation was performed by Turner *et al* (1981) who used a speciation model to predicted the expected association of cations with inorganic ligands within model seawater. However, the role of organic

material as a complexing ligand was not fully addressed and a number subsequent authors have examined the role of organic ligands in the speciation of dissolved trace metals (Wallace, 1982; Neubecker and Allen, 1983; Millero, 1990; Plavšić and Cosovic, 1994). Of the metals examined during this dissertation Cu is the most strongly associated with organic matter with an indication that dissolved Pb speciation is also influenced by organic matter while Zn predominately associates with inorganic ligands (Wallace, 1982; Mouvet and Bourg, 1983; Cabaniss and Shumann, 1988a, 1988b). However, the relative importance of the dissolved and particulate phases for various trace metals is dependent on their particle reactivity and metals such as Pb predominantly associated with the particulate phase while metals such as Cd exist primarily in the dissolved phase (Burton *et al*, 1993).

An understanding of the interaction of dissolved trace metal species with particulate matter is required to model the long range transport of trace metals in the coastal environment (Olsen *et al*, 1982; Morris, 1986; Santschi, 1989; Morris; 1990; Förstner, 1994; Millward *et al*, 1994, 1996; Turner and Millward, 1994). The partition coefficient (K_D) has been commonly used to measure the association of trace metals between the dissolved and particulate phase (for example Nyffeler *et al*, 1984).

$$K_D = \frac{C_p}{C_s} \quad 1.1.$$

where, C_s is the concentration of metal in the dissolved phase (w/v) and C_p is the concentration of metal in the particulate phase (w/w). The K_D concept assumes instantaneous and reversible equilibrium between the dissolved and particulate phases; homogeneity of particulate surfaces; and the speciation of the dissolved element is not complex (Millward, 1995).

Marine particles consist of the particle matrix (clay, silicate) and usually are coated heterogeneously with metal oxides and organic matter. Trace metals will adsorb to varying degrees to each type of material depending on its geochemistry. For example :

| | |
|-----------------|-------------------|
| Clay | Cs |
| Organic matter | Cu>Pb> Zn~Cd |
| Al/Fe/Mn oxides | most trace metals |

Further comments regarding the kinetics of trace metal uptake have been addressed in the introduction to Chapter 6. The particle population within any given water mass is a complex mixture of particles with different origins (fluvial, biological, sewage, industrial, atmospheric, resuspended sediment) and hence characteristics (composition, size, density, flocculation). These considerations mean that an examination of the processes of trace metal interaction with suspended particulate matter, not only requires an understanding of trace metal sorption with different particle coatings, but also a knowledge of the behaviour and composition of the particles within a given water mass.

1.4.2. Benthic Processes.

Within the coastal environment, variation in the trace metal content of particles results from the input of trace metals and geochemical/diagenetic processes. The classic description of early diagenetic processes is based on the progressive oxidation of electron acceptors as given by Froelich *et al* (1979) and Berner (1981) and allows a useful overview of the interaction of trace metals with particle coatings. Organic material deposited in sediment is decomposed microbially, the microbes utilise the available oxidants that yield the greatest free energy change per mole of organic carbon oxidised (Froelich *et al*, 1979). The sequential biological reduction of these oxidants O_2 , NO_3^- , Fe^{3+} , Mn^{4+} , SO_4^{2-} and CH_4 produce distinctive porewater profiles of these variables in deep sea sediments (Figure 1.6.). The depth into the sediment can be divided into zones of oxygen usage e.g. oxic and anoxic. The separation between these zones is often referred to as either the redox boundary or the oxidation front.

As the concentration of oxygen reaches zero, the manganese oxyhydroxides are reduced, releasing Mn (II) into the pore waters (Lynn and Bonatti, 1965). The concentration of Mn (II) at lower depths in the sediment core is controlled by the solubility product of the carbonate species. A similar behaviour is observed for Fe. Reduction of Fe (III) oxyhydroxides produces Fe (II) in the porewaters. The porewater Fe (II) and Mn (II) diffuse upward, across the redox boundary, precipitating into a metal rich band in the region of the redox boundary. The Fe rich bands tend to be closer to the redox boundary than the manganese rich bands, due to the rapid oxidation of Fe compared with Mn (Stumm and Morgan, 1981). In the lower depths of the core Fe is precipitated as the

sulphide by interaction with the H₂S produced by reduction of the SO₄ in the sulphidic zone (Sørensen and Jørgensen, 1987; Gaillard *et al*, 1989).

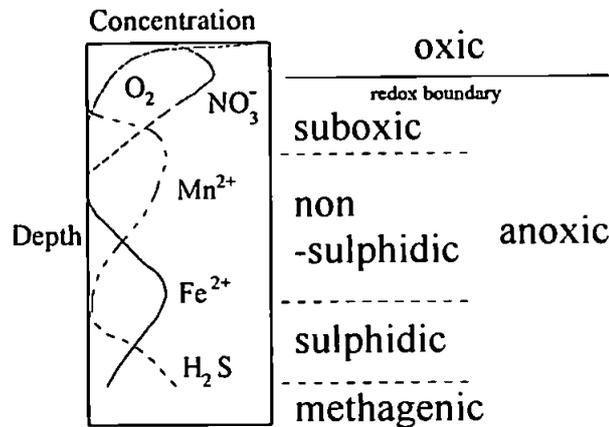


Figure 1.6. Schematic representation of the porewater profiles of O₂, NO₃⁻, Mn (II), Fe (II) and H₂S in deep sea sediments caused by early diagenesis.

The chemical changes occurring in the sediment core causes a decrease in the redox potential (E_h) with depth. The E_h (V) values are often expressed in terms of electron activity ($p\varepsilon$) a dimensionless value, the relationship between these two values is given in Equation 1.2. Some typical values of $p\varepsilon$ are given in Table 1.7.

$$p\varepsilon = \frac{F}{2.3RT} E_h \quad 1.2.$$

where, F = Faraday Constant ($9.64 \times 10^4 \text{ C mol}^{-1}$), R = Gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T = temperature (K).

Due to higher rates of sedimentation, and increased biological productivity of coastal waters the diagenetic zones occur within a much small sediment depth compared with deep sea sediments. The depth of the redox boundary will also be dependent on other variables including sediment substrate, oxygen content of the bottom water, and anthropogenic inputs. To some degree diagenetic processes will be perturbed, by superimposed anthropogenic inputs (Schmidt and Reimers, 1991) and the effects of resuspension and bioturbation. Bioturbation of the sediment can cause the direct introduction of oxygen below the redox boundary, causing a micro environment around the burrow (Santschi *et al*, 1990) and detrital feeders will cause a mixing of the upper layers of the sediment core. Bioturbation can have a significant effect on the sedimentary composition and solute

fluxes (Aller, 1990, 1994a, 1994b). The presence of macrofauna has been shown to enhance porewater fluxes by 20 - 30 % (Aller and Yingst, 1985). Resuspension of the sediment will also cause mixing and under the influence of the prevailing current, the advection of resuspended material. Clearly, the core profile of coastal sediments are a record of a complex mixture of geochemical, physical and biological interactions (Aller, 1994b).

Table 1.7. Reaction constants for diagenetic reactions. ΔG° = Gibbs free energy per mole of 'Redfield Ratio' (Redfield, 1958) organic matter; $p\epsilon^\ddagger$ = electron activity (estimated for aquatic conditions).

| Oxidant | | ΔG° kJ mol ⁻¹ | $p\epsilon^\ddagger$ |
|-----------------|---|--|----------------------|
| O ₂ | Reduction → H ₂ O | -56367 | +13.75 |
| NO ₃ | Denitrification → N ₂ | -53540 | +12.65 |
| NO ₃ | Reduction → NH ₄ | -48592 | +6.15 |
| Mn (IV) | Birnessite δ-MnO ₂ → Mn (II) | -54600 | +8.50* |
| Mn (IV) | Pyrolusite α-MnO ₂ → Mn (II) | -51596 | - |
| Fe (III) | Hematite Fe ₂ O ₃ → Fe (II) | -24915 | -1.67* |
| Fe (III) | Limonitic Goethite FeOOH → Fe (II) | -23501 | - |
| SO ₄ | Reduction → H ₂ S | -6715 | -3.50 |

† Froelich *et al*, 1979; ‡ Stumm and Morgan, 1981. * values of non specific metal oxides

The flux of trace metals from the sediment porewater into the overlying water column can be obtained with a knowledge of the porewater profiles in the surface sediment and the concentration in the overlying water column. The flux of solute (g m² s⁻¹), J_i , from the sediment water interface is given by Fick's First Law (Equation 1.3.), knowing the porosity, ϕ , and the difference in porewater concentration of the solute, ∂C_i (g m⁻³), across the sediment depth, ∂x (m); an estimate of the benthic dissolved trace metal fluxes can be obtained.

$$J_i = -\phi D_s^i \left(\frac{\partial C_i}{\partial x} \right) \quad 1.3.$$

According to Ullman and Aller (1982) the value of θ^2 can be estimated from Equation 1.4.

$$\theta^2 = \phi F \quad 1.4.$$

$$D_s^i = \frac{D_o^i}{\theta^2} \quad 1.5.$$

where , D_s^i is the bulk sediment diffusion coefficient ($m^2 s^{-1}$), D_o^i is the free solution diffusion coefficient of the solute ($m^2 s^{-1}$), and θ^2 , the geometric tortuosity. Values of the formation resistivity factor ($F = R_s/R_w$, where R_s and R_w , are the electrical resistivities of the saturated bulk sediment and the interstitial water, respectively) for coastal sediments are given by Ullman and Aller (1982) and typically range between 1.2 and 2.0 to a depth of 5cm in muddy sediment. Substitution of Equation 1.4. into Equation 1.5. and subsequent substitution of the modified Equation 1.5. into Equation 1.3. gives the following -

$$J_i = -\frac{D_o^i}{F} \left(\frac{\partial C_i}{\partial x} \right) \quad 1.6.$$

Equation 1.6. can be used to give a first estimate of the trace metal benthic fluxes across the sediment-water interface.

The geochemical alteration of particulate matter has a number of important considerations for trace metal distribution (Shaw *et al*, 1990). The redox condition will affect redox sensitive metals and the resultant changes to the trace metal speciation can affect their phase associations. As previously mentioned the two most important metals to be affected are Fe and Mn, other trace metals are readily associated with Fe and Mn oxides (Hem, 1978; Hem *et al*, 1989; Klinkhammer *et al*, 1982; Balistrieri and Murray, 1986). Consequently, the dissolution and precipitation caused by the alteration of the oxidation state of Fe and Mn will release and concentrate trace metals on the particle as a function of geochemical or diagenetic alterations (Duchart *et al*, 1973; Shaw *et al*, 1990; Gerringa, 1991). The release of trace metals into the dissolved phase and/or porewaters can cause fluxes of these trace metals from the sediment-water interface into the overlaying water. Resuspension of the upper surface of the sediment containing diagenetically mobilised trace metals will alter the particulate trace metal burden of the water column. Benthic fluxes will contribute to the trace metal burden of the overlaying water, and are subject to industrial inputs possibly causing continual pollution problems in the future (Kitts *et al*, 1994).

1.4.3. Particle Tracing Techniques: $^{206}/^{207}\text{Pb}$ isotopic ratio.

As previously mentioned in Section 1.4.2. the characteristics and composition of particles can depend on their source. The use of $^{206}/^{207}\text{Pb}$ isotopic ratio provides a convenient method of distinguishing between natural and anthropogenic modified particles (providing they are contaminated with Pb), Williams *et al* (1994). Other chemical tracers have been used such as Nb (Grant and Middleton, 1990) as a marker for TiO_2 processing effluent, but this is only practical in a limited number of analyses and situations.

Australia imports 79% of the lead into Britain (predominantly as bullion, 180,000 tonnes), one of its principal uses is as a petrol additive (Figure 1.6.). During the combustion of leaded petrol, lead is released as an aerosol into the environment to be deposited in the local environs. The lead will also undergo long range aeolian transport and has been found in some of the most remote regions of the earth (Chester *et al*, 1983, Kersten *et al*, 1991a, Rosman *et al*, 1993). After deposition, lead can be washed and removed by precipitation (the precipitation itself may also contain aeolian lead) via normal weathering processes into the local sewage industry, ultimately to be transported to estuaries and hence into coastal waters. Additionally, coastal waters will also gain aeolian inputs directly, but as a more diffuse input (Kersten *et al*, 1992). Imports of Australian and Canadian lead have low $^{206}/^{207}\text{Pb}$ isotopic ratio compared with naturally weathered lead (e.g. pre-industrial lead, Holderness Cliffs, $^{206}/^{207}\text{Pb}$ isotopic ratio: 1.23). These differences can be used to differentiate between anthropogenic and naturally occurring lead. Table 1.8. illustrates the variation of the $^{206}/^{207}\text{Pb}$ isotopic ratio due to the mixing of natural lead with anthropogenic lead in the environment. In addition, as a representation of available $^{206}/^{207}\text{Pb}$ isotopic ratio data, it highlights the small amount of data currently available for the UK. It should also be noted that although the dominant source of lead in the environment is from petrol additives, local anomalies may be present due to industrial effluents e.g. Albright and Wilson ($^{206}/^{207}\text{Pb}$ isotopic ratio: 1.84). The phosphate rock processed is enriched in U which is a parent of Pb ($^{206}/^{207}\text{Pb}$ isotopic ratio: 2.70).

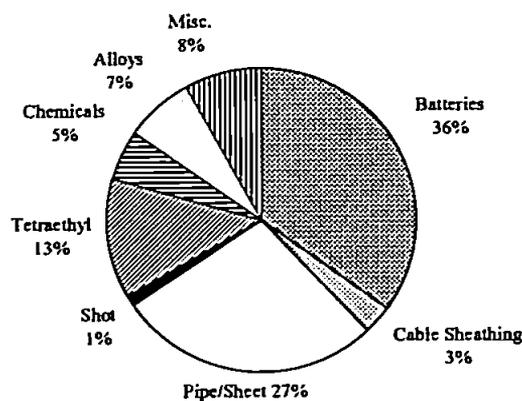


Figure 1.6. Principal use of lead during 1992, in the UK

Table 1.8. Comparison of $^{206}/^{207}\text{Pb}$ isotopic ratios obtained from different sources.

| Sample | $^{206}/^{207}\text{Pb}$ | Sample | $^{206}/^{207}\text{Pb}$ |
|---------------------------------|---------------------------------------|-------------------------------|--------------------------|
| Broken Hill, Australia, ore | 1.04 ^b | British Columbia, Canada, ore | 1.07 ^b |
| BP Petrol | 1.07 ^c | | |
| London, Air | 1.13 ^d , 1.10 ^e | Paris air | 1.10 ^f |
| Arctic, Air | 1.16 ^g | Rainwater, Scotland | 1.08 - 1.12 ^a |
| Dogger Bank | 1.18 ^b | Humber | 1.17 ^b |
| Thames | 1.17 ^b | Weser | 1.17 ^b |
| Elbe | 1.17 ^b | Rhine | 1.17 ^b |
| Rhone | 1.15 ^f | Loire | 1.15 ^b |
| Seine | 1.15 ^f | Gironde | 1.18 ^b |
| Sediment, Swansea Bay | 1.14 ^d | Surface soils, Scotland | 1.15 - 1.16 ^a |
| pre-industrial sediment, France | 1.20 ^f | | |

a Bacon *et al*, 1992; b Kersten *et al*, 1992; c Kersten pers. comm.; d Hamilton and Clifton, 1979; e Chow *et al*, 1975; f Elbaz-Poulichet *et al*, 1986; g Sturges and Barrie, 1989a.

1.4.4. Modelling Approaches to Sediment Transport.

The modelling of fine sediment transport in relation to the distribution of trace metals (referred here as a Fine Sediment Transport Model for Metals, FISTRAMM) poses many problems which have not been fully addressed. Classically FISTRAMMs have been based on mud transport models which have included a chemical component. This chemical component in FISTRAMMs can vary due to i) no consideration for trace metal removal

(Prandle *et al*, 1993), ii) simple uptake of the trace metal onto the particle using a constant K_D (ECoS, Plymsolve, 1991), and iii) a more complex approach of adsorption and desorption of the trace metal and removal during the settling of the particle (NORPOL, Murphy and Odd, 1993). However, each model can only be as good as the information currently available and currently a number of issues have not been addressed:

- i. Variation of the speciation of dissolved trace metals, particularly with regard to the fate of industrial discharges e.g. trace metals from the highly acidic TiO_2 processing discharge in the Humber mouth, will undergo a variety of speciation changes each having a different reactivity towards the resident particle population.
- ii. Variation in particle composition due to anthropogenic inputs and the mixing of particle populations from different source regions and the subsequent effect the mixing will have on the partitioning of trace metals within this region e.g. whether the mixing of Holderness particles with Humber particles in the Humber plume is an additive process.
- iii. The reactivity of trace metals towards marine particles is not instantaneous and hence, the residence time that the trace metals are exposed to the particle population is an important factor to whether equilibrium is reached.
- iv. Removal of particulate metals can occur by settling of the suspended particles to the sediment bed, but each metal may associate with a different particle populations depending on their composition and hence may exhibit dissimilar settling velocities to the bulk suspended particles.
- v. Once settled these metals may be resuspended and hence contribute further to the particulate burden of the water column. If this resuspension is coincident with different water conditions (e.g. change in the tide) the resuspended particulate metals may undergo sorption processes.
- vi. After deposition the particulate trace metals will participate in diagenetic processes and could flux as a dissolved species into the overlying water column and undergo sorption processes.
- vii. Benthic biota can cause resuspension of particulate metals in areas not normally associated with physical resuspension events (e.g. tidal).

To include all of these issues in a single suitable model would be unreasonable but to consider an amalgamation of individual models (tidal, mud transport, metal..... models)

each requiring the input from one another would provide a composite model to deal with such complex matters (Huthnance *et al*, 1993).

1.5. Aims of the Study.

The aim of this study was to examine the long range transport of particulate trace metals in coastal waters thereby assisting the development of predictive models. Some of the issues highlighted in Section 1.4.4. have been used as the basis to assist in the development of a fine sediment transport model for trace metals. To achieve this aim, trace metals were examined spatially and temporally in the Irish Sea and North Sea. Sampling occurred during multi-disciplinary collaborative work aboard *R.R.S. Challenger*. At selective sites during these cruises samples were used to examine geochemical processes. Particular emphasis was placed on the sorption of trace metals with suspended particulate matter and their association with particles of different settling characteristics. The culmination of this dissertation is to produce a conceptual model for a fine sediment transport model for metals (FISTRAMM) in coastal waters.

Chapter 2 - Sampling and Methodology.

Chapter 2 - Sampling and Methodology.

2.1. Sample Collection.

2.1.1. Overview of Sampling Strategy.

Spatial and temporal samples were collected during three multi-disciplinary cruises aboard *R.R.S. Challenger* (Table 2.1. and Figure 2.1.). All cruises occurred during winter, consequently the suspended particulate matter (SPM) was primarily lithogenic in character. Sample collection and treatment were kept consistent, thereby allowing direct comparisons to be made between the Irish Sea and the North Sea study areas.

Table 2.1. Details of scientific cruises aboard *R.R.S. Challenger* (Figure 2.1.).

| Cruise | Date | Location |
|-----------|-----------------------|----------------------------------|
| CH88A/92 | 20 Jan. - 4 Feb. 1992 | North Eastern Irish Sea |
| CH99/92 | 6 - 21 Dec. 1992 | North Sea - LOIS RACS study area |
| CH108A/93 | 9 - 24 Nov. 1993 | North Sea - LOIS RACS study area |

The primary objective of cruise CH88A/92 was to investigate sediment resuspension processes in the coastal waters of the north eastern Irish Sea. Cruise CH99/92 was exploratory in nature, its objective being to provide preliminary data from the LOIS RACS study area. The first official cruise of the LOIS RACS project was CH108A/93.

The objective of the chemistry component of each cruise, was the examination of the sediment - water exchange processes and their impact on long range transport of pollutant trace metals. This was achieved by temporal and spatial collection of SPM and sediments, and in the case of CH88A/92 sediment porewaters. The following experiments and analyses were performed to understand the factors influencing the long range transport of pollutants:

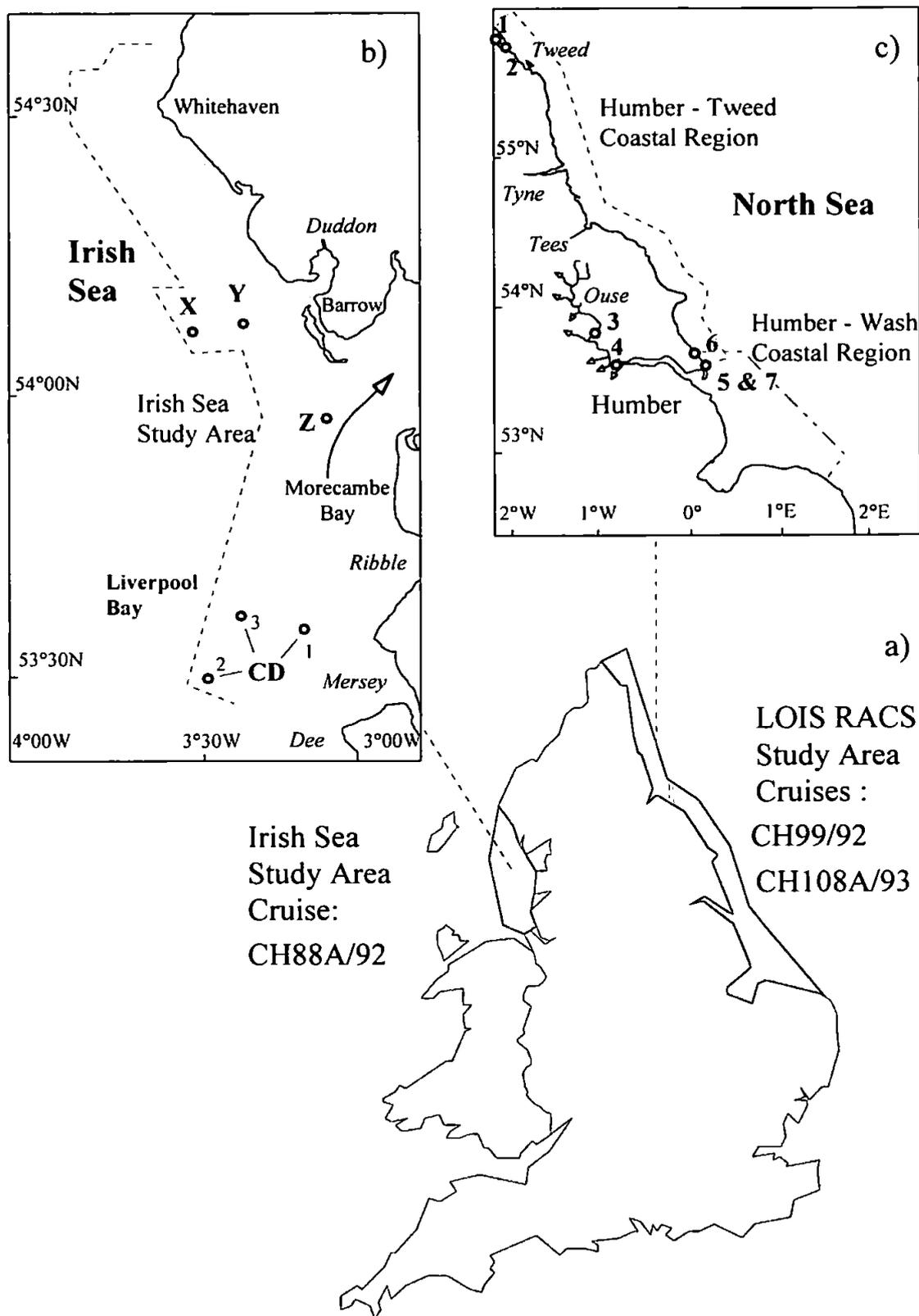


Figure 2.1. Study areas for cruises CH88A/92, CH99/92 and CH108A/93. a) General overview of the two study areas, b) Irish Sea study area - showing sites X, Y, Z and CD (CD consists of three widely spaced sampling points), no trace metal sampling occurred at site X and c) LOIS RACS study area - showing the two coastal regions sampled during both cruises, numbers indicating additional land-based sampling points (Table 2.2.)

- i) analysis of trace metals with contrasting geochemistries.
- ii) measurement of the $^{206}/^{207}\text{Pb}$ stable isotopic ratio, to discern the association of anthropogenic components with particulate matter.
- iii) unique settling experiments, investigating the settling characteristics of particulate trace metals and its influence on pollutant advection.
- iv) examination of the sorptive characteristics of selected SPM samples, by the selective partitioning of radionuclides.

After collection, samples were handled within a containerised clean laboratory, situated on the aft deck of *R.R.S. Challenger* (Morley *et al*, 1988). Prior to, and throughout each cruise, the laboratory was cleaned and the Milli-Q system of ultra pure water was made operational.

2.1.2. Suspended Particulate Matter.

During CH88A/92 the majority of the suspended particulate matter (SPM) samples, were obtained during tidal cycles at sites Y and Z, with additional sampling occurring at site CD (Figure 2.1a.). Water samples were primarily collected near the bottom of the water column, and additional samples were taken from the top and middle of the water column, to coincide with settling velocity tube (SVT) experiments. Samples of SPM were obtained from the near surface water of the Humber Estuary and Humber Plume region during CH99/92.

Samples of SPM were acquired during CTD profiling, using acid washed 10 l Go - Flo (General Oceanics) water bottles, attached to the CTD rosette. Pressure valves were set to allow the bottle to open at 10m depth, to minimise contamination during deployment and by the surface microlayer. After recovery the Go - Flo bottles were removed from the CTD rosette and prior to fixing to lugs on the laboratory's exterior, the samples were homogenised by inverting the bottles. The bottles were rigged to allow pressure filtration of the sample from within the laboratory (Morley *et al*, 1988). The filters were pre-cleaned in 1M HCl (AristaR, BDH) for 24 h then rinsed with ultra pure water (Milli - Q), and weighed after drying. Filters were loaded and removed from cleaned Teflon filter presses,

inside a laminar flow hood. The samples were filtered (0.4 μ m poresize; \varnothing 142mm, Nuclepore) to give loadings of several tens of mg of material. After filtration the SPM was rinsed with <20 ml of ultra pure water to remove any salts. Spare filters were retained as blanks. The volume filtered was recorded to allow the concentration of SPM to be calculated. The filters were stored at -18 °C prior to analysis.

2.1.3. Sampling of Sediments.

Three methods of sediment sampling were employed, *viz.* Day grab, box core and multicore, depending on the sample requirements. The Day grab was used to obtain surface sediment samples. A surface scrape of the sediment was taken using a plastic spatula and stored in a plastic container at - 18 °C until required for analysis.

Sediment samples retrieved by box coring were used to obtain sediment depth profiles. Providing the sediment surface of the box core was undisturbed, the overlying water was siphoned until approximately a 5 cm depth remained. The redox potential of the first 10cm was measured by insertion of an Eh probe into the sediment surface. The data obtained (Rowden pers. comm.) were latter converted into values of electron activity ($p\epsilon$) using Equation 1.2. A number of limitations should be borne in mind when using measurements of the electron activity in this manner. Oxygen can be introduced into the deep sediment layer by the insertion of the probe thereby perturbing the oxidation state near the probe. The relationship between theoretical and experimental redox potential is not ideal due to the variability in nature of the redox state of the metals and particle types. Hence, the measured redox potential will only provide an indication of the likely geochemical processes occurring.

A pre-cleaned clear plastic tube was inserted into the sediment surface. The open end was sealed with a plastic cap, and the surrounding sediment was removed to reveal the base of the tube, which was sealed with another plastic cap. The sediment core was immediately removed for processing and a visual description of the core was recorded. Cores were also obtained opportunistically during test runs of a multicorer, owned by Dunstaffnage Laboratory (CH99/92). The considerations were the same as for box cores, except that the sediment had already been sampled using a plastic tube.

Sediment cores taken during CH88A/92 were handled within a 'white spot' N₂ atmosphere, and the O₂ content (< 0.5 %) of the glove bag was monitored to ensure that the redox integrity was maintained for porewater extraction (Colley, 1992).

The sediment was extruded by applying a piston to the base of the core. The overlying water was removed and the sediment core was sectioned into suitable intervals (normally 1cm intervals for the first 10cm then 2cm intervals for the remainder of the core). The final interval in contact with the atmosphere and the piston, was discarded. The sediment slices were transferred to clean centrifuge tubes and centrifuged at 3000 rpm for 60 min at 7°C (CH88A/92), 3000 rpm for 10 min at 6°C (CH99/92). The supernatant was discarded if the porewaters were not required (CH99/92). Otherwise, the porewaters were drawn into acid-washed plastic syringes. Filter holders containing 5µm and 0.45µm poresize cellulose acetate filters (MiniSart filters, Sartorius) were attached in line to the end of the syringe. The porewaters were filtered directly into acid-cleaned plastic sample containers, volumes typically ranging from 5 - 25ml. The porewaters were immediately acidified to approximately 1% v/v with conc. HNO₃ (AristaR, BDH).

2.1.4. Sampling using Settling Velocity Tubes.

Figure 2.2. illustrates the main components of the SVT. The tube was designed at the University of Wales, Bangor (see Section 5.1.) (Jago *et al*, In preparation) and is a bottom withdraw tube of the type described by Owen (1976). Before deployment the SVT was cocked by drawing the tube back, against the tension of elastic strings, until it locked into the open position, and then it was lowered horizontally to the required water depth. Plate 2.1. illustrates two SVT's being prepared for deployment. The length of the tube is approximately 1m. In Plate 2.1. adjustments are being made to the trigger mechanism prior to cocking the SVT. The instrument can be triggered by two methods, depending on the sample depth. For surface samples, tension is manually applied to the trigger line which releases the tube. For near bottom samples, the line is kept taut by a weight. As the weight approaches the sea bed, the tension in the line is released - firing the tube. After firing, the tube closes and seals against the base plate, trapping a horizontal section of the



Plate 2.1. Two SVT's being prepared for deployment.

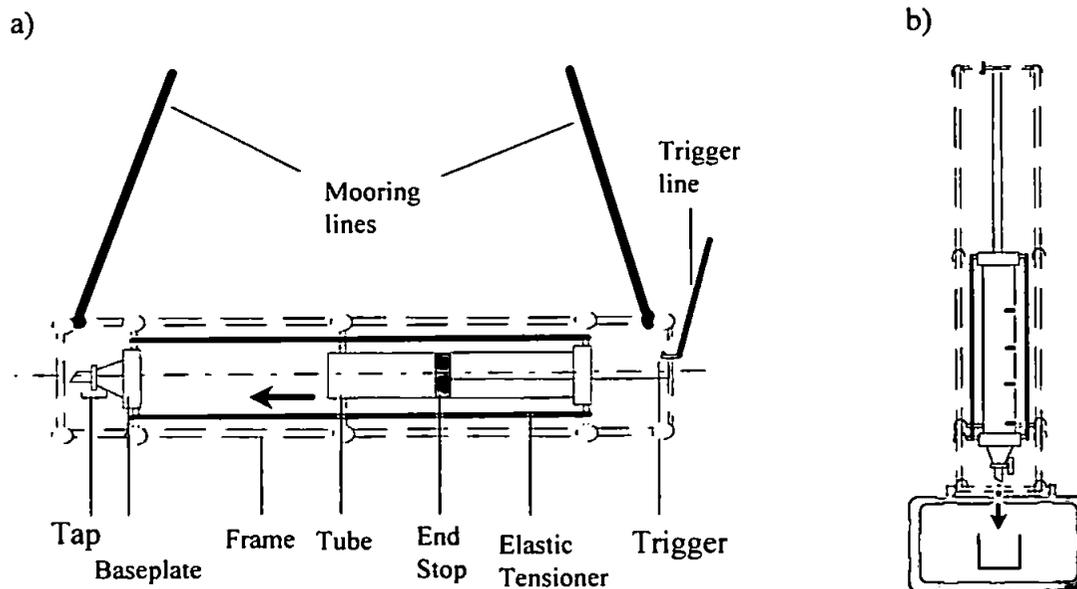


Figure 2.2. Schematic representation of a Settling Velocity Tube (SVT). a) Diagram illustrates the SVT in the process of sampling, b) SVT in vertical position resting on a stand at the start of an experiment (thermal jacket not shown). A sample was taken by raising the container to the tap (through the open framed stand) and opening the tap.

water column (Figure 2.2a.). Immediately following sampling, the SVT was kept horizontal and the sample homogenised by raising either end of the tube and by rotation. The tube was placed in a frame in the vertical position, with the tap at the bottom and a timer was immediately started (Figure 2.2b.). The tube was encased by an insulating jacket, minimising the thermal effects on settling measurements. At selected time intervals (5, 20, 80 and 280 min) 1 l samples were drawn off. The final fraction was retained as the residual fraction (>280 min). Each fraction was immediately filtered under gravity through acid cleaned filters (0.4 μ m poresize; \varnothing 142mm, Nuclepore), held in Teflon filter presses. The samples were stored at -18°C prior to analysis.

2.1.5. Additional Samples.

Prior to cruises CH99/92 and CH108A/93 shore based samples were collected to complement sampling during these respective cruises.

The riverine and marine samples were collected using acid cleaned carboys, which were rinsed with the sample several times before taking the final sample. Immediately on joining the ship, the samples were filtered under gravity as described for the SVT samples.

Samples of Holderness Cliff material were taken using a Teflon spatula and were immediately sealed in secure plastic bags. On joining the ship these samples were frozen at -18°C until required for analysis.

Table 2.2. Additional samples collected prior to cruises CH99/92 and CH108A/93.

| Cruise | Sample Description | Site | Fig. 2.1.c Ref. | Position |
|-----------|--------------------|-----------------------|-----------------|-------------------------|
| CH99/92 | River end member | Border Bridge, Tweed | 1 | 55° 46'.4 N 02° 00'.7 W |
| | | Union Bridge, Tweed | 2 | 55° 45'.2 N 02° 06'.3 W |
| | | Naburn, Ouse | 3 | 53° 54'.3 N 01° 05'.1 W |
| | Sea water | Boothferry, Ouse | 4 | 53° 43'.8 N 00° 53'.2 W |
| | | Easington, Holderness | 5 | 53° 38'.6 N 00° 07'.1 E |
| CH108A/93 | Cliff Material | Moat Farm, Holderness | 6 | 53° 47'.9 N 00° 04'.2 W |
| | | Easington, Holderness | 7 | 53° 38'.6 N 00° 07'.1 E |

2.1.6. Particle Sizing.

During cruises CH88A/92 and CH108A/93 selected SPM samples were examined using a Malvern Laser Particle Sizer Model 2200 (Bale *et al*, 1984). The Malvern Laser Particle Sizer uses a 3mW laser ($\lambda = 632.8\text{nm}$) and a 100mm (focal length) receiving lens giving measurements in the size ranges 1.9-188.0 μm for 15 component size bands (Table 5.3). Calibration was achieved using glass spheres ($56.8 \pm 4.7 \mu\text{m}$, Polysciences Inc.). Results were considered acceptable for an obscuration of >0.01 and a log error of <5 (Bale pers comm.).

2.2. Partition Experiments.

2.2.1. *Experimental Procedure.*

Radiochemical experiments were carried out during cruises CH88A/92 and CH99/92 to examine the extent of metal uptake by marine SPM. The radiotracers were prepared as a cocktail from original stock solutions of a range of γ -emitting metals of varying geochemistries (^{109}Cd , ^{51}Cr , ^{137}Cs , ^{59}Fe , ^{54}Mn and ^{65}Zn in 1M HCl). The cocktail was freshly prepared prior to each cruise. Spikes of the cocktail were added, to 50ml samples retained in plastic reaction vessels. Control of pH in the reactors was achieved by addition of weak alkali solution. Solutions were kept at ambient seawater temperature (typically 6 - 7°C) by retaining the reactors in a flow cell connected to the non-toxic supply. Samples were prepared for geometric correction (i.e. different geometries of dissolved and particulates phases) by spiking pre-filtered seawater and a filter paper with the cocktail.

Three types of experiments were undertaken during CH88A/92 - 5 day K_D values, kinetic studies and K_D values of fractions obtained from the SVT sampling. Similarly during CH99/92, kinetic experiments were carried out and also performed on fractions from the Humber SVT experiment. Additional mixing experiments were performed during CH99/92. All radiochemistry was performed in an isolated area in the interior of the containerised clean laboratory on the ship. All radiochemical work was performed within the guidelines for their safe use on NERC vessels. This included pre- and post-monitoring of the radioactivity background.

2.2.2. *Five day K_D Values.*

Duplicate sub-samples (50mls) taken from the surface, middle and bottom of the water column at site Z, were spiked with 20 μl of radiotracer cocktail. The solutions were incubated for five days with frequent stirring, pH and O_2 contents were monitored throughout (see Table 2.3) the incubation period. After sampling, the solutions from each of the experiments were immediately filtered through pre-weighed filters (0.45 μm , Millipore) using a microfiltration apparatus. The filters and filtrates were retained for later analysis.

Table 2.3. Conditions for five day kinetic experiments.

| Cruise | Site | Sample | Depth (m) | Salinity $\times 10^{-3}$ | Temperature ($^{\circ}\text{C}$) | pH | O ₂ (%) |
|--------|------|---------|-----------|---------------------------|------------------------------------|-----|--------------------|
| CH88A | Z | surface | 2.3 | 32.3 | 6.4 | 7.6 | 100 |
| | | middle | 10.4 | 32.5 | 6.5 | 7.6 | 100 |
| | | bottom | 18.4 | 32.9 | 6.7 | 7.6 | 100 |

2.2.3. Kinetic Experiment.

Trace metal reactivity of Irish Sea particles was examined, by spiking a continuously stirred bulk sample of SPM from the bottom of the water column, at sites Y and Z (Table 2.4.). Periodically 50ml were removed for filtration as described above and five individual 50ml samples were spiked with 25 μl of cocktail during CH99/92 and reactors were removed at suitable intervals for filtration.

Table 2.4. Conditions for kinetic experiments.

| Cruise | CH88A/92 | CH88A/92 | CH99/92 | CH99/92 |
|------------------------------------|----------|----------|------------|--------------|
| Location | Site Y | Site Z | Holderness | Humber Mouth |
| Duration (days) | 5 | 11.5 | 5 | 5 |
| spike volume (μl) | 200 | 150 | 125 | 125 |
| Sample volume (ml) | 400 | 250 | 250 | 250 |
| Salinity | 33.4 | 32.9 | 33.4 | 32.9 |
| Temperature ($^{\circ}\text{C}$) | 7.78 | 6.68 | 7.8 | 6.7 |
| pH | 7.4 | 7.97 | 7.7 | 7.7 |
| O ₂ (%) | 100 | 100 | 100 | 100 |

2.2.4. Settling Fraction K_D Values.

Novel partitioning experiments were performed on the ship using sub-samples from the SVT fractions. From each fraction, 50ml samples were taken and treated as previously

described to establish 5 day K_D s. This work allowed the examination of radiotracer uptake of different particle settling fractions.

2.2.5. *Mixing Experiments.*

The prime interest during CH99/92 was the reactivity and mixing between Humber and Holderness particles within the Humber plume. To mimic this situation, a mixing experiment was devised, where aliquots of Holderness and Humber samples were combined in varying proportions to produce a mixing series (% Humber material - 0, 20, 40, 60, 80, 100). To each of these 50ml solutions a 25 μ l spike of the cocktail was added and the solutions were allowed to incubate for 5 days.

Immediately on returning from the cruises, measurements of the radioactive filters and filtrates were undertaken. Samples were counted for 1000s on a high purity Ge crystal coaxial detector connected to a Canberra Series 80 Multichannel Analyser. The counts were corrected for the different geometries of filter pads and solutions. Wall adsorption was found to be negligible (Turner *et al*, 1992b; Turner and Millward, 1994).

2.3. Sample Treatment and Analysis.

2.3.1. *Selection of Digest for Determining Particulate Trace Metals in Particles.*

The interpretation of particulate metal data is strongly dependent on the method of sample treatment prior to analysis. Many papers have examined the effects of different sample digests (Chester and Hughes, 1967; Tessier *et al*, 1979; Luoma and Bryan, 1981; Kersten and Förstner, 1986; van Valin and Morse, 1982; Tipping *et al*, 1985; Rule and Alden, 1992.). Each extraction procedure examines an operationally defined fraction of trace metals (except for total digestion) which have been loosely associated with geochemical phases (see Martin *et al*, 1987 and references therein).

The extraction procedure chosen to extract the samples for this study, would need to be consistent for samples, which consists of SPM and sediments. The samples to be extracted would be -

- i) predominantly oxidic in nature
- ii) oxide coated
- iii) have varying anthropogenic contents
- iv) have variable organic content
- v) have variable texture

The use of 1M HCl was chosen for a number of reasons:-

- i) it is a single reagent method, which could minimise the potential for contamination
- ii) it has been successfully used for the North Sea (Turner, 1990; Tappin *et al*, 1995)
- iii) it has been suggested that it is a reliable and consistent method for assessing the bioavailability of trace metals (Luoma, 1983)
- iv) it has been used successfully in stable lead isotopic ratio determinations (Chow and Patterson, 1962; Ng and Patterson, 1982; Hopper *et al*; 1991, Williams *et al*, 1994; Millward *et al*; 1994)

Although extraction procedures have been well described for trace metals, the dependence of stable lead isotopic ratios (Sections 2.4.3. and 1.5.) on digest methodology is unknown. A sequential extraction experiment was devised to examine the effect of extractants on the $^{206}/^{207}\text{Pb}$ isotopic ratio. Standard sediments (MESS-1, BCSS-1) and two Irish sea sediments (GW9 - Offshore of the Esk Estuary; Z 0-1 - Site Z) were sequentially and non sequentially digested with 25% HOAc, 1M HCl, 1M HNO₃ and HF with *aqua regia* (data for site Z is shown in Figure 2.3.).

The non - sequential digestion examined the behaviour of each extractant on the sediment. It can be seen from Figure 2.3. that HOAc does not remove a large proportion of the lead (~30 - 50%). The majority of the Pb (~80%) was removed by HCl (% Pb extracted) and ~20% of the Pb remained in the sample matrix, which could be extracted by HNO₃ and HF.

The sequential extraction provides an insight to the specific phase being attacked by the digest e.g. the sequential HF leach will only release metals held in the particle matrix. There is a negligible difference for extraction of Pb between the HCl digest and the HNO₃ digest. The matrix bound Pb is removed only by using HF. The Pb extracted from the matrix is characterised by a high ^{206/207}Pb isotopic ratio. Thus, the bulk of the lead present is extracted by HCl and is of low isotopic ratio i.e. anthropogenic lead.

These results suggest that the anthropogenic lead was surface adsorbed onto the sediment. Extraction by HNO₃ and HF will remove the remaining lead of high isotopic ratio i.e. natural background lead incorporated in the matrix lattice. However, the overall effect of using HNO₃ or HF is a relatively small increase in the isotopic ratio, due to the high percentage of non radiogenic lead in the samples.

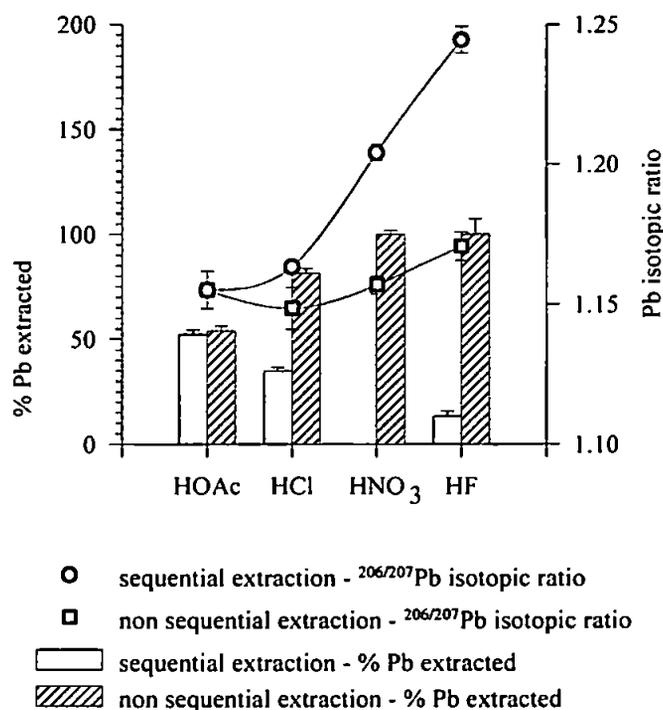


Figure 2.3. Data from sequential and individual (non-sequential) sediment extraction experiments at site Z, Irish Sea. The graphs show that only ~20% of the Pb is associated with the matrix and is characterised by a high ^{206/207}Pb isotopic ratio. Concentrations have been normalised to the HF value for the non-sequential extractions and normalised to the sum of the sequential digests (additivity has been assumed).

The results of HF digests of MESS-1 and BCSS-1 are given in Table 2.5 and show reasonable agreement with the certified values. Analysis of the standard sediments required significant alteration to the optimised GFAA temperature programs obtained for the sediment samples, collected from the Irish and North Sea. This suggests that the matrix of the standard sediments are different to that of the sediments collected from British coastal waters.

Table 2.5. Tabulated data for the total digestion of standard sediments, indicated are the certified values (National Research Council, Canada, 1987) and measured values.

| | | Fe* (mg g ⁻¹) | Mn (µg g ⁻¹) | Pb (µg g ⁻¹) | Cd (µg g ⁻¹) | Cu (µg g ⁻¹) |
|--------|-----------|------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| MESS-1 | Certified | 30.5 ± 1.8 | 513 ± 25 | 34.0 ± 6.1 | 0.59 ± 0.10 | 25.1 ± 3.8 |
| | Measured | 27.6 ± 0.6 | 438 ± 17 | 29.9 ± 0.2 | 0.51 ± 0.02 | 27.3 ± 0.6 |
| BCSS-1 | Certified | 32.9 ± 1.0 | 229 ± 15 | 22.7 ± 3.4 | 0.30 ± 0.10 | 18.5 ± 2.7 |
| | Measured | 29.4 ± 0.7 | 204 ± 16 | 19.9 ± 1.5 | 0.41 ± 0.07 | 16.0 ± 1.4 |

*Fe values have been converted from %Fe₂O₃ to mg/g.

Metals associated with sedimentary material are subject to the grain size effect (Ackermann *et al*, 1983), resulting in the coarse sediment components (of low metal content e.g. sand) giving significant variability during analysis. To reduce this variability a number of techniques have been employed:

- i) comparison of the metal concentration with non anthropogenically influenced elements e.g. Al, Li, Rb or Fe (Balls, 1986; Ridgeway and Price, 1987; Dehairs *et al*, 1989; Grant and Middleton, 1990; Loring, 1990; 1991)
- ii) size fraction determination, usually <63µm fraction which corresponds to sand - silt interface (Ackermann *et al*, 1983; Cauwet, 1987; Krumgalz, 1989; Turner *et al*, 1993; Morrissey *et al*, 1994)

The former technique is only suitable when complete digestion of the sample occurs. Separation of the < 63µm fraction can be performed in a number of ways. Dry sieving is not suitable, as the clay content tends to cause caking. Wet sieving can be performed with

or without dispersion. This was examined using sodium hexaphosphate as a dispersant, and the results are given in Table 2.6.

Dispersing the sediment leads to an enhanced desorption of metals, which is highlighted by the large change in isotopic ratio, from 1.214 to 1.153 in the filtrate. As previously discussed (Sections 1.5. and 2.3.1.1.) this decrease in isotopic ratio is indicative of the removal of surface bound anthropogenic lead.

Table 2.6. The effect of sediment dispersion on metal determination.

| Parameter | No dispersant | Dispersant |
|-------------------------------------|---------------|------------|
| % <63 | 4.9 | 7.5 |
| Fe (% desorbed) | 0.00 | 1.48 |
| Mn (% desorbed) | 0.00 | 0.27 |
| Zn (% desorbed) | 0.14 | 1.49 |
| Isotopic Ratio of filtrate solution | 1.214 | 1.153 |
| Isotopic Ratio of digest solution | 1.164 | 1.161 |

2.3.2. Treatment of Particulate Samples.

All equipment was acid cleaned prior to use, by soaking in detergent (Decon) for 24h, then rinsed with Milli-Q, 50% v/v HNO₃ for 24h, then rinsed with Milli-Q and soaked in 50% v/v HCl for a further 24h, and finally rinsed in Milli-Q and allowed to dry at room temperature under cover.

Filter samples were removed from storage and allowed to thaw at room temperature, in a laminar flow hood. The filters, with their associated SPM were weighed and immediately placed into acid cleaned Teflon beakers and 10ml of 1M HCl was added to the beakers. The beakers were covered and left for 24h in a laminar flow hood. The digests and aliquots (of 1M HCl, totalling 10ml) used to wash the beakers, were filtered. The filtrate was retained and only made up to 25ml in acid cleaned volumetric flasks immediately prior

to analysis. Procedural blanks (no filter) were performed for each batch of digestions. Filter blanks were also run with the samples.

Filtering for CH88A/92 SPM was achieved by withdrawing the digest into an acid washed plastic syringe, and then filtered directly into a volumetric flask using a syringe attached to a MiniSart Filter (0.45 μ m, cellulose acetate). Each filter was rinsed with 10ml of 1M HCl prior to use. This was considered sufficient to remove any filter contamination, but it was later found that the acid attacked the filter housing (see later discussion). Significant blank contamination was found for Cd and Zn, resulting from the filter housing. All further filtering was performed as described below.

The digest and washings for each sample were filtered under vacuum using an acid rinsed cellulose acetate membrane filter (0.45 μ m poresize; \varnothing 47mm, Sartorius). The filtrate was retained in a 100ml side arm flask and transferred to an acid cleaned 25ml volumetric flask. The side arm flask was rinsed and the washings were transferred to the volumetric flask. Samples taken from the settling tube experiments were treated in an identical manner.

As previously mentioned, problems were encountered with the use of MiniSart filters with 1M HCl. MiniSart are integral filters and holders, designed to attach to the end of a syringe. Only Zn and Cd results showed signs of contamination. To examine the extent of the contamination, duplicate MiniSart filters were sequentially eluted with aliquots of 1M HCl, and the resulting filtrates analysed for Zn and Cd. The weights of metals contained within each filtrate were determined and summed (Figure 2.4.). Initial rapid depletion of Cd and Zn was observed. However with greater volumes, Cd appeared to be released. A plot of the actual concentrations measured in each elutant volume is show in Figure 2.4c.), which shows the large release of Cd after the third aliquot has been filtered. The release of cadmium was assumed to be the result of the breakdown of the filter holder material, and that the initial release of Zn and Cd was due to the release of surface adsorbed metals. The average loading for the filters was 11mg of Zn and 0.7 mg of Cd. The duplicate samples used in this experiment, highlights the variable composition of the Minisarts, and consequently the initial flushing of filters with 1M HCl was underestimated, to compensate for the contamination problem. It is apparent from this experiment that even with the initial washing of the filters, the samples were heavily contaminated with Cd and the results for this metal have been omitted. The relative contamination due to Zn was less and

the results have been included, though caution should be applied. There was no evidence of possible contamination by other metals.

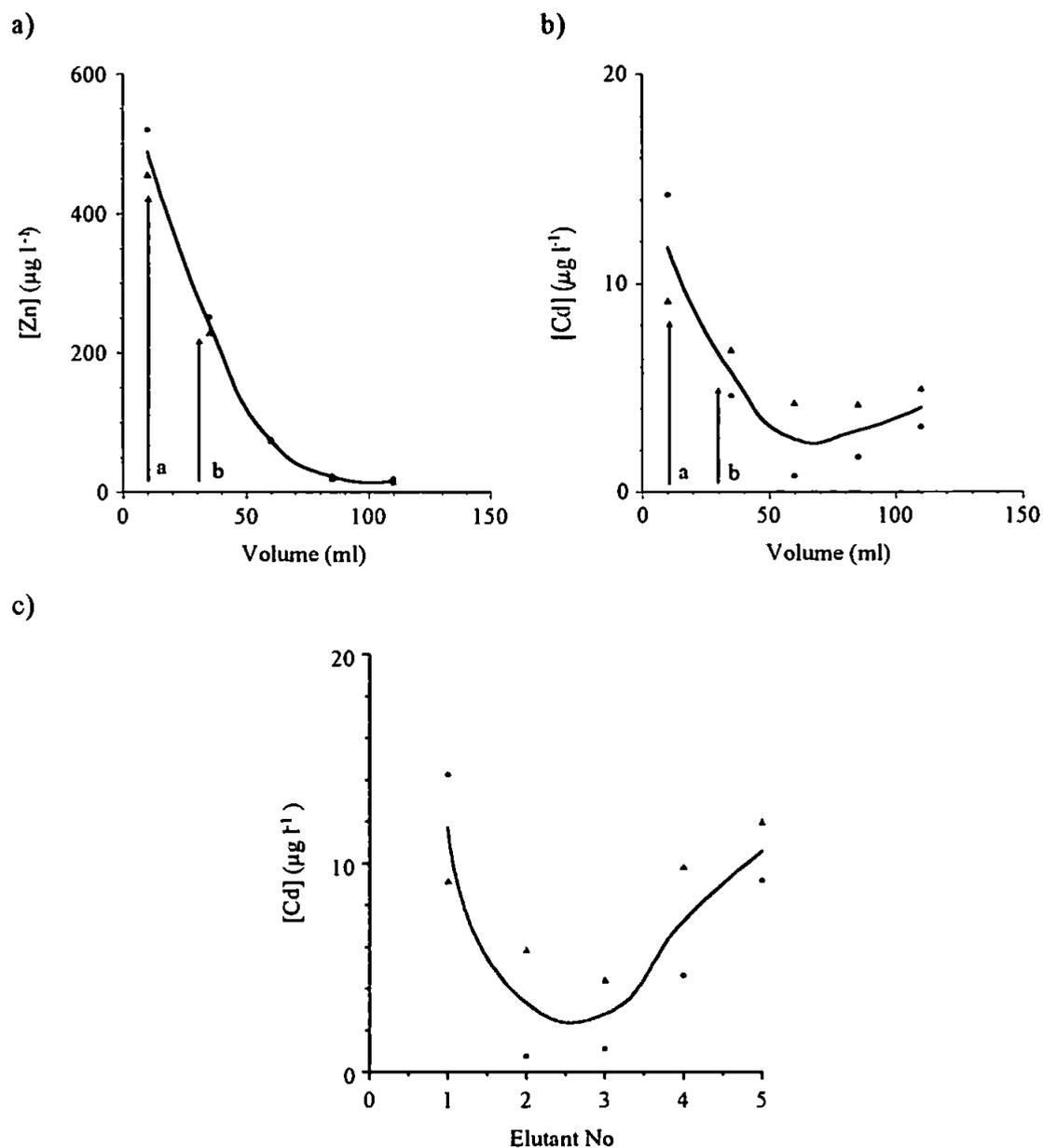


Figure 2.4. Graphs showing the change in concentrations of Zn and Cd after sequentially eluting two replicate MiniSart filters with 1M HCl. a) variations of Zn with elutant volume, b) variations of Cd with elutant volume and c) variation of Cd for each elutant. Line a indicates the volume used to pre-rinse the filter. Line b indicates the volume of sample passed after the rinse i.e. the sum of the rinse volume and the sample volume.

2.3.3. Treatment of Sediment Samples.

Sediment samples were allowed to thaw to room temperature. Handling of CH88A/92 core sediments was performed in a N₂ atmosphere. Small amounts of sediments were wet sieved through a 63µm Nylon sieve directly onto a preweighed acid washed cellulose acetate filter (0.45µm poresize; Ø47mm, Sartorius). The <63µm sediment fraction was obtained by applying a vacuum and then mechanically stirring the sediment sample in a Nylon sieve (Figure 2.5.). This set up has a number of advantages: i) the sediment is washed of salts, ii) separation of both >63µm and <63µm fraction occurs contiguously and iii) wet sieving inhibits caking of the sediment.

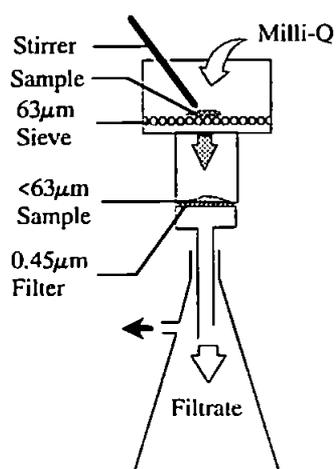


Figure 2.5. Arrangement of apparatus for isolation of <63µm sediment fraction.

After separation the >63µm fraction was washed from the surface of the sieve into a preweighed weighing boat. Both the <63µm and >63µm fraction were dried in an oven at 40°C, then weighed. Calculation of the % <63µm was made.

Approximately 0.3g of <63µm sediment was weighed directly into acid cleaned plastic digestion vessels. To each vessel 10ml of 1M HCl was added and the sample was stirred. The samples were left overnight inside a laminar flow hood, after ensuring effervescence (due to dissolution of carbonates), had finished. The sediment digests were then filtered as previously described for the SPM. Sediment digests were made up to 50ml volume.

2.4. Instrumentation.

The sample digests were analysed for Fe, Mn, Zn, Cd, Ca (insufficient sample volume did not allow analysis of Ca for CH88A/92 SPM), Co, Cu, Pb and ^{206/207}Pb stable isotopic. Measurements of Fe, Mn, Zn, and Ca were performed using flame atomic absorption spectroscopy (flame AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) was used to determine Cd, Co, Cu and Pb; GFAAS was also used to determine Pb and Cu in CH88A/92 porewaters by direct injection. Isotopic ratios were determined using inductively coupled mass spectrometry (ICP-MS). Full instrumental conditions are given in Appendix A.

2.4.1. Flame Atomic Absorption Spectroscopy (Flame AAS).

Metal analyses by flame AAS were obtained by linking the flame AAS (Instrumentation Laboratory (IL) 151 atomic absorption spectrophotometer in flame mode for CH88A/92 samples, GBC dual beam atomic absorption spectrophotometer in flame mode for all other samples) to a microcup (Berndt, 1981; Statham, 1983). The microcup allowed minimum sample volumes to be analysed (200µl), and this was particularly important for SPM digests due to the low sample volume of SPM digests.

The instrument was configured to read transient signals, usually achieved by increasing the read time, the signal was recorded using a chart recorder (IL 151 flame AAS) else digitally (GBC flame AAS). Peak height rather than peak area was used for absorbance measurements, as the peak area was sensitive to injection volume. The optimum aspiration rate was 4 ml min⁻¹, greater rates resulted in splashing of the sample during injection into the microcup, slower rates resulted in sensitivity loss due to peak broadening. The flame height was optimised (4.5 arbitrary units) for Fe, Mn and Zn. A slightly lower flame height was required (5.0 arbitrary units) for Ca.

An air-acetylene flame was used to determine Fe, Mn and Zn in digest solutions. Background correction (deuterium continuum) was required for Zn. A nitrous-acetylene flame was used to determine Ca, hence an ionisation buffer was required (samples were diluted with KCl solution to give a final buffer solution of 2000 mg l⁻¹). Analysis of Fe

and Mn in porewaters used a nitrous-acetylene flame to minimise salt interferences. Zn was undetectable in porewaters.

Table 2.7. Blank concentrations and detection limits for analysis by flame AAS.

| Cruise: | Blank values (mg l ⁻¹) | | | Detection limits (3σ, mg l ⁻¹) | | |
|------------------|------------------------------------|---------|-----------|--|---------|-----------|
| | CH88A/92 | CH99/92 | CH108A/93 | CH88A/92 | CH99/92 | CH108A/93 |
| SPM | | | | | | |
| Fe | 0.22 | 0.25 | 1.07 | 0.54 | 0.50 | 0.73 |
| Mn | 0.04 | 0.16 | 0.03 | 0.16 | 0.17 | 0.03 |
| Zn | 0.21 | 0.10 | 0.02 | 0.19 | 0.15 | 0.02 |
| Ca | - | 9.5 | 2.0 | - | 2.78 | 5.01 |
| Sediment | | | | | | |
| Fe | 0.86 | 1.05 | | 1.21 | 0.65 | |
| Mn | 0.08 | 0.05 | | 0.08 | 0.02 | |
| Zn | 0.04 | 0.01 | | 0.02 | 0.03 | |
| Ca | 5.07 | 0.93 | | 3.47 | 2.79 | |
| Porewater | | | | | | |
| Fe | 0.23 | | | 0.08 | | |
| Mn | 0.15 | | | 0.03 | | |

Blank values for SPM were filter blanks, whereas for sediment and porewaters procedural blanks were used.

The detection limits for flame AAS are given in Table 2.7. All were typically <10% of the sample measurement. Samples were reanalysed when either the correlation coefficient for the calibration, of four standards, was < 0.995, or if the sample relative standard deviation was >10%.

2.4.2. Graphite Furnace Atomic Absorption Spectroscopy (GFAAS).

Determination of marine samples by GFAAS is a more complex procedure than by flame AAS, as interferences are often caused by the sample matrix (Sturgeon, 1989). Reduction or elimination of these interferences, are achieved by the appropriate use of matrix modifiers (Tsalev *et al*, 1990) and optimisation of the GFAAS temperature program. These considerations were applied to each different metal and matrix analysed.

Because of matrix interferences, all GFAAS determinations were performed using method of additions calibrations and with background correction. The GFAAS used was a Perkin Elmer 4100ZL with Zeeman background correction connected to a Perkin Elmer AS-70 autosampler. Pyrolytically coated traverse heated graphite tubes, with an integral pyrolytic carbon platform were used throughout.

Identification of acceptable matrix modifiers was obtained by trial and error, based on previous experience. It was found that for nearly all determinations, matrix modification using Pd (500 mg l⁻¹ Pd with 1% NH₂OH.HCl in 1% HNO₃) was suitable (Schlemmer and Welz, 1986). High purity (99.999 %) Pd wire was dissolved in conc. HNO₃, and the addition of NH₂OH.HCl to a suitable dilution of the bulk Pd solution gave the modifier solution. The use of NH₂OH.HCl as a reducing agent for Pd was found to give enhanced sensitivity compared to a combination of Pd with MgNO₃ (as recommended by Perkin Elmer, 1991). For Cd determinations a NH₄H₂PO₄ modifier (2000 mg l⁻¹ PO₄ + 10 mg l⁻¹ MgNO₃) was used and an ammonium oxalate (3%) modifier was used for determinations of Pb in porewaters.

Optimisation of the temperature program is a complex process, often requiring the skill of the operator to interpret the changes in absorbance peak profiles. However, after checking the sample has dried smoothly, optimisation was achieved by cycling through the char and atomisation temperatures to give optimisation curves (see Figure 2.6). Ramp and hold times for the char and atomisation temperature were optimised, but were found to have a minimal effect on the overall optimisation. By a combination of the peak profile and the optimisation curves, a suitable temperature program was obtained.

Optimisation was performed for each metal determination in SPM, sediment and porewaters. Particular mention should be made of the difficulties associated with direct injection analysis of porewaters. Porewaters contain a high salt concentration, therefore problems were encountered with crystallisation of salt at the edges of the graphite tube, which had to be cleaned regularly. Optimisation of saline solutions are problematical, as NaCl has a broad band spectrum, and combined with the high salt content, produces a large background interference. Char temperatures in excess of 1000°C are required to

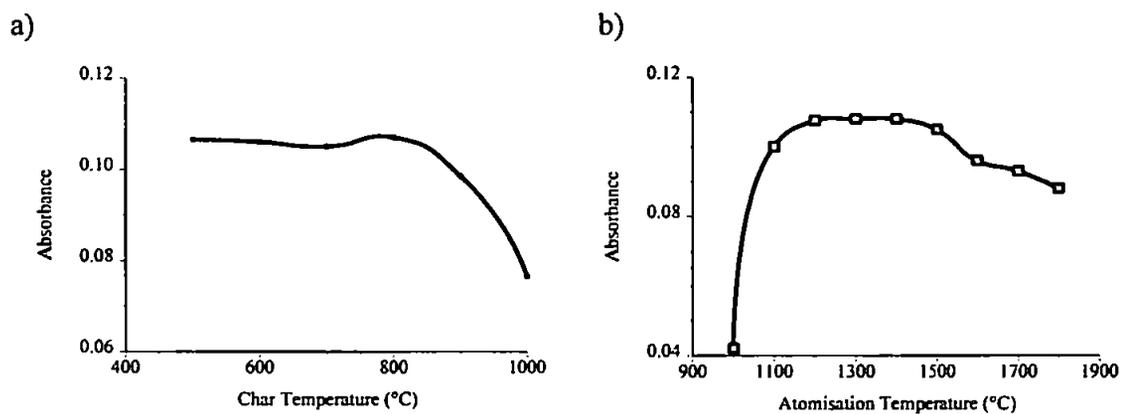


Figure 2.6. Optimisation curves for Cd in 1M HCl digest of SPM using PO_4^{3-} modifier. a) optimisation curve for char temperature, b) optimisation curve for the atomisation temperature.

Table 2.8. Blank values and detection limits for analysis by GFAAS.

| Cruise : | Blank values ($\mu\text{g l}^{-1}$) | | | Detection limits (3σ , $\mu\text{g l}^{-1}$) | | |
|------------------|---------------------------------------|---------|-----------|---|---------|-----------|
| | CH88A/92 | CH99/92 | CH108A/93 | CH88A/92 | CH99/92 | CH108A/93 |
| SPM | | | | | | |
| Pb | 2.3 | 11.1 | 1.9 | 6.6 | 4.2 | 4.5 |
| Cu | 10.1 | 7.0 | 9.1 | 14.1 | 2.3 | 1.3 |
| Co | 8.2 | 1.4 | 0.4 | 2.8 | 2.0 | 0.4 |
| Cd | - | 3.6 | - | - | 0.4 | - |
| Sediment | | | | | | |
| Pb | 5.3 | 7.3 | | 6.8 | 8.9 | |
| Cu | 3.6 | 2.0 | | 4.0 | 2.3 | |
| Co | 0.2 | 0.2 | | 6.3 | 0.9 | |
| Cd | 5.9 | 0.8 | | 4.0 | 0.02 | |
| Porewater | | | | | | |
| Pb | 0.0 | | | 3.9 | | |
| Cu | 0.2 | | | 5.6 | | |

Blank values for SPM were filter blanks, whereas for sediment and porewaters procedural blanks were used. Injection volume : $5\mu\text{l}$.

volatilise the salt. It can be seen from Figure 2.6a. conventional optimisation of Cd in a saline solution would result in very low sensitivity.

The detection limits for GFAAS are given in Table 2.8. All values were typically $<10\%$ of the sample measurement except Cd, and samples were reanalysed when either the

correlation coefficient for the calibration, of three standard additions, was < 0.995 or if the sample relative standard deviation was $> 10\%$.

2.4.3. Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

High precision measurements for isotopic ratios can be obtained using thermal ionisation mass spectrometry (TIMS) (Ng and Patterson, 1982; Maring and Duce, 1990). However, this technique does not lend itself to routine analysis. ICP-MS though an order of magnitude less precise is a rapid method with sufficient precision to measure $^{206}/^{207}\text{Pb}$ isotopic ratios to three decimal places (Hinners *et al*, 1987, Sturges and Barrie, 1989b, Kersten *et al*, 1992).

Sample digests were analysed for stable lead isotopic ratios using ICP-MS (VG Plasmaquad PQ2-Turbo ICP-MS, Fisons Instruments). Calibration was achieved using NIST-981 common Pb isotopic standard. Determinations of ^{202}Hg , ^{204}Pb , ^{206}Pb , ^{207}Pb and ^{208}Pb were obtained, with values of ^{202}Hg being used to correct the ^{204}Pb value for ^{204}Hg . Contributions of ^{204}Hg to ^{204}Pb were typically $< 1.5\%$. A relative standard deviation of 0.5% ($n = 20$) for the $^{206}/^{207}\text{Pb}$ isotopic ratio was obtained for multiple runs of the same sample, (0.6% , Sturges and Barrie, 1987; 0.3% , Miyazaki and Reimer, 1993).

2.5. Quality Assurance.

Standard sediments have often been used to give quality control to analyses, of marine sediments (Law *et al*, 1989, Schmidt and Reimers, 1991, Camacho-Ibar *et al*, 1992). The certification of these sediments are only valid for total digestion of the sediment, and therefore, are of little value when examining partial digestion of sediment samples e.g. 1M HCl. As previously mentioned (see Section 2.3.1.) the analyses of standard sediments were found to require different conditions to that applied to the samples, consequently the analyses of standard sediments may not be a reflection of the sediment samples. This conclusion highlights a clear need for standard sediments to be made readily available, which are certified for partial digestion, and reflect the nature of British sediments. Replicate analyses were performed during sediment digests and typical results from an

Irish Sea replicate sediment is given in Table 2.9. As part of a different study (Turner pers. comm.), two samples were analysed for the $^{206/207}\text{Pb}$ isotopic ratio by an independent laboratory (Kersten pers. comm.), see Table 2.10.

Table 2.9. Analysis of duplicate samples of an Irish Sea sediment (GW6). Indicated are the mean trace metal concentrations of the duplicate digests (samples 1 and 2) and the standard deviations associated with the triplicate measurement of each digest.

| Sample | Element | | | | |
|--------|---------|--------------------------|--------------------------|--------------------------|--------------------------|
| | | Ca (mg g ⁻¹) | Fe (mg g ⁻¹) | Mn (µg g ⁻¹) | Zn (µg g ⁻¹) |
| 1 | | 33.3 ± 0.8 | 7.8 ± 0.1 | 692 ± 5 | 98 ± 2 |
| 2 | | 32.6 ± 0.6 | 7.4 ± 0.0 | 637 ± 29 | 104 ± 3 |
| | | Pb (µg g ⁻¹) | Cd (µg g ⁻¹) | Cu (µg g ⁻¹) | Co (µg g ⁻¹) |
| 1 | | 69 ± 5 | 3.7 ± 0.2 | 10.9 ± 0.8 | 44.5 ± 1.5 |
| 2 | | 77 ± 2 | 3.2 ± 0.1 | 12.1 ± 0.4 | 40.3 ± 3.9 |
| | | i.r. | | | |
| 1 | | 1.181 ± 0.001 | | | |
| 2 | | 1.179 ± 0.005 | | | |

i.r. - $^{206/207}\text{Pb}$ isotopic ratio

Table 2.10. Comparison of independent $^{206/207}\text{Pb}$ isotopic ratio analyses of Irish Sea sediments.

| Irish Sea Sediment | Kersten | This Study |
|--------------------|---------------|---------------|
| GX2-A | 1.172 ± 0.002 | 1.173 ± 0.001 |
| GW7 | 1.177 ± 0.002 | 1.184 ± 0.003 |

In addition, to the criteria previously mentioned (calibration - $r > 0.995$, sample - $< 10\%$ rsd), consistency of analysis was monitored using the characteristic mass (m_0 for GFAAS) and the characteristic concentration (m_c for flame AAS) for each analysis run. The characteristic mass/concentration is that required to give a 1% absorbance (taken as 0.0044 A). As an example Cu is shown in Figure 2.7. Increases in m_0 (i.e. decreasing sensitivity) were observed prior to the graphite tube replacement. Concentrated samples

also showed increases in m_o , which suggests the presence of interfering components, causing the variability within each analysis run. These observations, highlight the need to use standard addition as the mode of calibration. Analyses by flame AAS do not have the same problem with interference and consequently such variation in m_c was not observed.

Table 2.11. shows the m_o and m_c observed for the metals analysed during this study. The predicted and observed m_c for flame AAS are comparative, and not surprisingly the m_o of metals analysed by GFAAS tend to be larger than predicted. The documented values of m_o are performed on idealised, acidified standards with minimum interferences, whereas the values of m_o obtained during this study are derived from complex solutions, using different temperature programs and matrix modifiers to those recommended for acidified standard solutions.

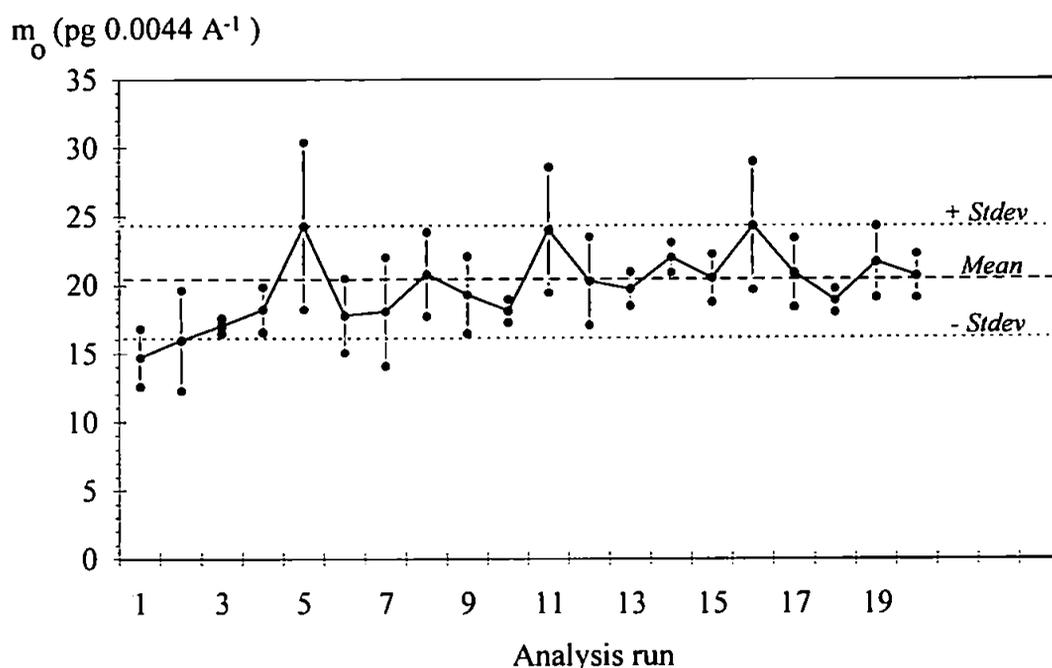


Figure 2.7. Graph showing variation of the mean m_o for each batch of Cu analyses. Error bars indicate the \pm standard deviation, to illustrate the variation of m_o during each batch of analyses. Indicated as dashed lines, are the overall mean (*Mean*) and standard deviations (\pm *Stdev*).

Table 2.11. Table comparing the m_o and m_c obtained during this study and those documented (Perkin Elmer, 1991).

| | Documented | | This study | | Units per 0.0044 A | |
|-----|---------------|----|---------------|----|-----------------------|---------------------|
| | mean | sd | mean | sd | m_o | m_c |
| Cd | 1.3 ± 0.3 | | 1.9 ± 0.4 | | pg | |
| Co | 17.0 ± 3.4 | | 21.0 ± 3.1 | | pg | |
| Cu | 17.0 ± 3.4 | | 20.4 ± 4.1 | | pg | |
| Pb | 30.0 ± 6.0 | | 37.0 ± 8.9 | | pg | |
| Fe | 0.40 ± 0.08 | | 0.37 ± 0.09 | | | µg ml ⁻¹ |
| Mn | 0.040 ± 0.008 | | 0.040 ± 0.003 | | | µg ml ⁻¹ |
| Zn | 0.008 ± 0.002 | | 0.010 ± 0.003 | | | µg ml ⁻¹ |
| Ca* | | | 1.0 ± 0.1 | | | µg ml ⁻¹ |

* no m_c is available for the analysis of Ca using nitrous/acetylene flame.

2.6. Conclusion.

Throughout this work care has been taken to ensure that the analysis is of the highest quality. In the pursuit of this aim, problems have been encountered and overcome. This has shown the need for deliberation when making the smallest changes to methodology. The selective use of methodologies during this work allows the results to be compatible with the existing North Sea Database (Lowry *et al*, 1992; NSTF, 1993).

Chapter 3 - Trace Metals in British Coastal Waters.

Chapter 3 - Trace Metals in British Coastal Waters.

3.1. Introduction.

Particulate trace metal distributions in coastal waters are a complex interplay between the hydrodynamic conditions, and trace metal sources and sinks, all of which are highly changeable, both spatially and temporally. Anthropogenic inputs of trace metals into coastal water can result from varied sources, such as discharges by industry (directly or indirectly via adjacent estuaries); aeolian deposits, and from the reintroduction of relic contamination from sediment resuspension and porewater diffusion. These anthropogenic signals will be superimposed onto natural background trace metal signals, which can be derived from the normal weathering processes and offshore sources. This chapter will examine the distribution of particulate trace metals in the coastal waters of the Irish Sea and the North Sea. The discussion will involve an interpretation of the geochemical processes involved in their long range transport.

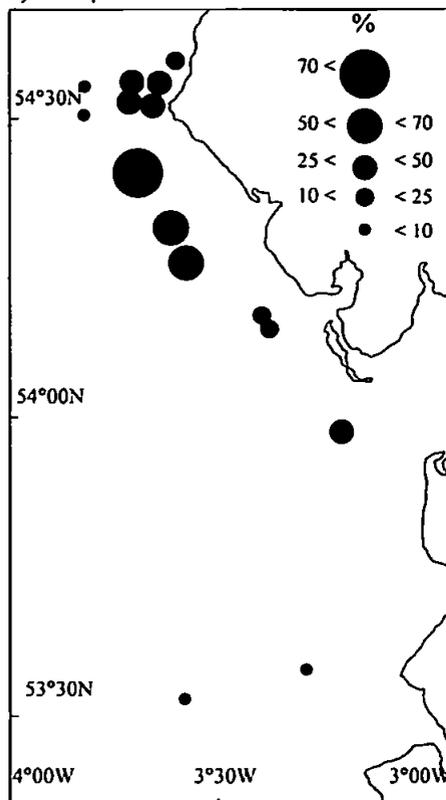
Though coastal seas are subject to considerable anthropogenic inputs, they exhibit quite different characteristics which are highlighted by the transport and behaviour of the trace metals in these regions. Particulate samples of suspended particulate matter (SPM) and sediment were examined for a selection of trace metals chosen by their differences in geochemical behaviour. Each coastal sea will be considered independently and then compared.

3.2. Trace Metals in the North Eastern Irish Sea.

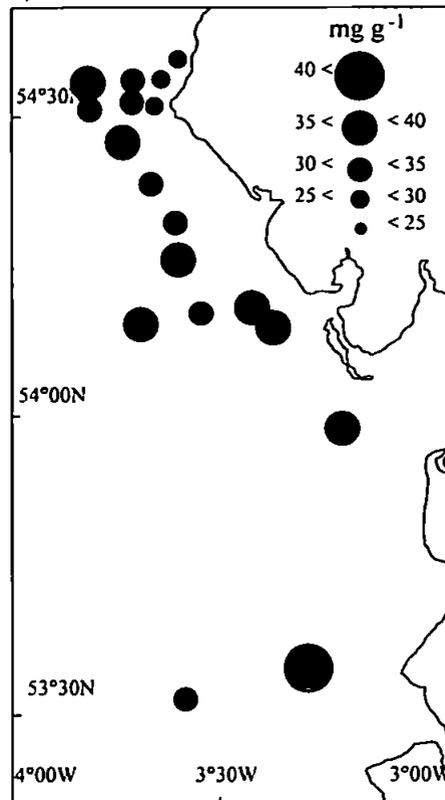
3.2.1. *Trace Metals in Bed Sediments.*

The grain size distribution of bed sediments in the region was determined from the fractions passing a 63 μ m sieve. The results show coarse sediments are located in the south of the region with finer sediments further north, followed by a region of coarser material (Figure 3.1a.). This distribution was generally matched by changes in Ca content of the sediments with the highest values being found with coarse materials (possibly

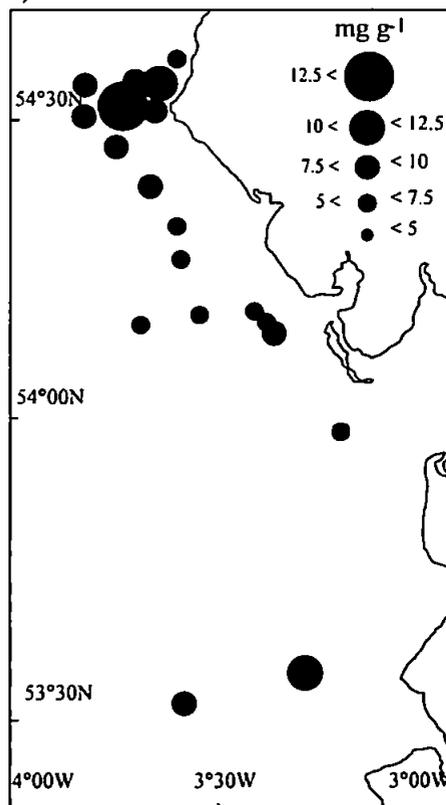
a) $<63\mu\text{m}$



b) Ca



c) Fe



d) Mn

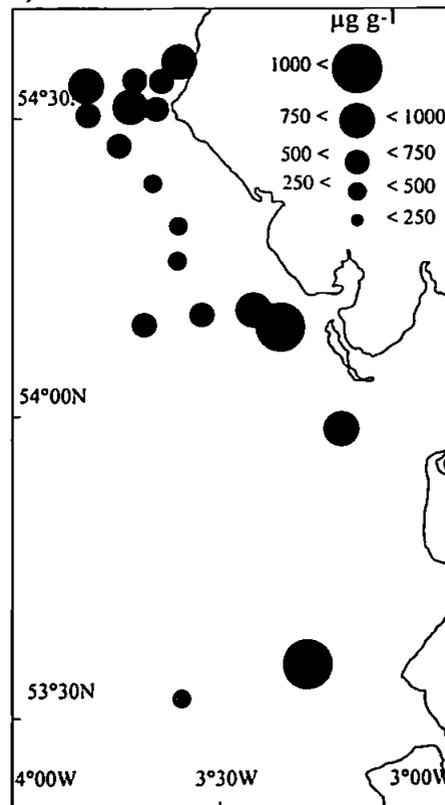
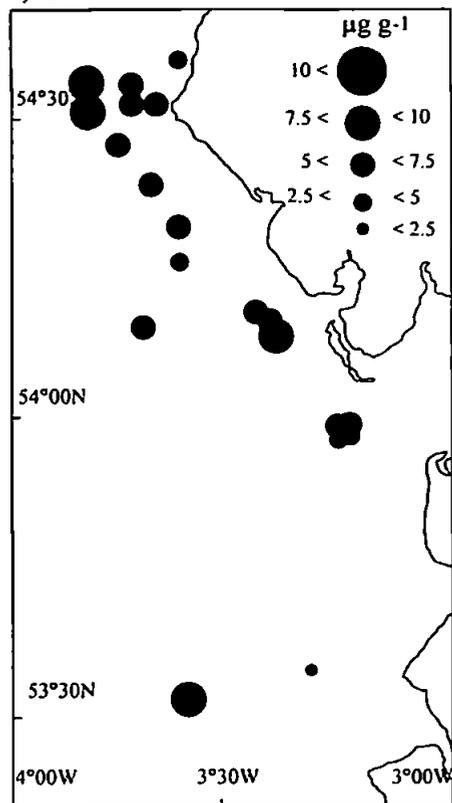
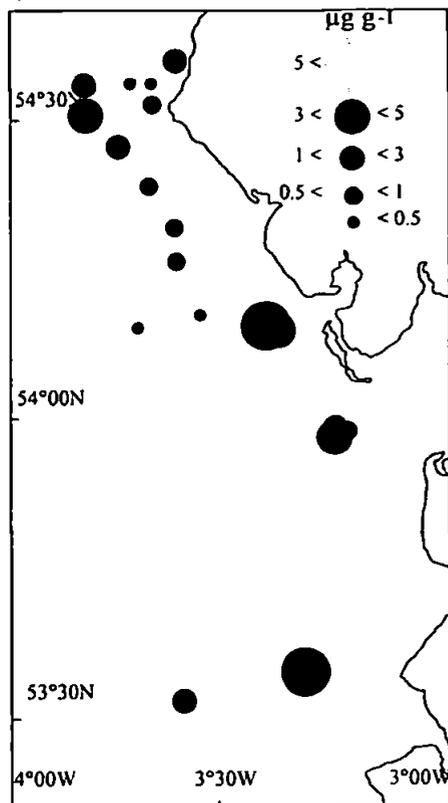


Figure 3.1. Distribution of surface sediment data in the North Eastern Irish Sea, a) % $<63\mu\text{m}$ b) Ca c) Fe d) Mn e) Co f) Cd g) Cu h) Zn i) Pb j) $^{206}/^{207}\text{Pb}$ isotopic ratio. Metal data was obtained from $<63\mu\text{m}$ fraction available to 1M HCl leach.

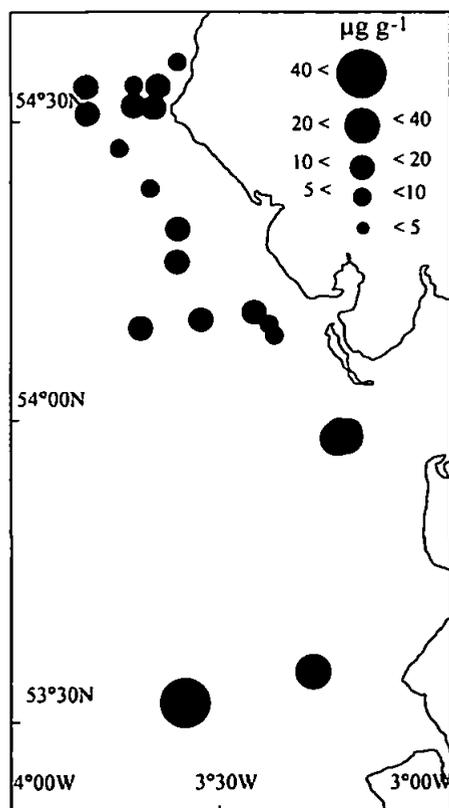
e) Co



f) Cd



g) Cu



h) Zn

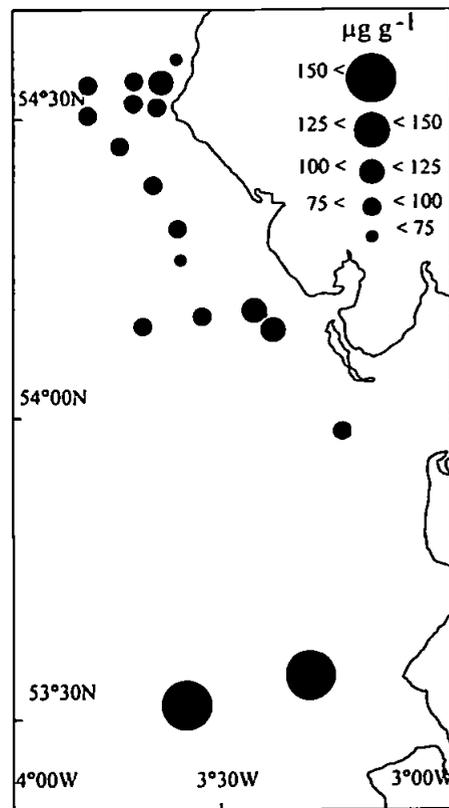


Figure 3.1. continued

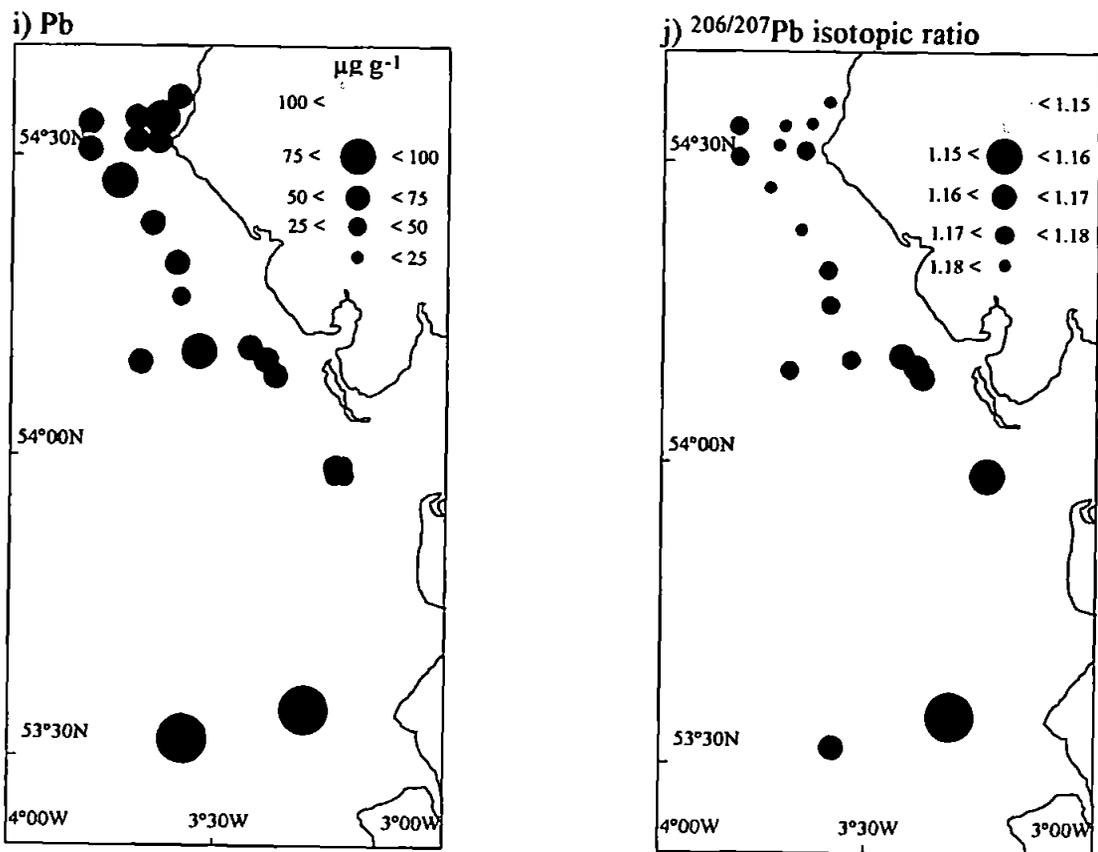


Figure 3.1. continued

calcareous shells) and the lowest with finer silty material (Figure 3.1b). The Fe and Mn oxide phases of the sediment show relatively low concentrations in the finer materials but significant concentrations were found in the vicinity of 54° 30' N where industrial inputs are present. Cobalt tends to follow a similar distribution to Mn.

The distribution of Cd showed the highest concentrations in samples closest to estuaries, which may suggest that Cd is transported via riverwater inputs into this region. Similar distributions are shown for Cu, Zn and Pb (Figures 3.1g., 3.1h. and 3.1i.) with the highest concentration in Liverpool Bay and a progressive decrease in concentrations occurring in a northward direction. As observed with the Fe, Mn and Co, the concentration of these metals increases offshore of Whitehaven, at a latitude about 54° 30' N. Whitehaven is a known discharge point for a phosphate rock processing plant (NRA, 1991). The plant is consented to discharge Cd, Cu, Pb and Zn, together with other metals e.g. Cr, Hg, Ni (NRA, 1991), and the pH of the effluent is typically 2.0 (NRA pers. comm.).

The trend in $^{206/207}\text{Pb}$ isotopic ratio in surface sediments, indicated anthropogenic Pb in the vicinity of Liverpool Bay (high Pb concentrations are also present) and a progressive dilution of this signal northward (Figure 3.1j.). Perturbations in the $^{206/207}\text{Pb}$ isotopic ratio around Whitehaven may have resulted from the high uranium content in phosphate ores (McCartney *et al*, 1992) and the ores relative enrichment of ^{238}U (Section 4.2.). However, though the $^{206/207}\text{Pb}$ isotopic ratio has been used to indicate anthropogenic sources, in this case it is complicated by the high $^{206/207}\text{Pb}$ isotopic ratio of the rock being processed (Table 3.1.). A number of samples around Whitehaven had $^{206/207}\text{Pb}$ isotopic ratios of 1.20 yet values of 1.17 - 1.18 were found along the Cumbrian coast, suggesting the influence of the Whitehaven discharge in the immediate vicinity.

A correlation matrix of metal concentrations can be a useful tool to examine potential relationships between different metals (Table 3.1.). Some of the highest correlations were shown by Zn with Cu, Co and Pb. Except for Co these metals are considered to be pollutant metals and may suggest a potential dependence of these metals on an anthropogenic source. Fe is thought to be a 'geochemical carrier' and correlates with Zn, Co and Pb

Table 3.1. Correlation matrix indicating r-values ($p \leq 0.05$) for 1M HCl digestion of $<63\mu\text{m}$ size fraction of Irish Sea surface sediments.

| | % $<63\mu\text{m}$ | [Ca] | [Fe] | [Mn] | [Zn] | [Cu] | [Co] | [Cd] | [Pb] |
|---------|--------------------|-------|------|-------|-------|-------|------|------|------|
| [Ca] | | | | | | | | | |
| [Fe] | | | | | | | | | |
| [Mn] | | -0.58 | | | | | | | |
| [Zn] | | | 0.50 | | | | | | |
| [Cu] | | 0.60 | | | 0.74 | | | | |
| [Co] | | | 0.60 | | 0.70 | 0.41 | | | |
| [Cd] | | | | | | | | | |
| [Pb] | | | 0.50 | | 0.92 | 0.68 | 0.64 | | |
| Pb i.r. | | | | -0.40 | -0.60 | -0.56 | | | |

3.2.2. Sediment Cores.

3.2.2.1. Description of the Sediment Cores.

Immediately after taking the sediment core a visual description was recorded (Figure 3.2.). The cores were mainly sand with the exception of core Z which contained 20-40% <math> < 63 \mu\text{m}</math>. Core Z was obtained from the entrance to Morecambe Bay which is a potential source of these deposits. In the case of core Y1 a shell horizon was observed, but not in Y5 which was collected in the vicinity of Y1. Animal burrows were clearly visible in cores Y1, Y5 and CD2. Core CD2 was particularly inundated with fauna. This is likely a reflection of its location near the sewage and industrial waste dumping ground and, hence, is likely to be subjected to a high supply of organic carbon. Though no burrows were observed in core Z, an archive core at site Z did show burrows. The presence of fauna will result in bioturbation and mixing of the sediment core. In the Irish Sea two animals dominate sediment below 5cm - *Callinassa Subterranea* and *Maxmülleria Lankestri* (Kershaw *et al.*, 1992; Swift, 1993). These burrows will introduce pathways for oxygen penetration below the redox boundary (Santschi *et al.*, 1990) perturbing redox sensitive metals and metals associated with them.

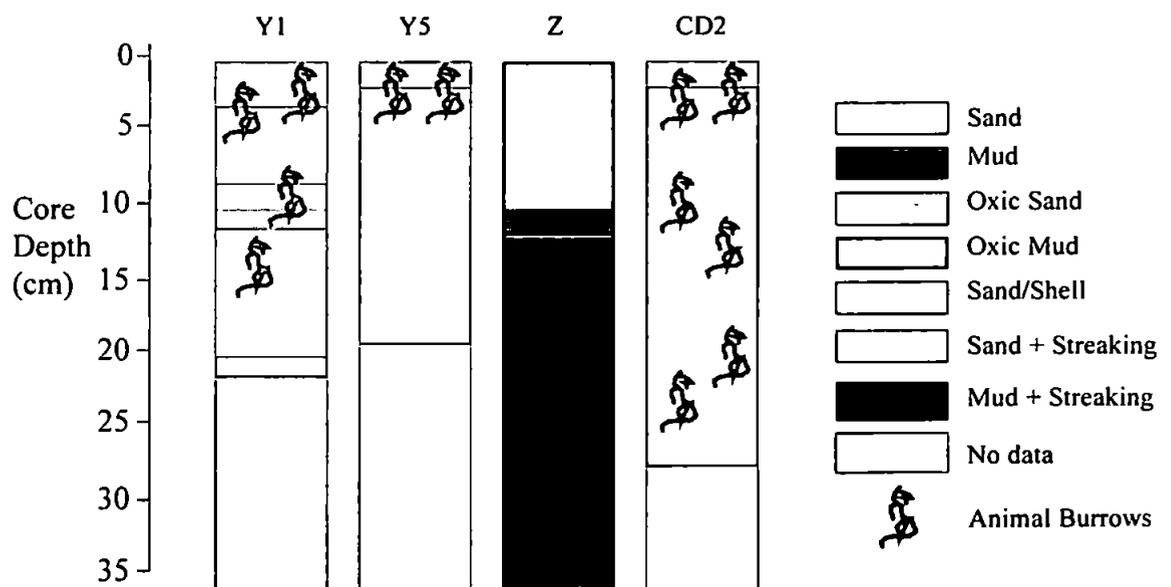


Figure 3.2. Visual description of sediment cores obtained from the north eastern Irish Sea (Figure 2.1. for site locations).

Core Z appeared to have the deepest redox boundary at about 10cm, whereas cores Y1, Y5 and CD2 had a redox boundary at a depth of 2-3 cm. The p_e profile for the sediment cores (Figure 3.3.) all showed a p_e range indicative of organic matter oxidation. The surface sediment p_e values for all sediment cores were sufficient for the reduction of O_2 , NO_3 and Mn (IV). The visually recorded oxic depths for these cores (Figure 3.2.) tended to be overestimated (see later). No Mn rich bands would be expected to form in the upper sediment layers and fluxing of Mn (II) would be possible from the sediment-water interface. The p_e value of 0 is the point where Fe (III) can be reduced, and oxidation of Fe (II) is inhibited. Whereas, a p_e value of approximately +1.5 allows the irreversible oxidation of Fe (II). Hence, the initial precipitation of diagenetically mobilised Fe would be expected at depths corresponding to approximate p_e values of 0 to +1.5. The visually observed redox boundaries for each of these cores were based on the colour change across the redox boundary and tend to coincided with this Fe precipitation depth. All of the sediment cores at a depth of 10cm approach the p_e value (-3.5) sufficient to reduce SO_4 to H_2S , formation of Fe sulphides would be expected below this depth. Dark streaking was observed in some of the cores at this depth (Figure 3.2.).

3.2.2.2. Dissolved and Particulate Trace Metals in Sediment Cores.

The $<63\mu m$ grain size, trace metal concentrations and $^{206}/^{207}Pb$ isotopic ratio profiles for cores Y1, Y5, Z and CD2 are given in Figures 3.4 to 3.7. respectively. Dissolved Fe, Mn, Cu and Pb in sediment porewaters are also indicated in Figures 3.4. to 3.7.

Cores Y1 and Y5 had $\sim 20\%$ $<63\mu m$ throughout while the muddier core Z was $\sim 45\%$ $<63\mu m$ in the upper 5cm but stepwise to $\sim 25\%$ $<63\mu m$ at the base of the core. The coarse nature of core CD2 was reflected in the $<63\mu m$ values of $\sim 5\%$ throughout the core, and a higher Ca concentration. Although, the concentrations of Ca in the profile were obtained from the $<63\mu m$ fraction the values may be considered indicative of fine shell fragments and Ca bearing minerals.

Core CD2 had the lowest porewater concentrations of Fe and Mn (Figure 3.4.) which was probably due to the coarse nature and mixing by bioturbation of the core (Figure 3.2.). Since the porewater Mn concentration was higher in the surface sediment layer compared

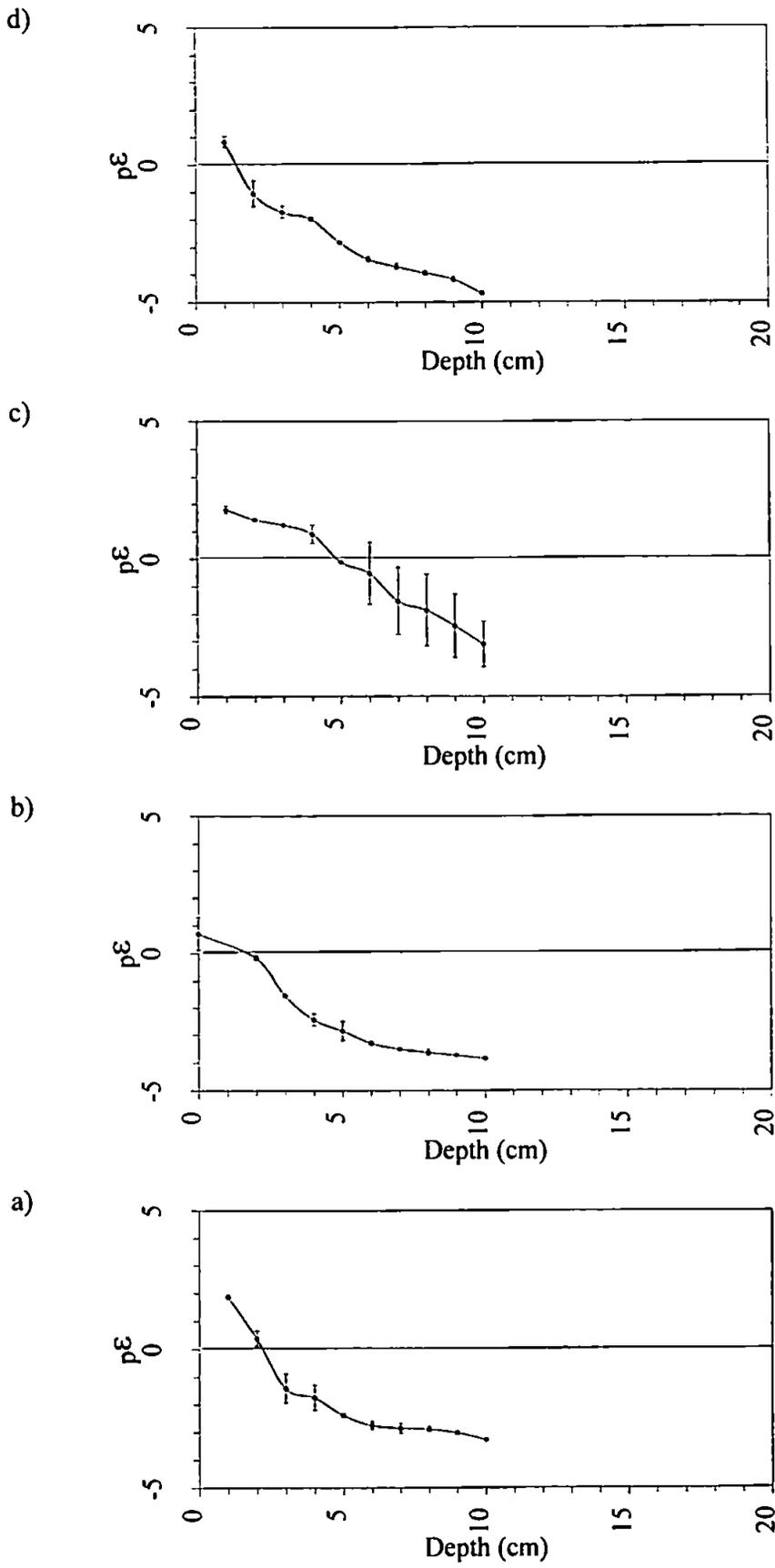


Figure 3.3. $p\epsilon$ profiles for sediment cores taken in the north eastern Irish Sea a) Y1, b) Y5 c) Z and d) CD2.

to the overlying water, Mn could flux into the water column. The concentration of particulate Mn appeared to be invariant and may be caused by the mixing effect of burrowing animals, though a slight maxima appeared to be present at a depth of ~8cm. A peak in particulate Fe was present at 4cm but was composed of a single high value and therefore must be treated with caution.

The Fe and Mn profiles for cores Y1, Y5 and Z appeared to be structured, implying diagenetic changes. The profiles of porewater Mn and particulate Mn for cores Y1 and Y5 were similar. Both cores showed a broad dissolved Mn peak from ~3cm to ~12cm. Above 3cm increases in particulate Mn implied precipitation of dissolved porewater Mn. However, the depth appears to be barely sufficient to fully oxidise dissolved Mn. A similar situation was observed in core Z but the porewater peak of dissolved Mn was much better defined. Reduction of Fe could have occurred at a depth of 10cm in cores Y1, Y5 and Z. Peaks in particulate Fe were associated with the maximum observed in dissolved Fe concentrations, though for core Y1 it was situated a few centimetres above the dissolved Fe maximum. Two large peaks, which may be a single peak, of particulate Fe occurred below the dissolved Fe maximum at a depth of ~15cm in core Z. Associated with this peak were maxima in other trace metal profiles (Co, Zn, Cd, and Pb) which suggested that the dissolved Fe peak(s) at 15cm were not analytical artefacts. Less well defined maxima in these metals appeared to be associated with the particulate Fe peak at 10cm. This may suggest that the deposition of particulate Fe co-precipitates these metals. The peak at 15cm may be a relic peak associated with anthropogenic input but since large inputs of not only Zn, Cd, Pb but also Fe and Co would be required this may be unlikely. If a large deposition of sediment occurred, a sharp change in sediment redox conditions would result causing a shift upwards of the redox boundary leaving diagenetically formed metal rich band lower in the core, while at the same time fresh precipitation would occur at the new redox boundary. A situation similar to this occurs in turbidic deep sea sediments. Sediments accumulating on the upper continental shelf fail catastrophically, to be transported as gravity flows, and deposited on the adjacent abyssal plain causing alterations in the redox nature of the original sediment (Wilson *et al*, 1985; 1986). However, pollutants arriving at site Z could occur during winter storms which transport organic rich land derived material from within Morecambe Bay.

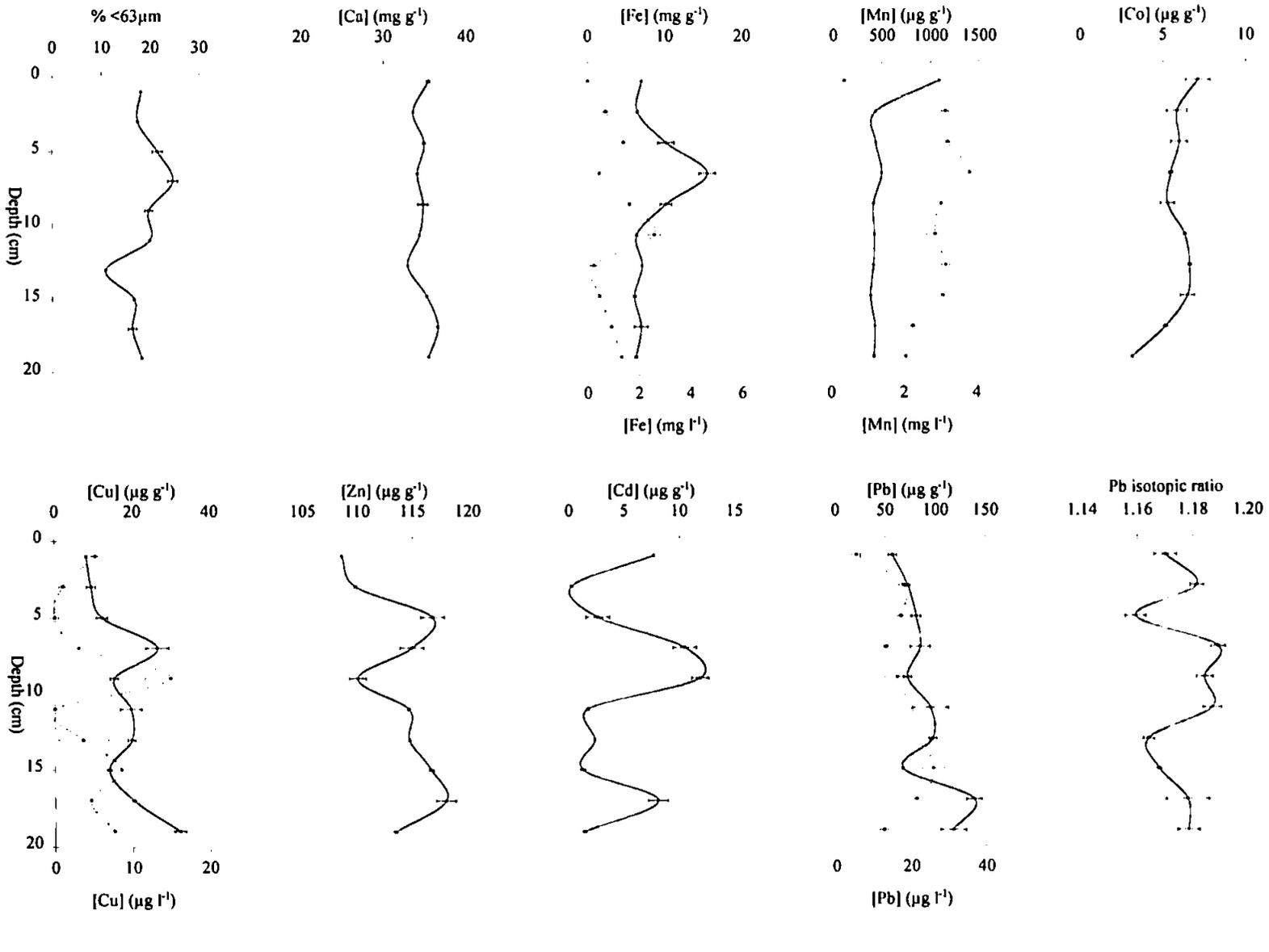


Figure 3.4. Trace metal core profiles for site Y1. <63µm sediment digest (---○---), porewater (---●---).

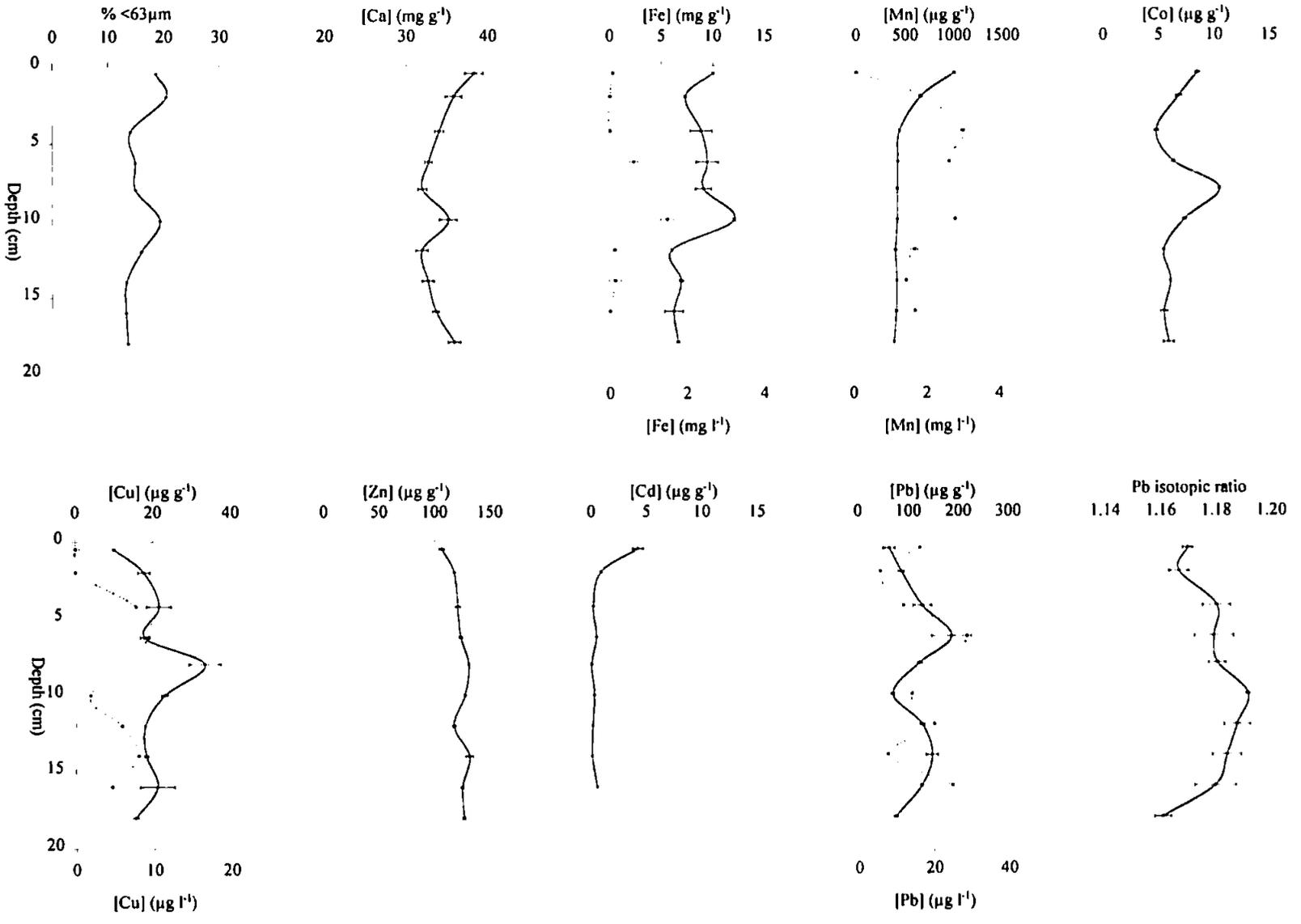


Figure 3.5. Trace metal core profiles for site Y5. <63µm sediment digest (—◆—), porewater (····●····).

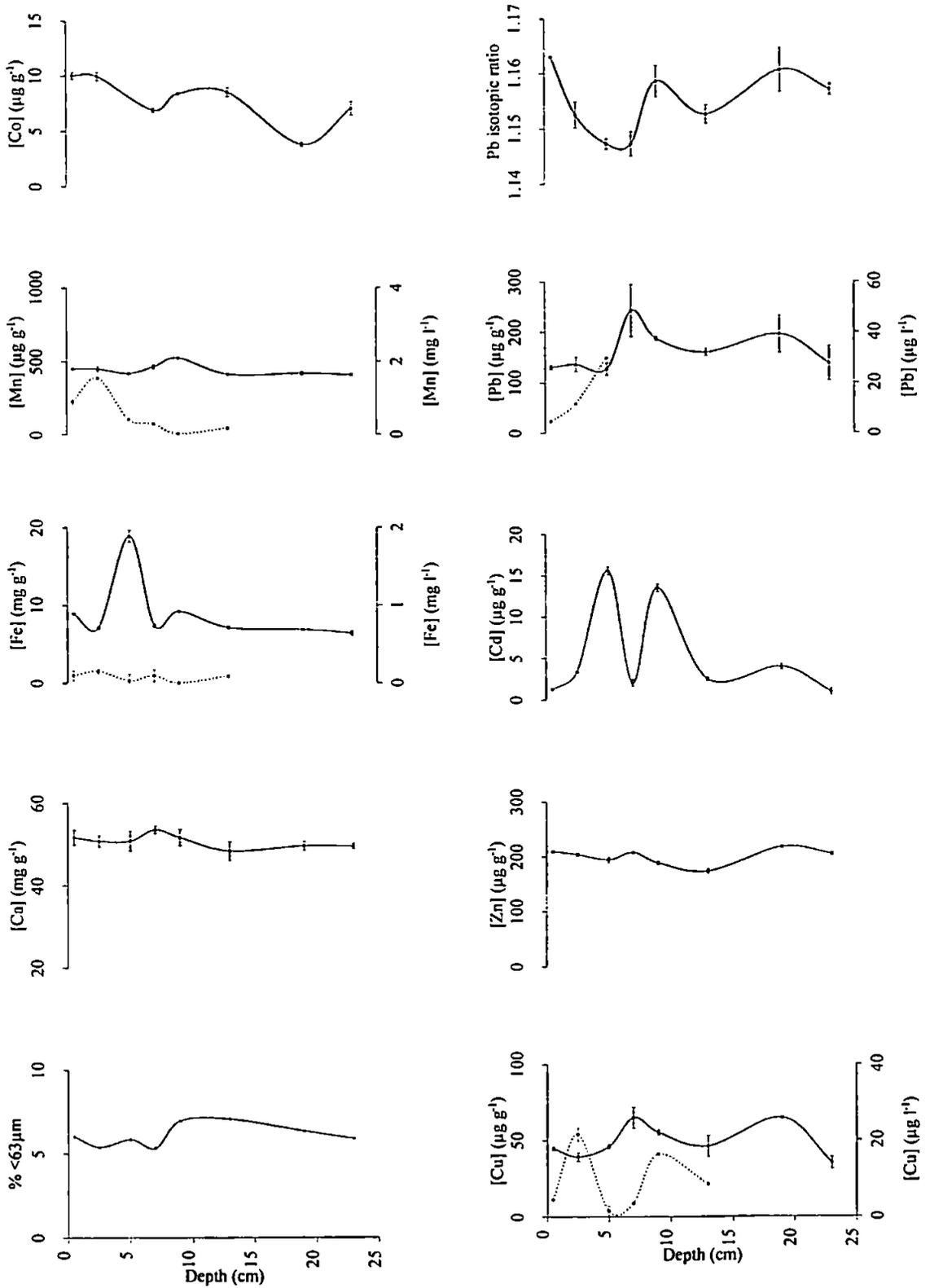


Figure 3.7. Trace metal core profiles for site CD2. $<63\mu\text{m}$ sediment digest (—◆—), porewater (—●—).

Some of the metals appeared to be fluxing across the sediment surface (Table 3.2). The observations suggest Mn, Cu and Pb were fluxing from cores Y1 and CD2, with Mn and Pb from core Y5, and Mn and Cu from core Z. Thus, the diffusion of Mn, Cu and Pb across the sediment water interface will contribute to the wider trace metal concentration range in this coastal region. Porewater fluxes for the area can be derived from Equation 1.6. using the approach adopted by Ciceri *et al* (1992), for a porosity of 0.9 and a grain coarseness given by $m=2$ (Table 3.2.), and temperature corrected diffusion coefficients from Li and Gregory (1974). Assuming the area of the north eastern Irish Sea is 2.3×10^9 m², comprising 20% gravel (represented by core CD2), 50% sand (represented by cores Y1 and Y5) and 30% mud (represented by core Z) the benthic fluxes of Cu and Pb are 92 and 60 kg d⁻¹ respectively. Data obtained by PARCOM (1991) showed that fluxes of Cu and Pb into the Mersey Estuary are of the order 49.6 kg d⁻¹ for Cu and 48.3 - 51.6 kg d⁻¹ for Pb, for Morecambe Bay the fluxes of Cu and Pb are 47.7 kg d⁻¹ and 55.6 - 75.5 kg d⁻¹, respectively. However, not all the metal may enter the Irish Sea because of the filtering capacity of estuaries and embayments (Zwolsman, 1994). The PARCOM (1991) fluxes are of the same order of magnitude as those obtained from porewater analysis given above. This suggests that as the pollutant sources in the Mersey and Morecambe Bay are reduced by tighter legislative control the fluxes of metals from the shelf sea sediments could become relatively more important.

It is highly probable that anthropogenic inputs occurred in these sediment cores particularly core CD2 which is situated in the vicinity of a sewage and industrial waste dumping ground. The cores are highly bioturbated and relatively coarse, again most significantly for core CD2. The data has shown that surface enrichment of particulate trace metals, and inferred benthic fluxes of dissolved trace metals occur. The sediments of the north eastern Irish Sea are not final sinks of trace metals in the area but represent temporary sinks because diagenetic processes will enrich the surface sediment and cause trace metals to flux across the sediment-water interface. Resuspension of the surface sediment will allow the trace metals to re-enter the water column until finally being removed from the region.

Table 3.2. Comparison of dissolved metal values from bottom waters and porewaters in the upper 1 cm of each core.

| Core | Y1 | Y5 | Z | CD2 |
|--|------------------------|------------------------|------------------------|------------------------|
| % <63µm Fraction | 18 | 19 | 46 | 6 |
| Mn(µg l ⁻¹) NE Irish Sea ⁺ | 1.95 | 1.95 | 1.95 | 1.95 |
| Porewater | 1960 | 2540 | 1120 | 910 |
| Flux (kg m ⁻² d ⁻¹) | 5.6 x10 ⁻⁶ | 7.3 x10 ⁻⁶ | 2.9 x10 ⁻⁶ | 2.8 x10 ⁻⁶ |
| Cu (µg l ⁻¹) NE Irish Sea ⁺ | 0.66 | 0.66 | 0.66 | 0.66 |
| Porewater | 5.22 | 0.00 | 40.80 | 4.50 |
| Flux (kg m ⁻² d ⁻¹) | 1.44 x10 ⁻⁸ | 0 | 1.14 x10 ⁻⁷ | 1.3 x10 ⁻⁸ |
| Pb (µg l ⁻¹) NE Irish Sea ⁺ | 0.11 | 0.11 | 0.11 | 0.11 |
| Porewater | 5.50 | 16.40 | 0.00 | 4.60 |
| Flux (kg m ⁻² d ⁻¹) | 2.24 x10 ⁻⁸ | 6.76 x10 ⁻⁸ | 0 | 2.01 x10 ⁻⁸ |

⁺ Values were taken from Preston (1973).

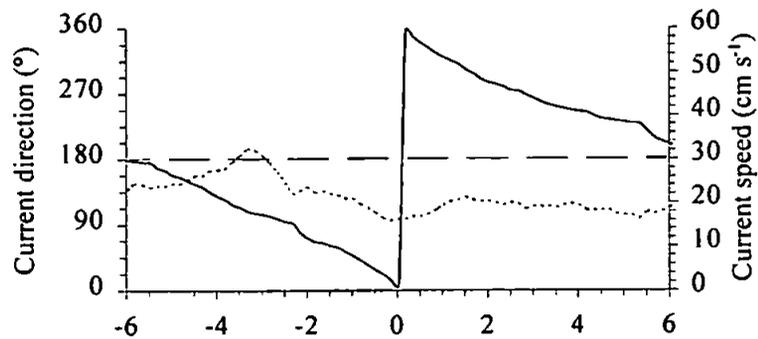
3.2.3. Trace Metals in Suspended Particulate Matter.

Samples of SPM were obtained at sites Y and Z (Figure 2.1.) during spring and neap tides. The measured variables are shown in Figures 3.9. and 3.10. for sites Y and Z respectively. Relatively few samples were obtained at Site Z due to logistical constraints. Typically, site Y was more saline and warmer than site Z and was considerably less turbid. These observations suggested that site Z was more strongly influenced by freshwater discharges than site Y. This was perhaps not surprising as site Z was positioned at the mouth of Morecambe Bay while site Y was north of Morecambe Bay (Figure 2.1.). Site Y was adjacent to the Duddon Estuary but the freshwater discharge from the Duddon River was low (5 m³ s⁻¹) compared to the total freshwater discharges from rivers in Morecambe Bay (71 m³ s⁻¹). This suggests that site Y was more representative of variations in coastal parameters, while site Z might be more heavily influenced by discharges from Morecambe Bay.

3.2.3.1. Variation of Particulate Trace Metal Concentrations at Site Y over a Tidal Cycle.

Examination of current speed and direction at site X (Figure 3.8.), to the west of site Y, showed a number of features distinguishing the neap and spring tides. The current speeds during the springs were almost double the current speeds at neaps which would increase resuspension and hence, higher concentrations of SPM during spring tides (Figure 3.9.). The increased turbidity resulted in lower suspended particulate metal concentrations due to dilution by sediment particles, which generally had lower trace metal concentrations (Table 3.3.). A critical erosion speed of 30 cm s^{-1} is representative of the current speed required for the resuspension of surface sediment of about $100\mu\text{m}$ grain diameter. Thus, the current speeds at neaps would not have caused substantial resuspension of fine sand. In contrast resuspension could have occurred throughout the spring tide because the critical erosion speed was exceeded for most of the tidal cycle. However, the asymmetry of neap tides may have caused the resuspension of material finer than $100\mu\text{m}$ from the

a)



b)

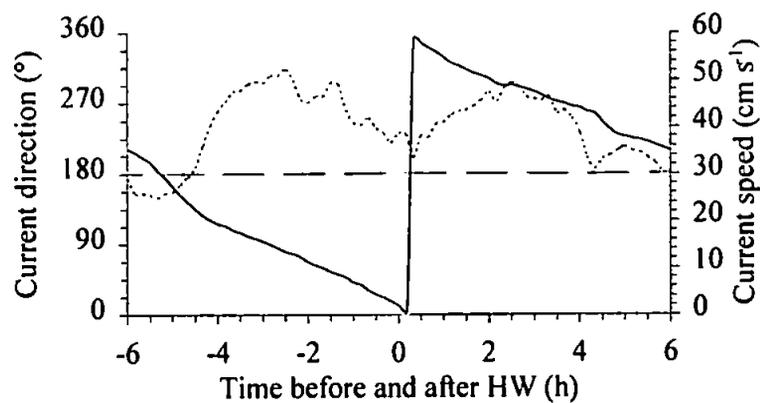


Figure 3.8. Current speed (---) and direction (—) measured at site X for the a) neap and b) spring tides. Indicated is the velocity 1m above the bed (— — —) required to mobilise particles of $>100\mu\text{m}$ in diameter (very fine to fine sand).

sediment surface. This material may have been of a different nature to the bulk sediment (Jago *et al*, 1993) and continual resuspension and settling of sedimentary material during flood-ebb and spring-neap cycles could give rise to a winnowing of particles comprising the sediment bed, resulting in a surficial layer of fine slow settling particles. Both the spring and neap tides do not exhibit zero current flow at the turn of the tide, such that at neaps the water flow was $\sim 15 \text{ cm s}^{-1}$ while at springs it was $\sim 25 \text{ cm s}^{-1}$, which ensured that some of the material of low settling velocity could remain in permanent suspension. Integration of the areas under the curves for the flood and ebb tides (Figure 3.8.) indicates residual current flows for springs and neaps of 1.9 cm s^{-1} and 2.5 cm s^{-1} respectively, in a north eastward direction. Thus, the predominant movement of particulate trace metals would follow the residual flow in a north eastward direction. An overall northward transport of anthropogenic Pb was indicated by the increasing $^{206/207}\text{Pb}$ isotopic ratio in surface sediment values from Liverpool Bay to the Cumbrian Coastline (Figure 3.1.).

Table 3.3. Mean SPM and $<63\mu\text{m}$ surface sediments trace metal values from the Irish Sea at sites Y and Z (Sp - spring tides, Np - neap tides). See Figure 2.1. for location of each site.

| Particulate Trace Metal Concentrations ($\mu\text{g g}^{-1}$, except Fe : mg g^{-1}) | | | | | | | |
|--|----------------|---------------|----------------|-------------|--------------|--------------|-----------------|
| | [Fe] | [Mn] | [Co] | [Cu] | [Zn] | [Pb] | Pb i.r. |
| Y | | | | | | | |
| SPM Sp | 8.4 ± 0.6 | 1095 ± 69 | 6.1 ± 3.2 | 16 ± 7 | 175 ± 31 | 94 ± 13 | 1.16 ± 0.02 |
| SPM Np | 11.0 ± 1.0 | 974 ± 115 | 9.4 ± 4.6 | 41 ± 22 | 426 ± 97 | 108 ± 23 | 1.16 ± 0.01 |
| Sediment | 8.5 ± 2.1 | 1049 ± 57 | 7.8 ± 1.0 | 9 ± 1 | 108 ± 1 | 60 ± 4 | 1.17 ± 0.00 |
| Z | | | | | | | |
| SPM Sp | 9.3 ± 0.5 | 1146 ± 67 | 9.4 ± 1.1 | 17 ± 7 | 213 ± 64 | 71 ± 32 | 1.16 ± 0.01 |
| SPM Np | 8.6 ± 0.6 | 1087 ± 82 | 7.4 ± 0.9 | 33 ± 14 | 201 ± 18 | 105 ± 26 | 1.14 ± 0.02 |
| Sediment | 6.2 ± 1.7 | 765 ± 102 | 4.6 ± 1.3 | 15 ± 7 | 89 ± 9 | 48 ± 13 | 1.16 ± 0.01 |
| CD1 | | | | | | | |
| Sediment | 12.3 ± 0.2 | 1137 ± 0 | ND | 33 ± 4 | 333 ± 4 | 164 ± 5 | 1.14 ± 0.00 |
| CD2 | | | | | | | |
| Sediment | 9.0 ± 0.1 | 452 ± 5 | 10.0 ± 0.1 | 45 ± 1 | 210 ± 2 | 130 ± 5 | 1.16 ± 0.00 |

Pb i.r. - $^{206/207}\text{Pb}$ isotopic ratio

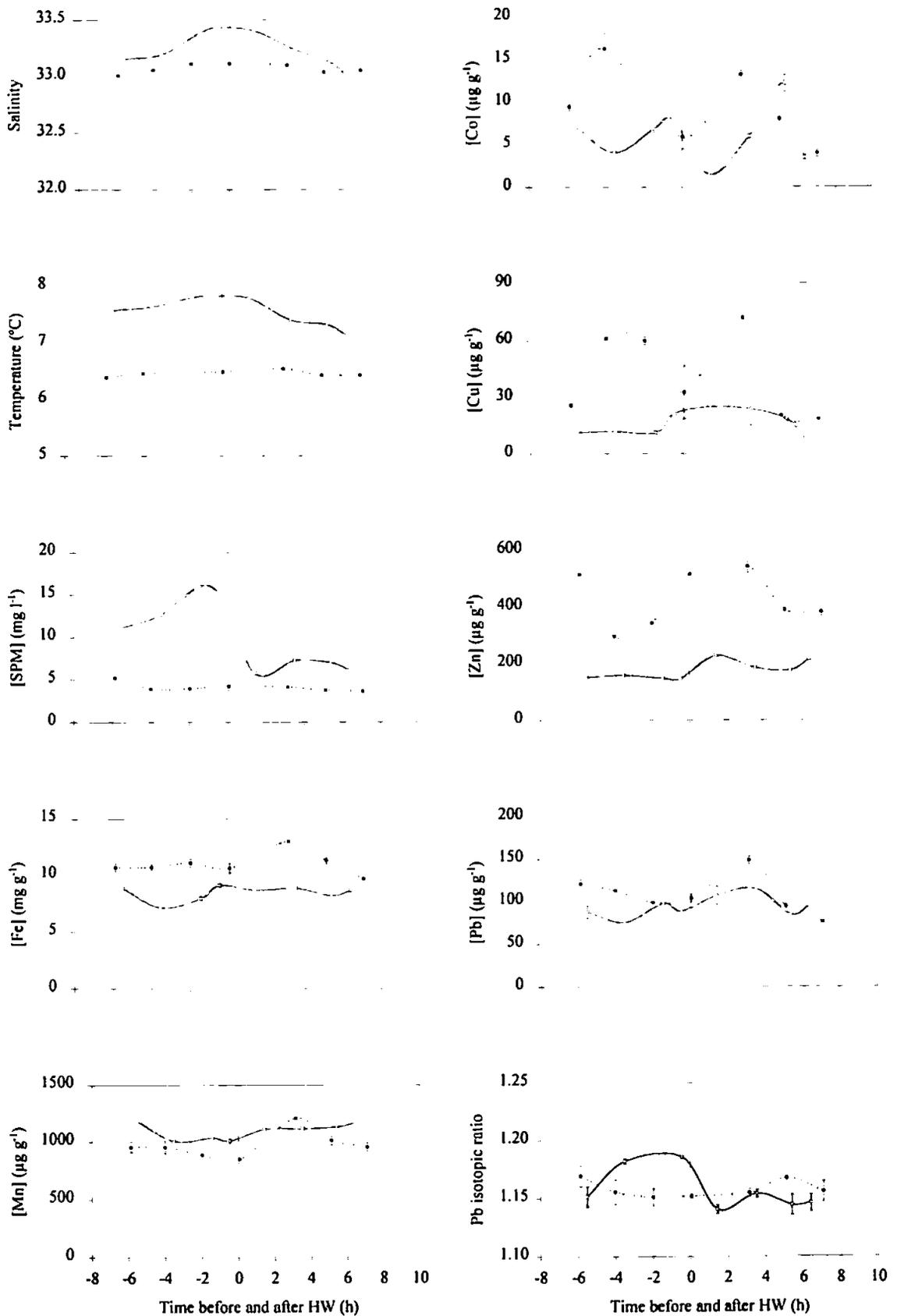


Figure 3.9. Variation of water conditions (Salinity, Temperature, SPM concentrations and particulate metal concentrations) at site Y, Irish Sea during a spring (○) and neap (●) tide.

Spring Tides at Site Y.

Generally the concentrations of suspended particulate trace metals were lower during the spring tide compared to the neap tide (Table 3.3.). A resuspension event was observed during the spring flood tide (Figure 3.9.). This resuspension would cause a lowering of SPM trace metal concentrations by resuspension of sediment with a lower metal content, (Table 3.3.). Since the SPM compared with the sediment contained a higher concentration of trace metals it must have either a) originated from an area of higher metal concentrations and been subsequently advected into site Y or b) metals are more reactive to the SPM e.g. small particles with higher specific surface areas, and the SPM represents a more reactive fraction of the resuspended sediment. The process of settling could isolate this more reactive fraction in the water column. The spring profiles for Fe, Cu, Zn, Pb and $^{206}/^{207}\text{Pb}$ isotopic ratio showed differences between flood and ebb tide.

The combination of Pb and $^{206}/^{207}\text{Pb}$ isotopic ratio measurements is a potentially useful tool to examine the movement of an anthropogenic particle active metal. The Pb profile (Figure 3.9.) clearly indicated a rise in Pb content from flood to ebb tide SPM. The $^{206}/^{207}\text{Pb}$ isotopic ratio showed two separate particle populations for the flood and ebb tide. The spring flood SPM had a higher $^{206}/^{207}\text{Pb}$ isotopic ratio than the ebb, which suggested that the flood tide contained more natural background lead while the ebb tide contained more Pb of anthropogenic origin. Consequently, considering the current regime for site Y (Figure 3.8.), the flood tide could advect offshore material, of higher isotopic ratio into site Y, while during the ebb tide, Pb of lower isotopic ratio, could be advected from landbased sources

Both Fe and Mn did not show strong variation during springs and neaps. Manganese concentrations in surface sediments from Liverpool Bay and site Y were similar. Consequently any combination of resuspended material and advected material would show little variation. Decreases in the spring flood concentrations occurred during the resuspension event and may be suggest the influence of mass dilution. The profiles for Cu and Co showed maxima during the flood and ebb period and had a similar pattern, while Zn appeared to only show maxima during the ebb tide. The increases in concentration of Zn, Co, Cu during the ebb tide may be explained in terms of material advected from the area of Liverpool Bay.

To summarise the dominating factors affecting the trace metal profile during the spring tide at site Y appears to be the direction of current. During the flood period, metal depleted offshore material is advected into the area, while during the ebb period the particles are anthropogenically enriched in selected trace metals possibly originating from the Liverpool Bay region.

Neap Tides at Site Y.

No resuspension was observed during the neap tide at site Y, yet variation in trace metal concentration was shown. The tidal asymmetry of the neap tide may result in the resuspension of a fine reactive surficial material from the sediment surface. The gravimetric determination of SPM is too insensitive to small variations in the SPM concentration. The neap profiles of Fe, Mn, Zn, Pb and $^{206/207}\text{Pb}$ isotopic ratio show differences between flood and ebb tides suggesting that the particle population was different, yet no variation in SPM was observed.

The neap tide showed little variation in $^{206/207}\text{Pb}$ isotopic ratio, the neap tide being less dynamic may have not been sufficient to advect sufficient quantities of material to alter the $^{206/207}\text{Pb}$ isotopic ratio. Hence, the values of the $^{206/207}\text{Pb}$ isotopic ratio during the neap tide were intermediate between that seen during the spring flood and ebb tide. The method of $^{206/207}\text{Pb}$ isotopic ratio employed is relatively imprecise and may not be sensitive enough to differentiate between these populations.

The neap profiles for Cu and Co showed maxima during the flood and ebb period and had a similar pattern, while Zn appeared to only show maxima during the ebb tides. These patterns were similar to that observed during the spring tide. However, the increase in metal concentrations during the spring ebb tide were explained in terms the advection of anthropogenic particles but the neap tide did not show a corresponding decrease in $^{206/207}\text{Pb}$ isotopic ratio during the ebb tide. The increases during the maximum flood and ebb period of the neaps may be indicative of resuspension of a fine metal rich material, which has been previously postulated.

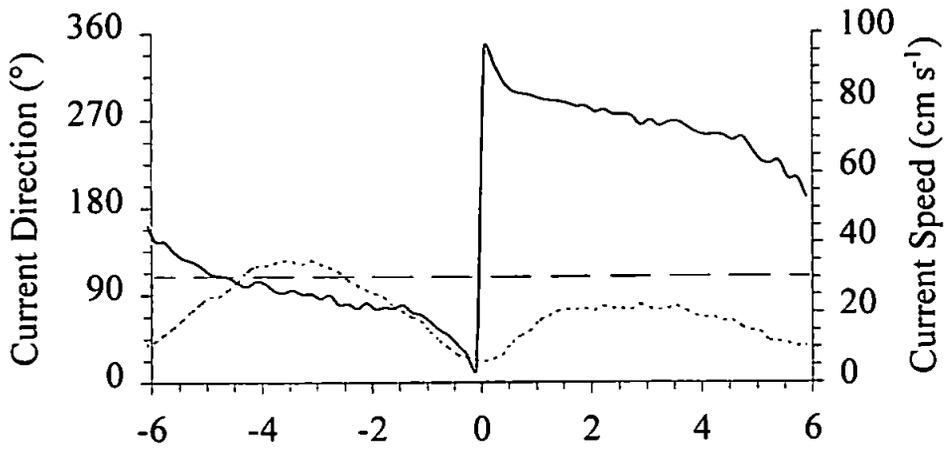
Inter-parameter correlations are poor for site Y during spring and neap tides. The preceding discussions for the spring and neap tides suggests that that the variation of metal concentrations may be a function of the influence of different sources (e.g. Seawge, industrial, fluvial) predominating during the tidal cycle rather than individual geochemistries. Suggesting trace metal concentrations were the product of the resuspension of metal rich fine material and the advection of polluted suspended particles.

3.2.3.2. Tidal Variation of Particulate Metals at Site Z.

The tidal conditions at Site Z (Figure 3.10.) are similar to Site X (Figure 3.8.), with the spring tide having higher current speeds. The current speeds during spring tides are expected to result in resuspension while the neap currents were not sufficient to induce the resuspension of sand sized material. A true slack water was not observed at Site Z (c.f. Site X), with a minimum current of $\sim 5 \text{ cm s}^{-1}$ during neaps and a minimum of $\sim 20 \text{ cm s}^{-1}$ during springs.

As previously mentioned the low number of samples available during the spring tide at site Z prevents a complete discussion of the factors affecting the variation of particle associated trace metals at this site (Figure 3.11.). The spring tide had high turbidities compared with neaps, this was also observed at site Y. Except for Pb, there appeared to be little variation in trace metal concentrations between springs and neaps even though major variations existed in turbidity. Examination of the data in Table 3.3. showed the particulate trace metal concentration in the surface sediment was lower than in the SPM for both the springs and neaps. This suggested that site Z may be dominated by advected particulate trace metals, rather than resuspension of surface sediments. In general terms the highest concentrations of Pb occur during the ebb tide which corresponded to the lowest $^{206}/^{207}\text{Pb}$ isotopic ratio.

a)



b)

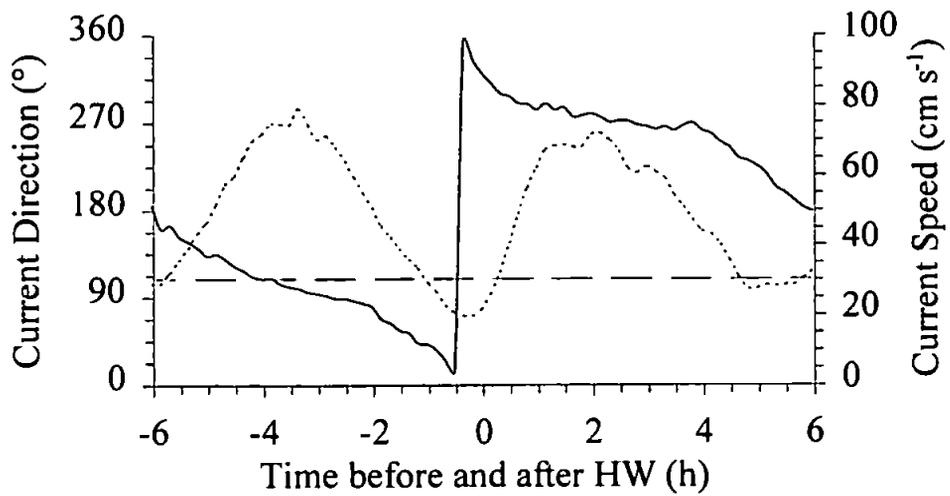


Figure 3.10. Current speed (-----) and direction (——) measured at site Z for the a) neap and b) spring tides. Indicated is the velocity 1m above the bed (— — —) required to mobilise particles of $>100\mu\text{m}$ in diameter (very fine to fine sand).

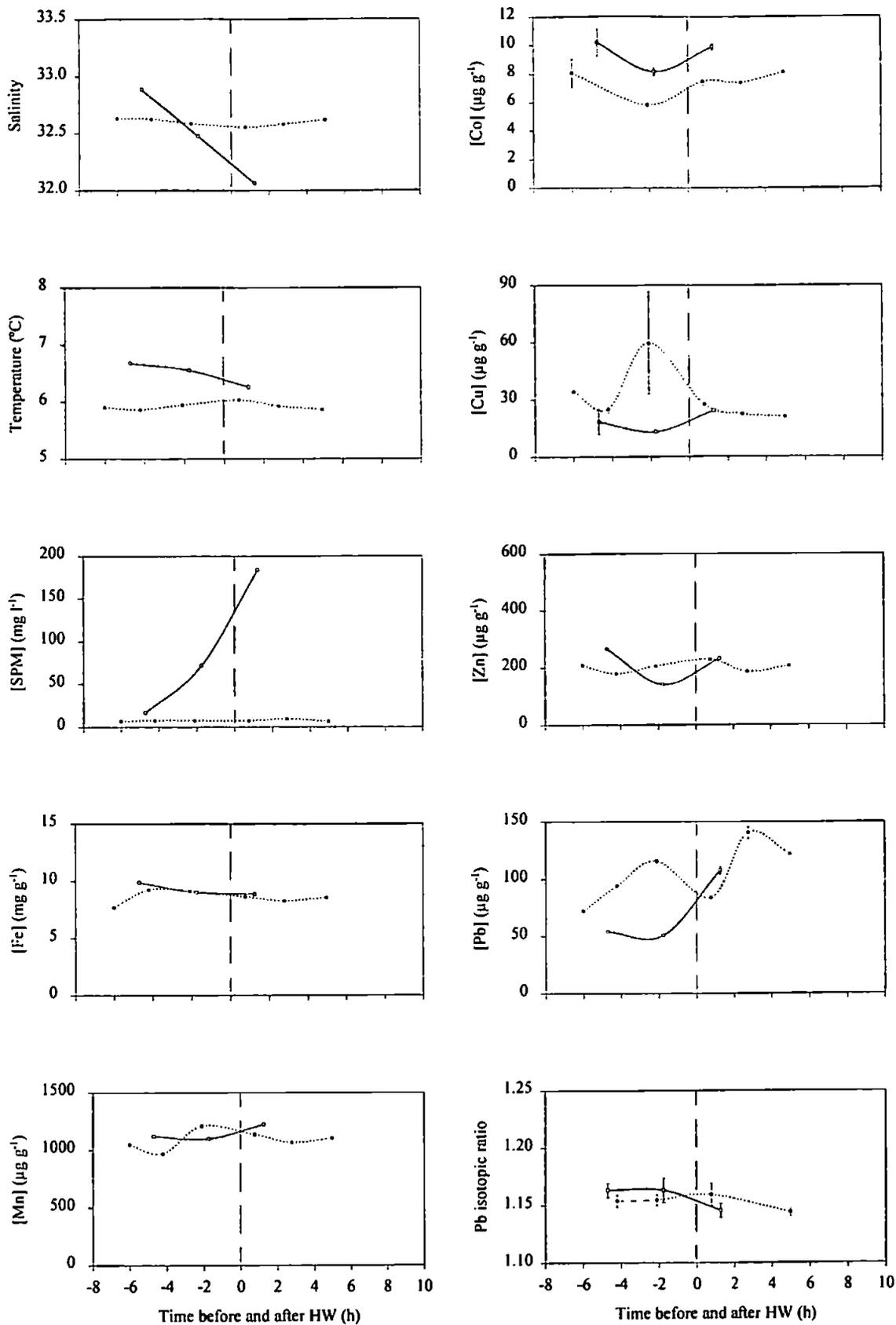


Figure 3.11. Variation of water conditions (Salinity, Temperature, SPM concentrations and particulate metal concentrations) at site Z, Irish Sea during a spring (—○—) and neap (---○---) tide.

3.3. Trace Metals in the LOIS Coastal Zone - North Sea .

3.3.1. Spatial Variation of Surface Sediments in the LOIS Coastal Zone.

Figure 3.12. illustrates the trace metal distribution in the $<63\mu\text{m}$ fraction of surface sediments in the LOIS coastal zone, clearly highlighted is the muddy area offshore of the Tees Estuary. The distribution of the % $<63\mu\text{m}$ size fraction suggested much of the area was coarse in nature, which prohibited the collection of a larger numbers of samples. The distribution in Figure 3.12a. mimicked that observed by the British Geological Survey in their sedimentary maps of the area (Sheets $54^{\circ}\text{N } 02'\text{W}$ and $53^{\circ}\text{N } 00'\text{W}$). The distribution of Ca (Figure 3.12b.) suggested the sediments in the Humber - Wash region were dominated by calcareous deposits. The Ca concentration was lower in the muddy regions. The mouth of the Humber Estuary had the largest concentrations of Fe, Mn and Zn, which may be due to metal rich (particularly Fe) industrial discharges (Figure 1.1.). Strong correlations were observed for Fe, Mn, Zn and Pb (Table 3.4.), and significant correlations of Cu with Fe, Zn and Pb were also observed, possibly due to their co-disposal by industry, while Co correlated significantly with only Fe and Mn. These correlations suggested a dependency of trace metal concentrations with ferro-manganese oxides. The sediment adjacent to the Tees Estuary had the highest concentrations of Cd and Pb in the area. The sediment in this area also had some of the lowest $^{206}/^{207}\text{Pb}$ isotopic ratios indicating that much of the Pb was anthropogenic. Information from PARCOM (1991) indicates that $>90\%$ of the Pb entering into Tees Bay is from industrial discharges.

Table 3.4. Correlation matrix of r -values ($p \leq 0.05$) for 1M HCl digests of the $<63\mu\text{m}$ size fraction of surface sediments in the LOIS coastal area.

| | % $<63\mu\text{m}$ | Ca | Fe | Mn | Zn | Cd | Co | Cu | Pb |
|------|-----------------------|----|------|------|------|----|----|------|----|
| Ca | | | | | | | | | |
| Fe | | | | | | | | | |
| Mn | | | 0.85 | | | | | | |
| Zn | | | 0.85 | 0.83 | | | | | |
| Cd | -0.44 | | | | | | | | |
| Co | | | 0.45 | 0.52 | | | | | |
| Cu | | | 0.44 | | 0.44 | | | | |
| Pb | | | 0.82 | 0.57 | 0.76 | | | 0.63 | |
| i.r. | 0.44 | | | | | | | | |

3.3.2. *Description of a Sediment Core from the Humber Mouth.*

The core was composed of approximately 50 % of $<63\mu\text{m}$ material, which was higher than the surrounding area, (which was dominated by sand and gravel). The Ca concentration which has been used to examine the amount of shell in samples, is high in this core yet the core is not coarse which suggests that calcareous material, possibly limestone, is present. The Holderness cliffs showed comparable Ca concentrations to the core, suggesting an origin for the fine material in the core.

The inter-parameter correlations observed for the surface sediment (Table 3.4.) were not observed for the sediment core (Table 3.5.), which may suggest that other processes (e.g. diagenesis) may affect trace metal association after deposition. For instance, a significant correlation between Co and Mn was obtained, and strong correlation between these two metals was previously observed (Sawlan and Murray, 1983). Yet, Fe did not correlate with any metals, this may be the result of temporal variability in the anthropogenic input of Fe deposited at this site. However, a linear increase in the ratio between Fe/Mn (Figure 3.13.) was observed. Suggesting that Fe precipitates become progressively more significant deeper in the sediment. The site is regularly resuspended by tidal action (Figure 3.18.) which would cause mixing and aeration of the upper sediment. This would cause trace metals to experience oxic or sub-oxic conditions (Section 1.4.), rather than complete anoxia, causing metal concentrations to become invariant. The steady rise in Fe/Mn ratio may be caused by the diagenetic release of Mn (suggested by its surface enrichment) while the sediment is not sufficiently anoxic to reduce Fe. Simple examination of the profiles in Figure 3.14 showed that in the upper sediment ($<10\text{cm}$) metals (Fe, Mn, Co, Zn, Cd, Pb) tended to be more enriched than in the lower sediment ($>10\text{cm}$), with small peaks in concentrations occurring coincident with peaks in % $<63\mu\text{m}$ fraction (Fe, Zn, Cd, Pb) which may suggest an enrichment of metals within the muddier layers of the core. Consideration of the Pb and $^{206}/^{207}\text{Pb}$ isotopic ratio profile suggested that at a depth of 2 to 5 cm the Pb is more anthropogenic in character. Copper has a mid core enrichment which is not observed with any of the other metals.

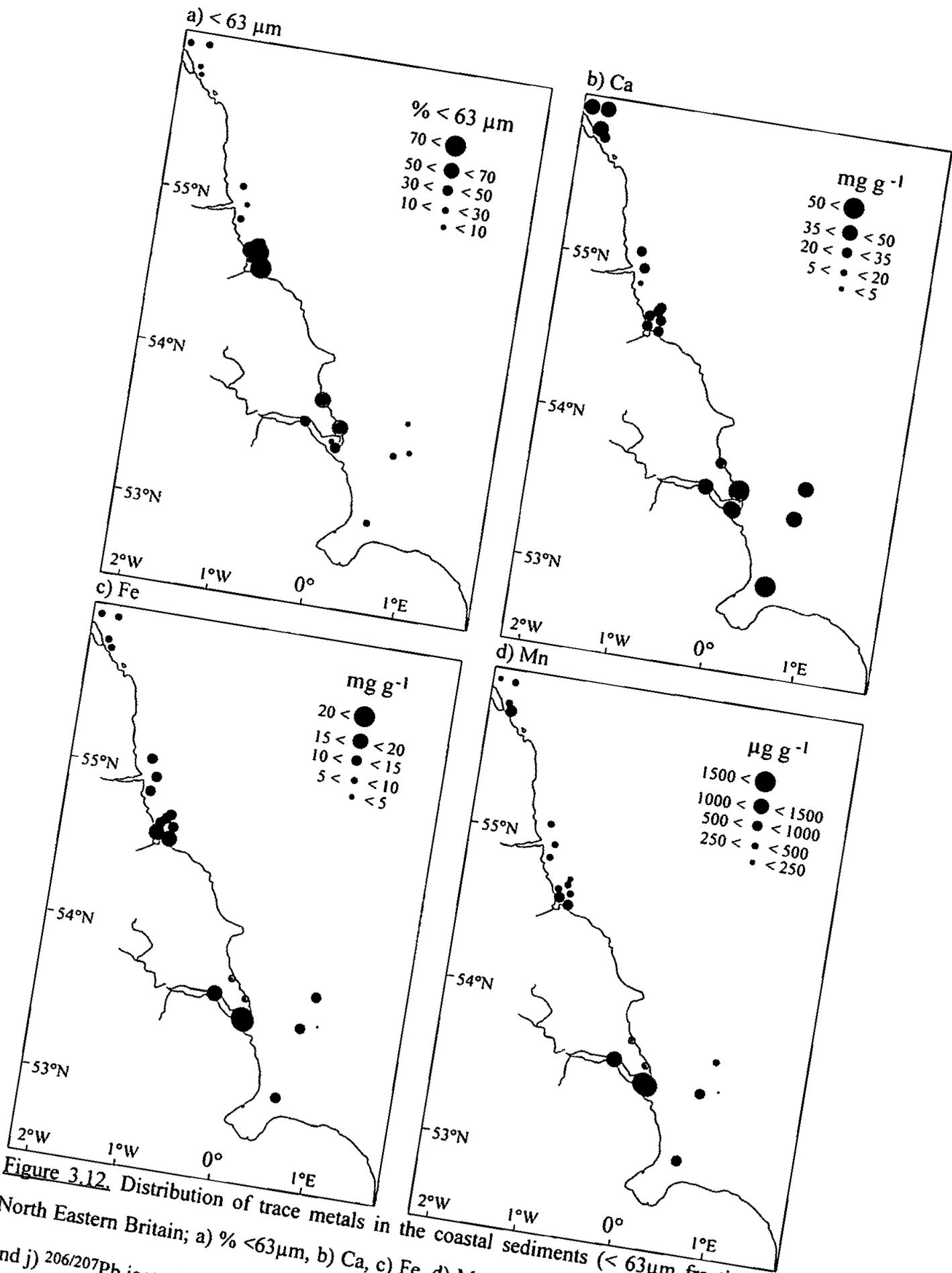
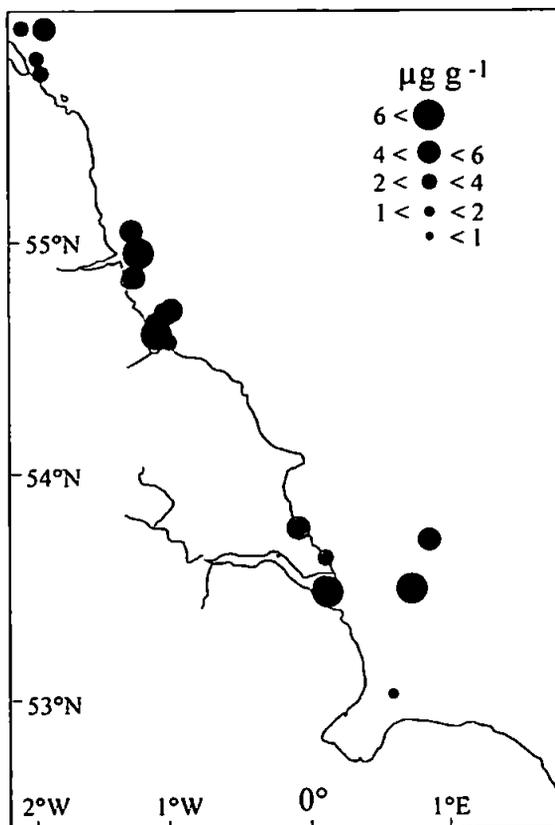
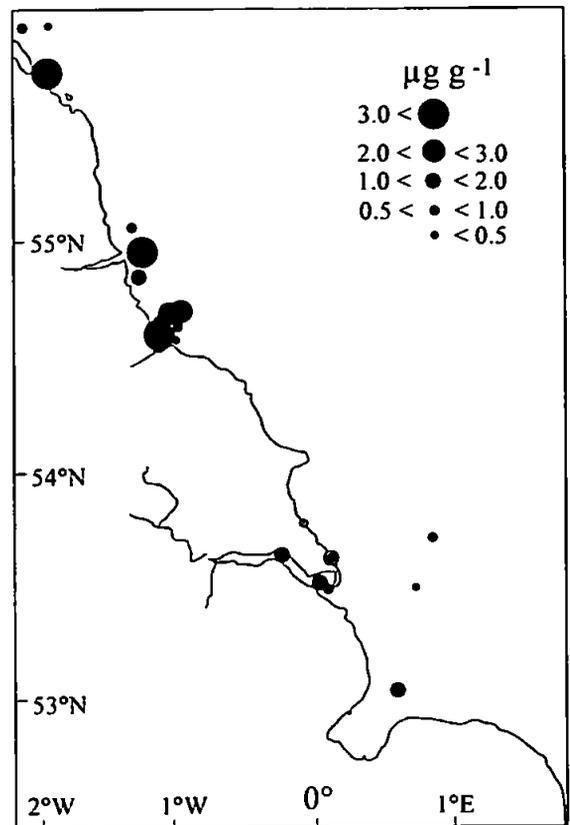


Figure 3.12. Distribution of trace metals in the coastal sediments ($< 63\mu\text{m}$ fraction) of North Eastern Britain; a) % $< 63\mu\text{m}$, b) Ca, c) Fe, d) Mn, e) Co, f) Cd, g) Cu, h) Zn, i) Pb and j) $^{206}/^{207}\text{Pb}$ isotopic ratio. ● shore based samples.

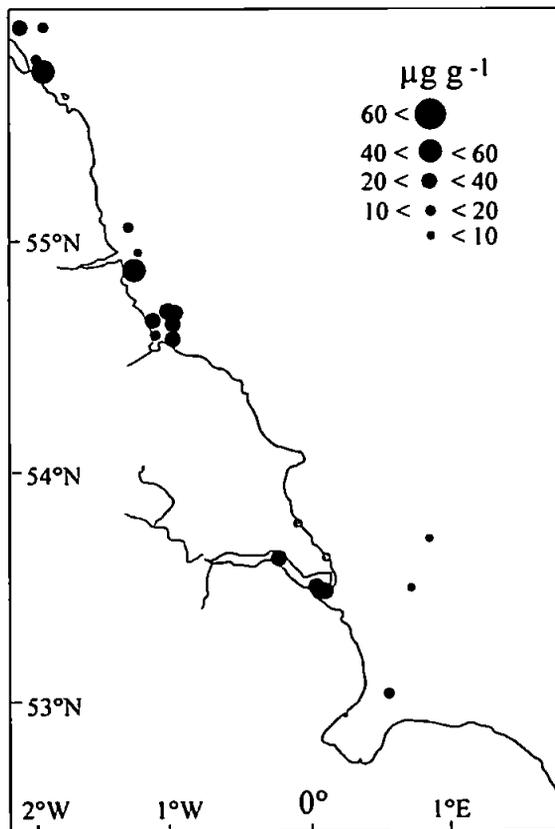
e) Co



f) Cd



g) Cu



h) Zn

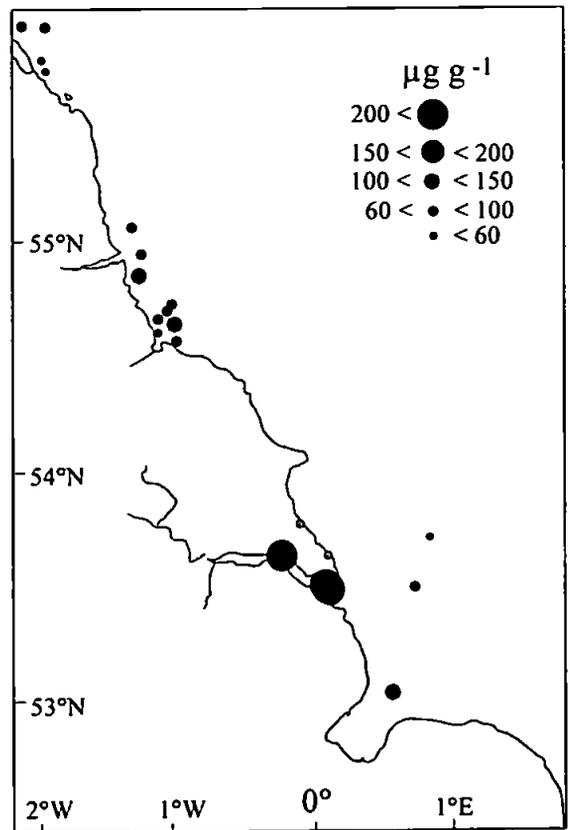
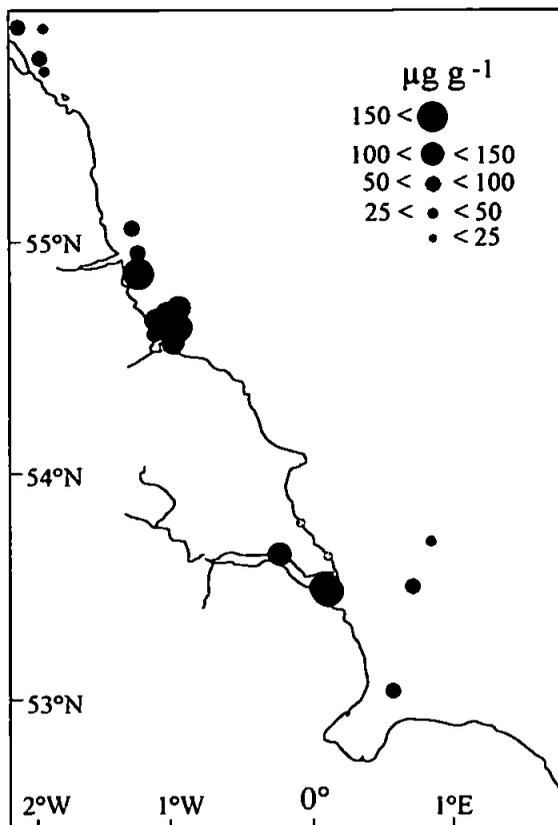


Figure 3.12, continued

i) Pb



j) ^{206/207}Pb isotopic ratio

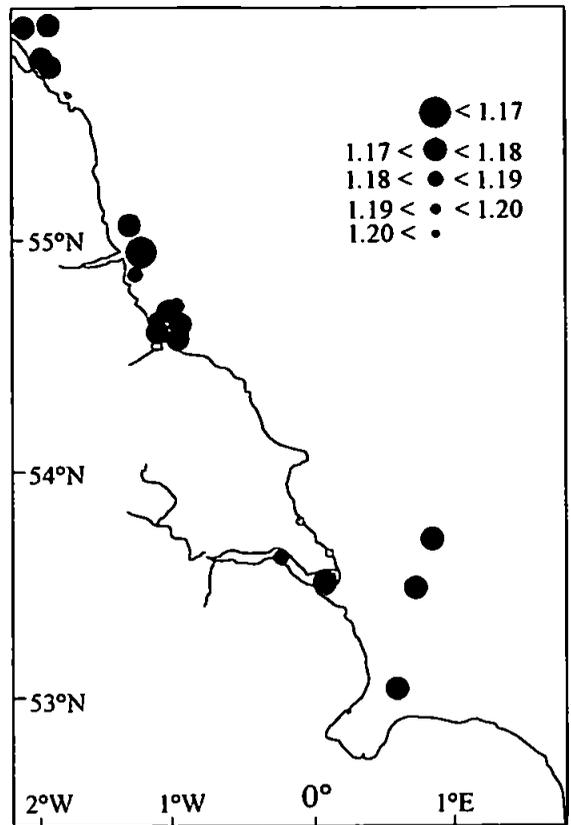


Figure 3.12. continued

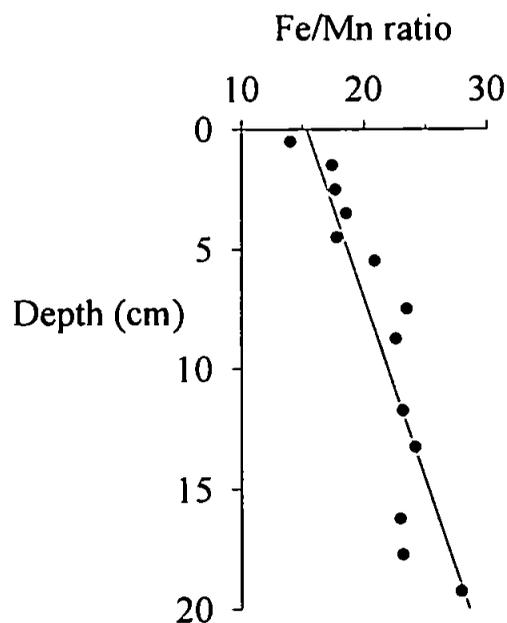


Figure 3.13. Progressive increase ($r^2 = 0.79$) in Fe/Mn ratio in a sediment core from the mouth of the Humber Estuary.

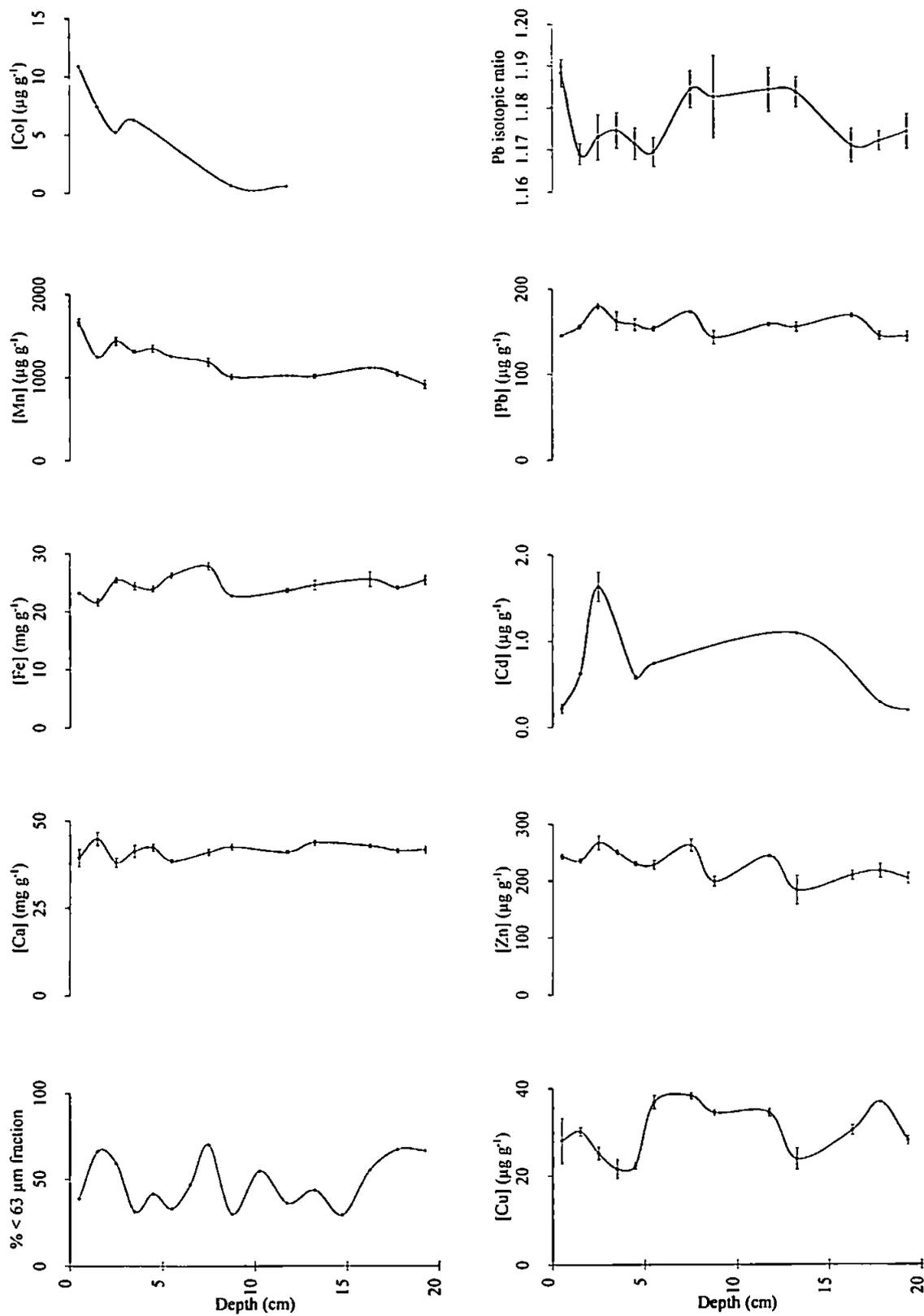


Figure 3.14. Sediment core profile taken during CH99/92 in the mouth of the Humber Estuary.

Table 3.5. Correlation matrix of r-values ($p \leq 0.05$) for trace metal concentrations obtained from a sediment core in the mouth of the Humber Estuary.

| | % fines | Ca | Fe | Mn | Zn | Cd | Co | Cu | Pb |
|------|---------|-------|----|------|------|------|----|----|----|
| Ca | | | | | | | | | |
| Fe | | | | | | | | | |
| Mn | | | | | | | | | |
| Zn | | -0.56 | | 0.63 | | | | | |
| Cd | | | | | | | | | |
| Co | | | | 0.91 | | | | | |
| Cu | | | | | | | | | |
| Pb | | | | | 0.61 | 0.93 | | | |
| i.r. | | | | | | | | | |

3.3.3. Spatial Variation of Suspended Particulate Matter in the LOIS Coastal Zone.

The highest concentrations of trace metals in the North Sea were shown to be adjacent to major freshwater sources (Figure 3.15.). The dominant inputs into this region are the Humber, Tees and Tyne. The Humber receives large discharges of Fe from the titanium processing industry (Newell *et al*, 1984). The Tees, and surprisingly the Tweed, are sources of Mn to the coastal waters. The Tweed has been considered a relatively pristine estuary (MAFF, 1992) but elevated levels of Mn have been previously observed for the Tweed (Laslett, 1995). Cobalt is discharged into coastal waters by all three of the industrialised estuaries. The highest concentrations of Cu were seen for the Tees. The highest concentrations of Zn were associated with the Tyne, Humber and Tweed but not the Tees. Cd appears to be significant for the Humber and the Tees, though two high Cd values were observed for the Tweed all other samples were not detectable and this may suggest that these values are suspect. Lead concentrations in coastal waters were highest adjacent to the Tyne and Tees estuaries, examination of the $^{206}/^{207}\text{Pb}$ isotopic ratio showed that both areas contained anthropogenic Pb, the coastal waters adjacent to the Tyne more so than the Tees. Pb refining industries are situated in this region and may suggest a source for this Pb. The observed distributions of suspended particulate trace metals were similar to the distribution based on industrial discharges (see Figure 1.1.), and suggest that the observed distribution are the result of anthropogenic inputs into this region.

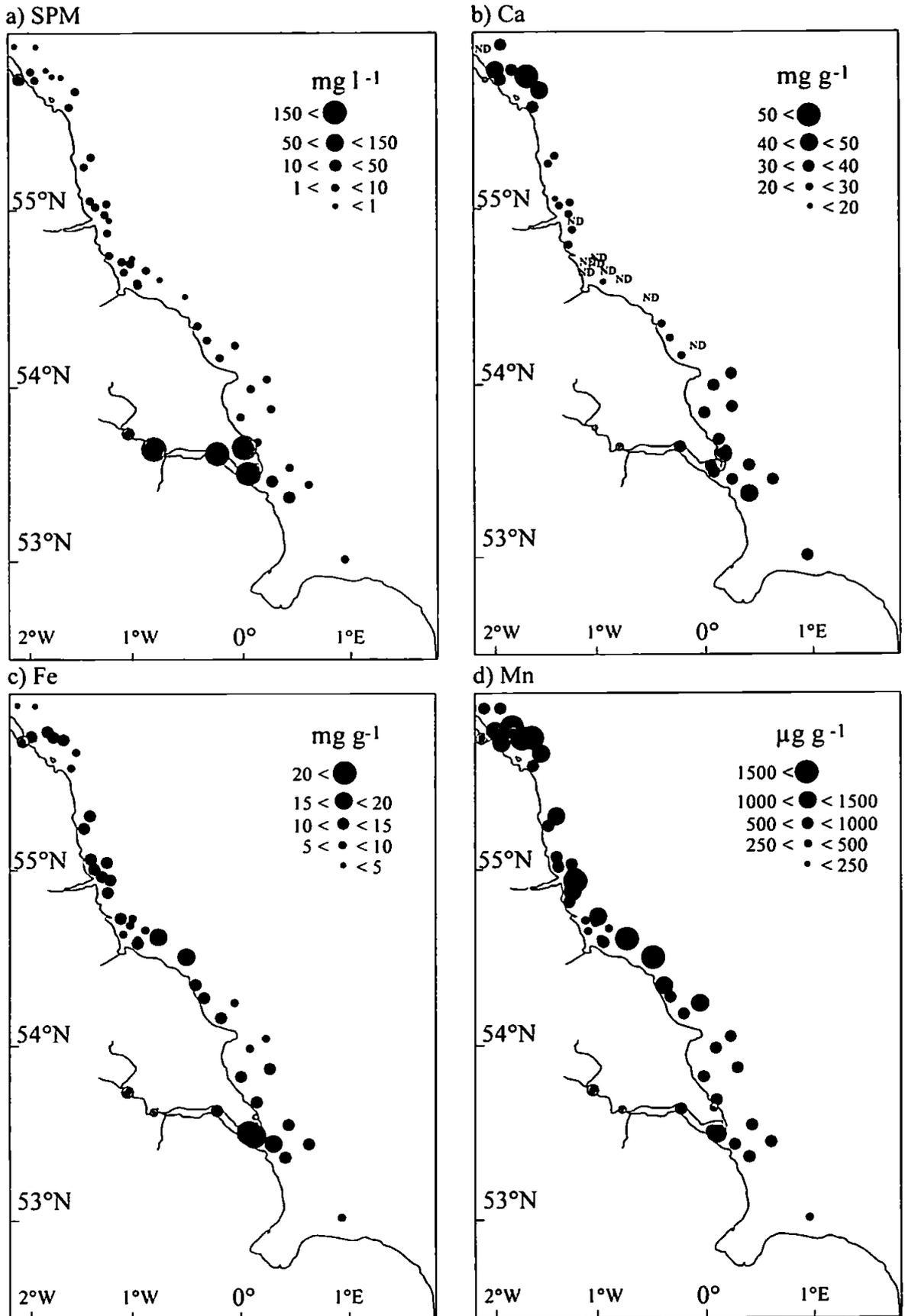
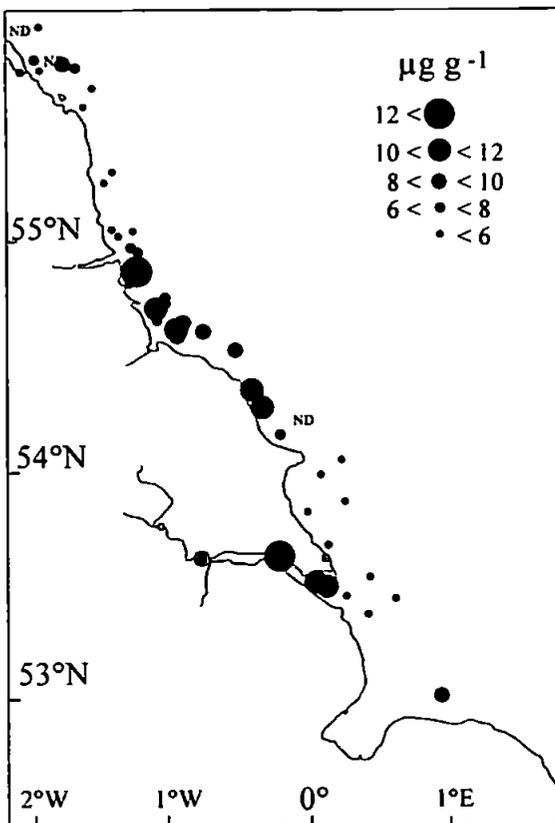


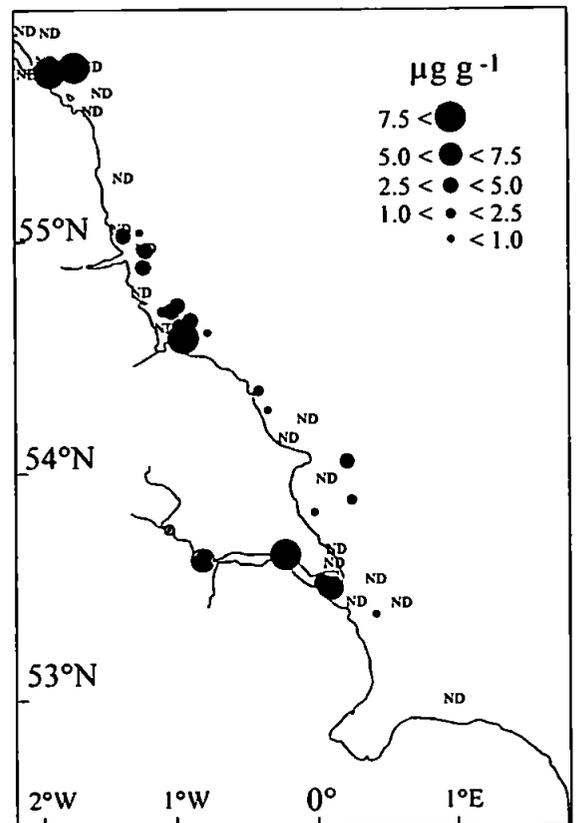
Figure 3.15. Distribution of particulate trace metals in the coastal waters of North Eastern Britain; a) SPM, b) Ca, c) Fe, d) Mn, e) Co, f) Cd, g) Cu, h) Zn, i) Pb j) ^{206/207}Pb isotopic ratio.

● shore based samples

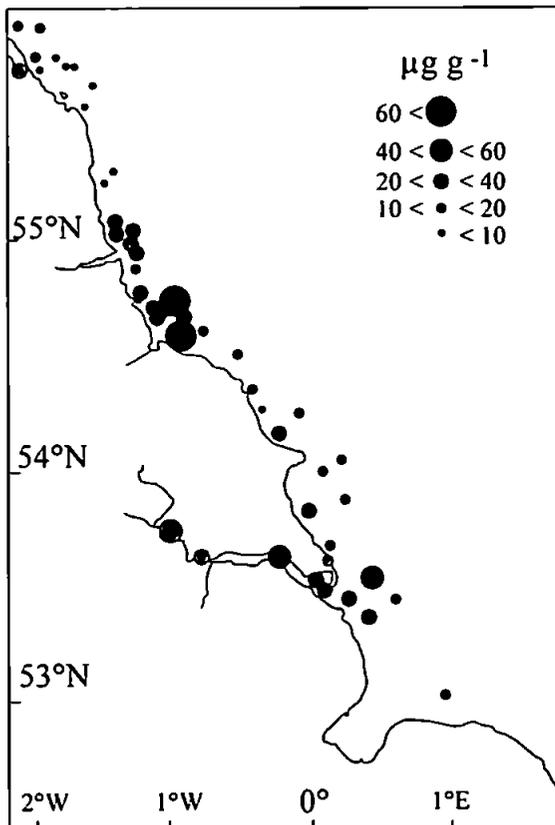
e) Co



f) Cd



g) Cu



h) Zn

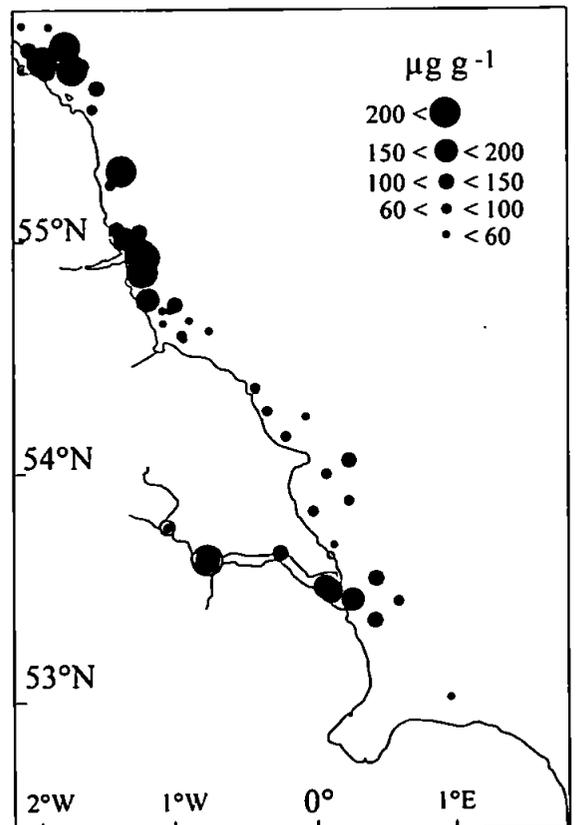
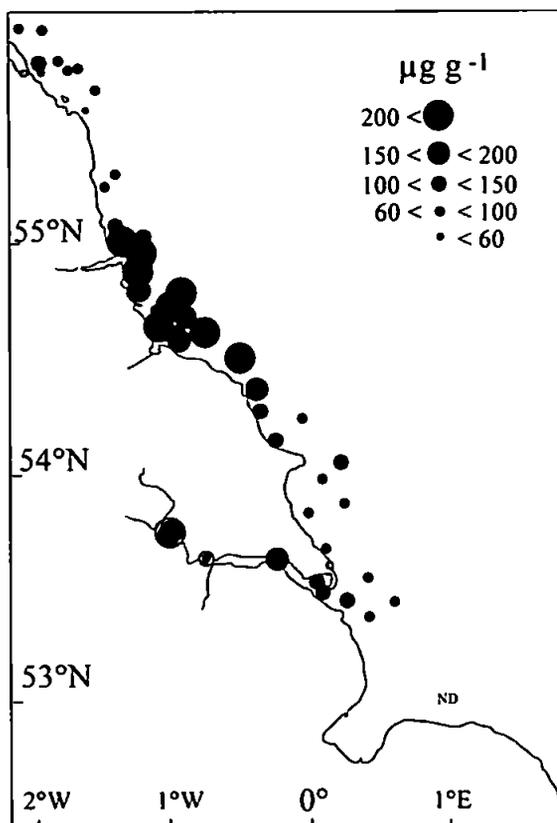


Figure 3.15. continued.

i) Pb



j) $^{206}/^{207}\text{Pb}$ isotopic ratio

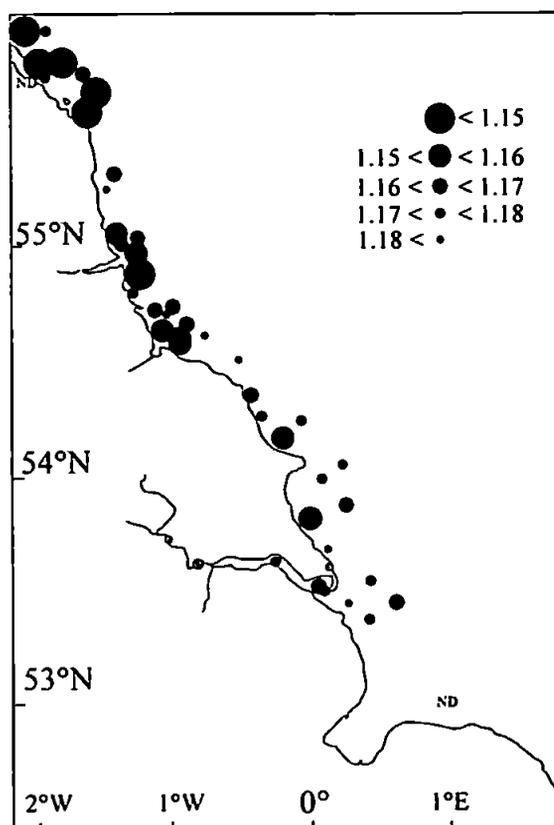


Figure 3.15. continued.

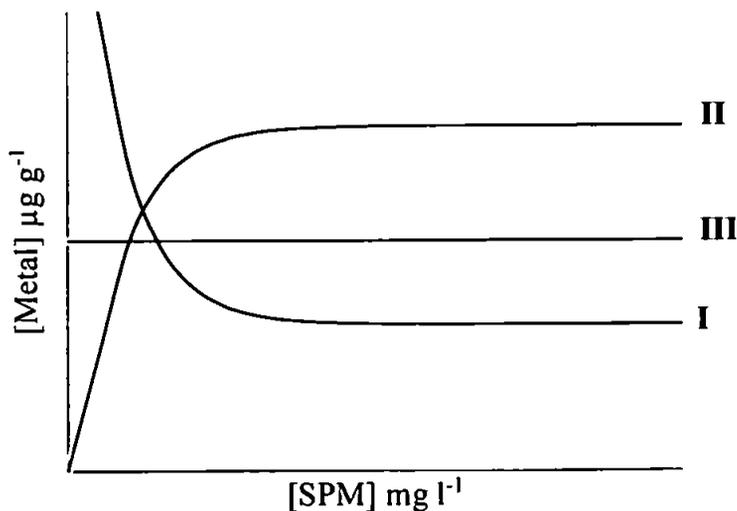


Figure 3.16. Representation of Type I, II and III trace metals behaviour as described by Duinker (1983).

Duinker (1983) proposed a model which described the distribution of particulate trace metals based on their relative association with permanently (P-SPM) and temporarily suspended particulate matter (T-SPM). The model assumes that the P-SPM is small, low

density material whereas the T-SPM is larger and more dense, and originates from either material in suspension or from the bottom sediment. Using this approach Duinker classified trace metals into three types based on their association with SPM fractions (Figure 3.16.) -

- Type I - Trace elements which preferentially associate with the P-SPM, typically Cu, Cd, Zn, Pb, organic C and organic N.
- Type II - Trace metals which preferentially associate with the T-SPM, typically Fe, Mn, Al, K and Ti.
- Type III - Trace metals which show no preference, typically Ca, Si and Cr.

Implicit in the Duinker model is the assumption that the SPM is a homogenous population without additional particulate or pollutant inputs within the region sampled. The model also assumes that slow settling particles are small and of low density, and faster settling particles are larger and of higher density, this assumption may not always be valid (e.g. floc formation, see Chapter 5). For some natural, and anthropogenically altered, situations these assumptions will not always be true and a degree of variability will be observed. However, the use of this model provides a useful way of examining the general behaviour over a large region, of particulate trace metals.

The variation of particulate trace metals with SPM in the North Sea coastal zone is shown in Figure 3.17. An algorithm has been derived for the fitted curves illustrated in Figure 3.17. (Equation 3.1.).

$$[M] = \frac{SPM^T [M]^T + SPM^P [M]^P}{SPM} \quad 3.1.$$

where, $[M]$ is the metal concentration, SPM is the concentration of SPM, superscripts T and P refer to temporarily and permanently suspended fraction. The equation was applied by using the average values of $[M]^T$, $[M]^P$ and SPM^P of the ten most turbid and ten least turbid samples to define the temporarily and permanently suspended fractions (Table 3.6.), SPM^T is a variable dependent on the value of SPM .

Some of the metals behaved as described by Duinker's model and can be divided into the different behavioural types.

- Type I - Mn, Pb, (Cd)
 Type II - Fe, Co, Cu, Ca
 Type III - Zn, ^{206/207}Pb isotopic ratio

Table 3.6. Mean values of the ten concentrations with the greatest and least SPM concentrations used as typical values for the permanently and temporarily suspended fractions.

| | SPM mg l ⁻¹ | Ca mg g ⁻¹ | Fe mg g ⁻¹ | Mn µg g ⁻¹ | Co µg g ⁻¹ |
|--------------------------------|---------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Permanently suspended fraction | 0.7 | 23.5 | 11.6 | 1853 | 5.8 |
| Temporarily suspended fraction | 88.0 | 36.4 | 16.4 | 924 | 11.0 |
| | Zn µg g ⁻¹ | Cu µg g ⁻¹ | Cd µg g ⁻¹ | Pb µg g ⁻¹ | Pb i.r.‡ |
| Permanently suspended fraction | 165 | 18.9 | 8.1† | 157 | 1.17 |
| Temporarily suspended fraction | 165 | 32.9 | 1.53 | 139 | 1.17 |

†Due to the number of Cd samples which were below the limit of detection the average SPM concentration for the permanently suspended fraction was 0.91 mg l⁻¹. The three most turbid samples were also excluded since these were polluted Humber Estuary samples ‡Pb i.r. - ^{206/207}Pb isotopic ratio.

No clearly discernible behaviour of Zn and ^{206/207}Pb isotopic ratio was observed. Both of which showed high values in sediments (Figure 3.12.) and SPM (Figure 3.15.) suggesting anthropogenic inputs within the region. The Humber and Tees estuaries are known to be pollutant sources of Cd (Taylor, 1979; Balls, 1985; Irion and Müller, 1990) with higher values of Cd observed in the turbid Humber samples. Iron is likely to be present as freshly precipitated oxides in the mouth of the Humber Estuary due to the acidic discharges by the titanium processing industry (Newell *et al*, 1984) which is the likely reason for the large variability observed in Figure 3.17.

Duinker found that the behaviour of Cu and Mn were expected to be Type II and Type I respectively, but in this work they behaved in the opposite manner. Copper is known to be associated with organic material (Cabaniss and Shuman, 1988a) and oxide coatings (Hem *et al*, 1989) which is typical of a Type I behaviour but Type II was observed. The Humber Estuary was until 1991 the site of a copper smelter and its catchment area is a highly

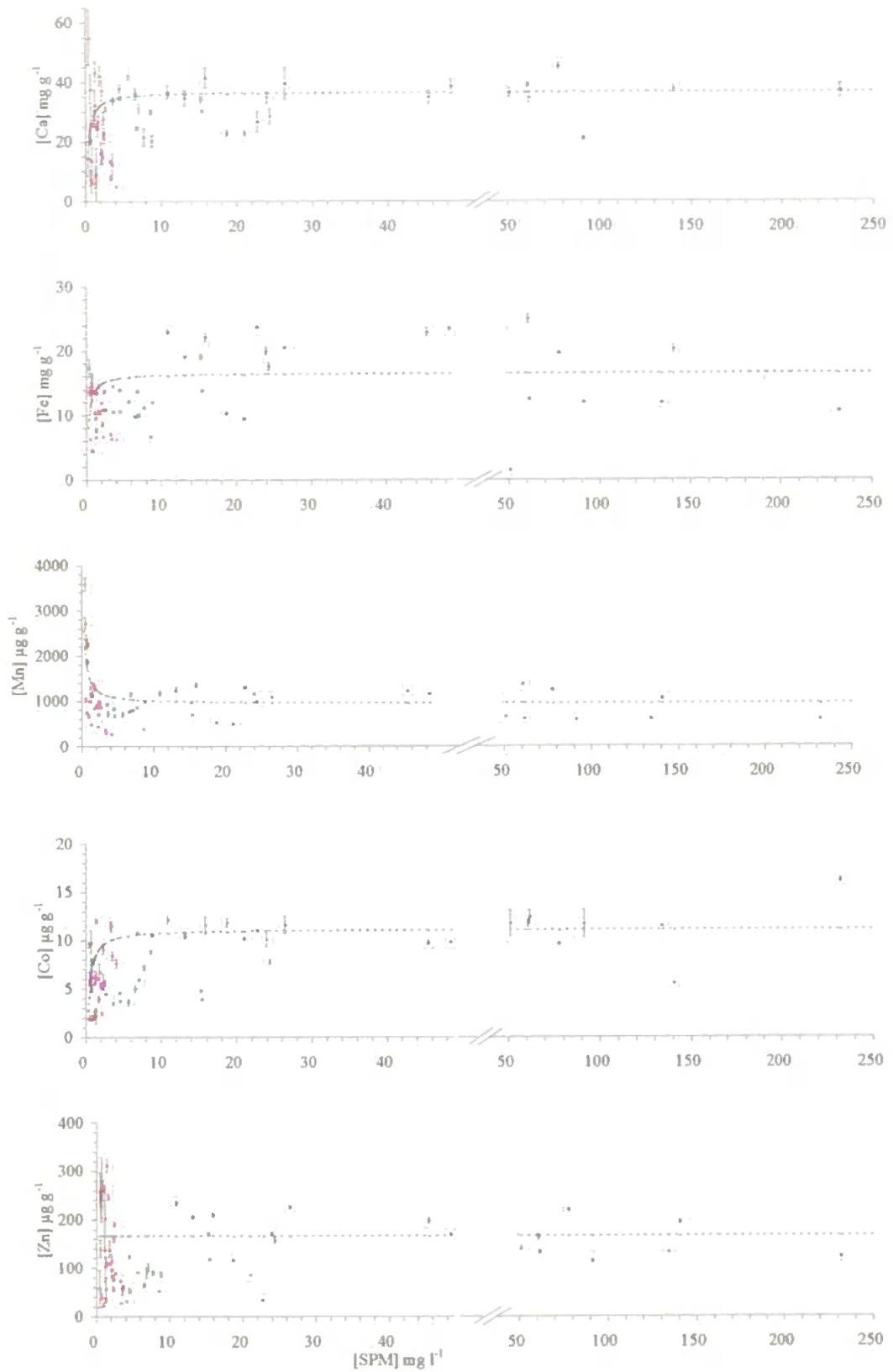
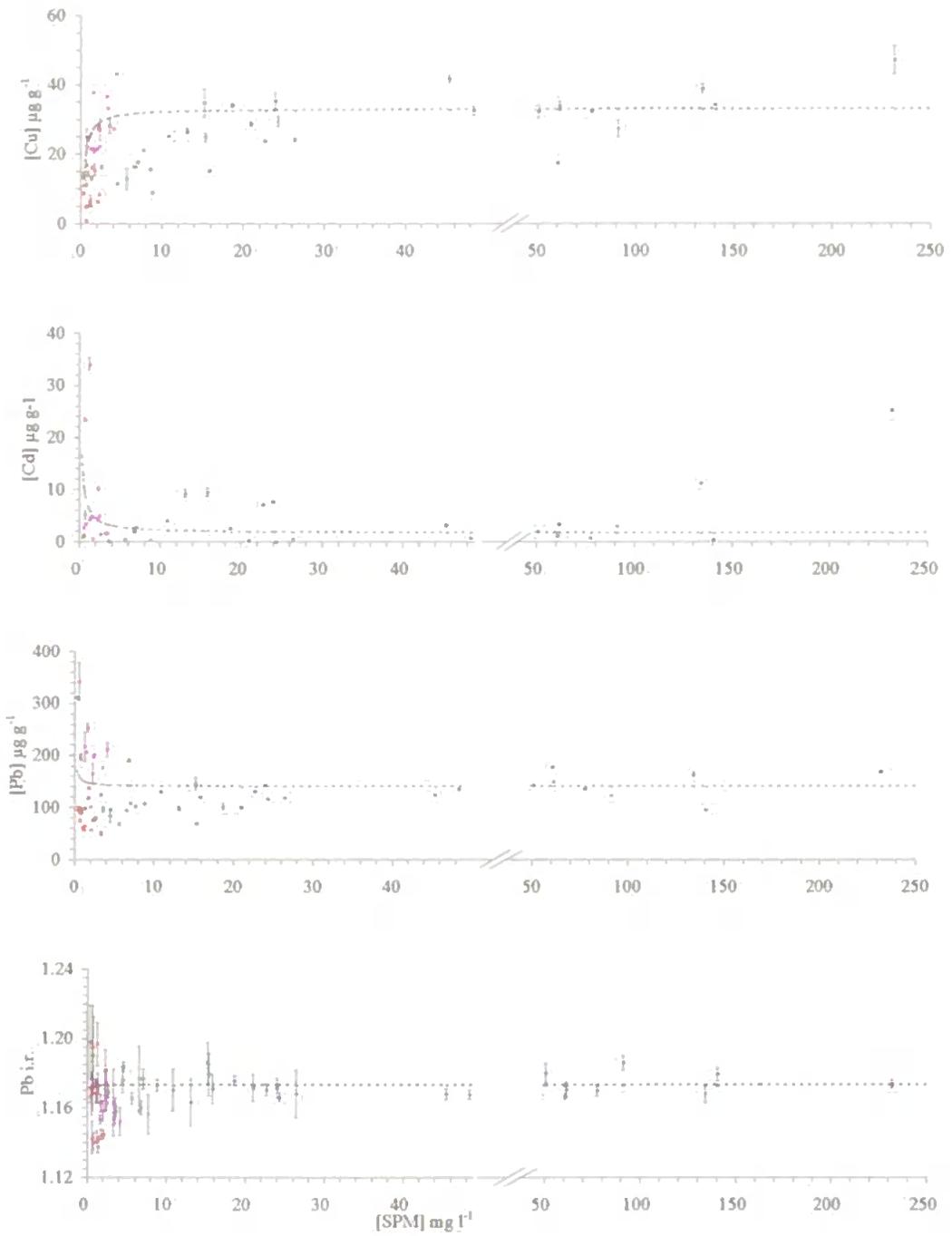


Figure 3.17. Comparison of trace metals concentrations versus SPM concentrations with regard to the Duinker (1983) model (see overleaf for key).



- Humber Estuary
- Coastal Waters - Tyne/Tees
- ▲ Coastal Waters - Tweed
- Coastal Waters - Humber

Figure 3.17. continued.

mineralised region, these considerations may suggest that the Cu is predominantly associated with mineral ores rather than organic matter and hence behaves in a Type II manner. Duinker suggested that Type I elements were associated not only with organic material but also with ferromanganese oxide coatings, the Type I behaviour of Mn suggests that the autocatalytic precipitation of Mn may still be occurring in the coastal waters.

The distinction of trace metals by their association with different settling fractions has been examined in Chapter 5 using a modified Owen Tube. The results of the Owen Tube work, given in Section 5.5.2., were not vastly dissimilar to those observed based on the Duinker model for the North Sea. The metals showing identical behaviour were Zn, Pb, and Cd. Most of the other metals showed no definite behaviour for the Owen tube.

3.3.3. Tidal Variation of Particulate Trace Metals at the Humber Mouth.

The tidal profiles of salinity and temperature showed relatively low values due to advection of fresher and cooler riverine water mixing with the warmer more saline coastal water. During flood and ebb periods resuspension events were observed, the SPM profile showed an increase in SPM concentration at -3h LW and at +2h LW. High water is the least turbid, presumably due to the settling of the resuspended material. This suggests that SPM at HW is the permanently suspended fraction and may be more offshore in nature since the flood tide would have just finished, and the resuspended material would be similar to sedimentary material, the similarity between surface sediment and suspended particulate trace metals (except for Cd) is clearly shown in Table 3.7. Thus, the tidal profiles are a series of different particle populations (as illustrated in Figure 1.3.) mixing and settling within this region. The discrepancy of Cd may be due to its association with organic matter and hence, a slower settling fraction (see Section 5.5).

A number of significant inter-parameters correlations ($p \leq 0.05$) were observed (Table 3.8.). SPM and Pb correlated negatively with salinity suggesting either a freshwater origin for the particulate Pb or pollutant inputs into less saline water. Strong correlations existed between Fe - Mn, and Mn - Zn, and a weaker correlation between Fe - Zn, which may indicate preferential adsorption of Zn by oxides of Mn compared with Fe oxides. Correlations were also observed between Ca - Mn and Ca - Zn. Of interest was the suggestion of a correlation between $^{206/207}\text{Pb}$ isotopic ratio with Fe and Mn. This may

mean that Pb of anthropogenic origin is preferentially associated with the ferromanganese coatings, further evidence of this is given from the sequential extraction described in Section 2.3.1.

Table 3.7. Average particulate trace metal concentrations (SPM) and <63µm sediment trace metal concentrations for the mouth of the Humber Estuary. Trace metal concentrations are those available to a 1M HCl digest.

| | Ca | Fe | Mn | Zn | Cu | Co | Cd | Pb | ^{206/207} Pb |
|--------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|-----------------------|
| | mg g ⁻¹ | mg g ⁻¹ | µg g ⁻¹ | i.r. |
| SPM | | | | | | | | | |
| Mean | 34 | 18 | 1010 | 174 | 29 | 10.8 | 3.7 | 128 | 1.17 |
| Stdev | 7 | 7 | 320 | 46 | 7 | 1.2 | 3.2 | 20 | 0.01 |
| n | 16 | 16 | 16 | 16 | 16 | 16 | 15 | 16 | 16 |
| <63µm Sediment | | | | | | | | | |
| mean | 39 | 21 | 1266 | 236 | 30 | 7.0 | 0.8 | 155 | 1.18 |
| stdev | 3 | 5 | 553 | 59 | 6 | 3.4 | 0.5 | 17 | 0.01 |
| n | 5 | 5 | 5 | 5 | 5 | 3 | 5 | 5 | 5 |

As observed with the Irish Sea, particulate Pb concentrations and the ^{206/207}Pb isotopic ratio do not correlate significantly. Though initially this may be expected the concentration of Pb need not be dependent on the anthropogenic content of that lead, i.e. low Pb values could be highly anthropogenic or of natural origin. The ^{206/207}Pb isotopic ratio was invariant throughout the flood and ebb periods but a rise was suggested at HW consistent with less anthropogenically derived Pb present at HW. The invariant nature of the ^{206/207}Pb isotopic ratio during the flood and ebb periods suggest that the Pb is of similar anthropogenic content during these periods of the tide.

The trace metal concentrations over a tidal cycle (Figure 3.18.) showed similar values of Fe, Mn, Co, Zn and ^{206/207}Pb isotopic ratios during the flood and ebb periods, which indicated that the material on the flood and ebb tide was geochemically similar and that the suspended material may advance and retreat over the tidal cycle. Other metals showed different profiles, Cu had a higher concentration during the ebb tide compared to the flood tide (95% confidence interval). Whereas, during the flood tide Cd concentrations showed

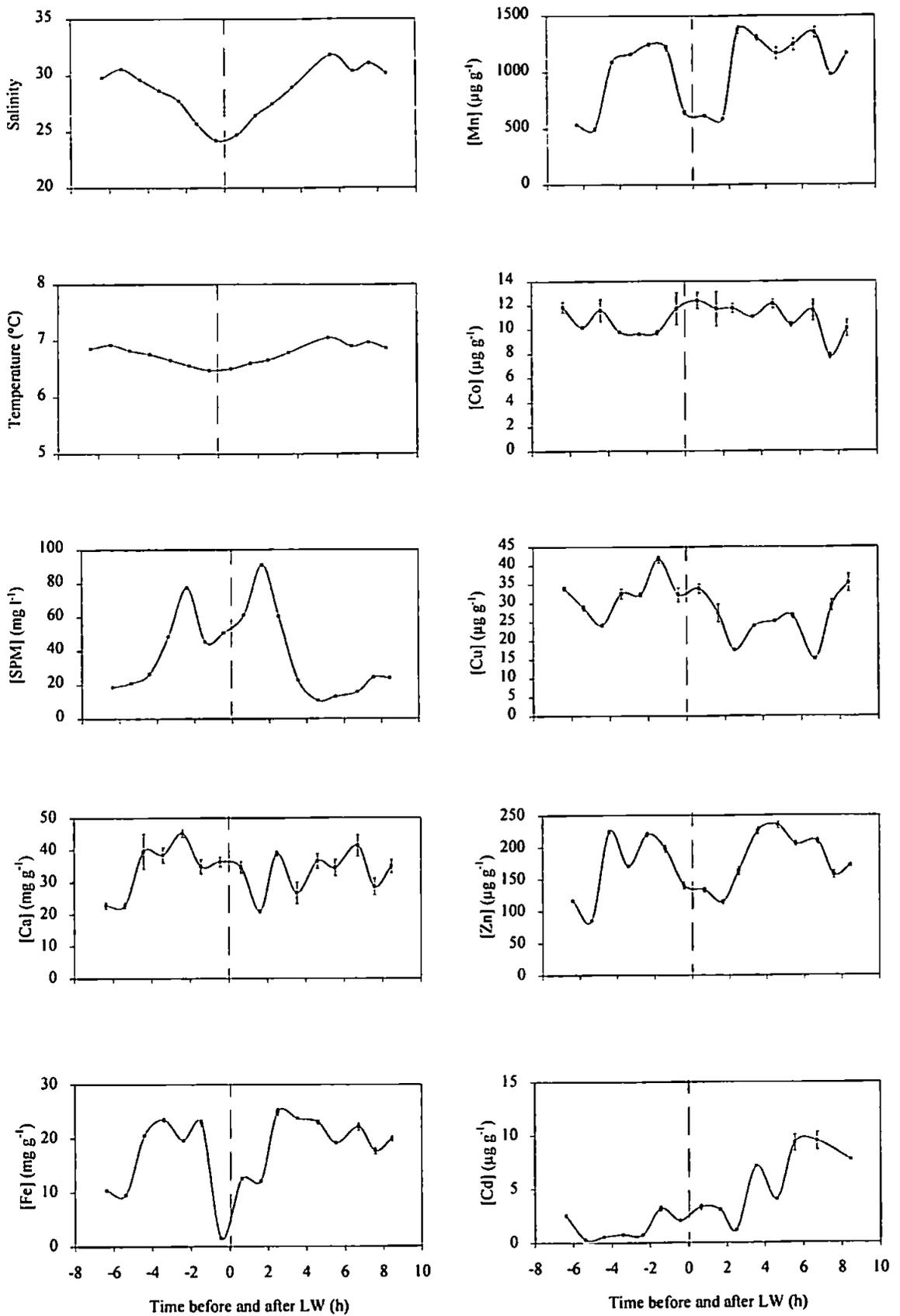


Figure 3.18. Variation of measured variables at the Humber mouth, North Sea during a neap tide.

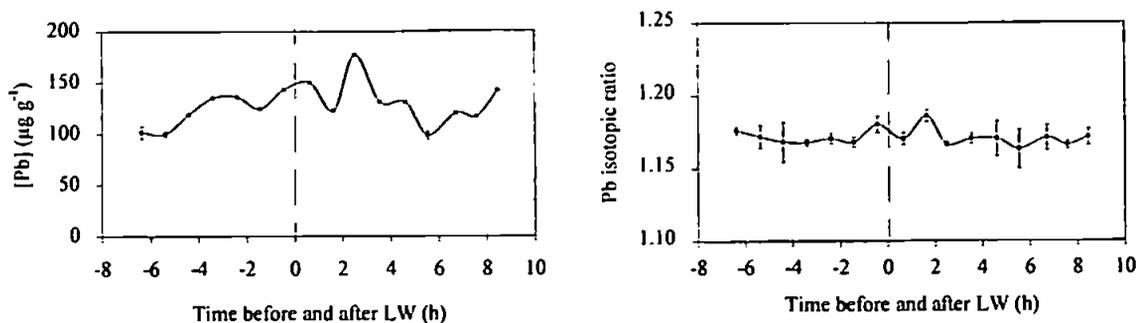


Figure 3.18. continued

a progressive increase. The sediment core taken in this vicinity showed high Cd concentrations in the surface 5cm (Figure 3.14.). Resuspension was observed during the ebb and flood tide (Figure 3.18.), but Cd only showed an increase during flood tide. The Humber Estuary is a known source of Cd (Balls, 1985) and the behaviour of Cd in this region requires further examination.

Table 3.8. Correlation matrix of r-values ($p \leq 0.05$) for SPM trace metal concentrations and other variables at the Humber mouth anchor station.

| | SPM | Salinity | Ca | Fe | Mn | Zn | Cu | Co | Cd | Pb |
|----------|-------|----------|----|-------|-------|-------|----|----|----|----|
| Salinity | -0.74 | | | | | | | | | |
| Ca | | | | | | | | | | |
| Fe | | | | | | | | | | |
| Mn | | | | 0.65 | 0.89 | | | | | |
| Zn | | | | 0.65 | 0.73 | 0.85 | | | | |
| Cu | | | | | | | | | | |
| Co | | | | | | | | | | |
| Cd | | | | | | | | | | |
| Pb | 0.50 | -0.58 | | | | | | | | |
| i.r. | | | | -0.66 | -0.64 | -0.51 | | | | |

Table 3.9. Comparison of particulate trace metal flux outputs with total flux inputs to the Humber Estuary.

| | | Salinity | Flow† | SPM | Ca | Fe | Mn | Zn | Cu | Co | Cd | Pb |
|---------------------------------------|----------------------|----------|--------------------------------|--------------------|--------------------|---------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| | | | m ³ s ⁻¹ | mg l ⁻¹ | kg d ⁻¹ | kg d ⁻¹ | kg d ⁻¹ | kg d ⁻¹ | kg d ⁻¹ | kg d ⁻¹ | kg d ⁻¹ | kg d ⁻¹ |
| Particulate trace metal output | | | | | | | | | | | | |
| CH42 (1) | Dec-88 | 30.8 | 405 | 55 | | 64500 | 1780 | 298 | 55 | 34 | 0.6 | 185 |
| CH42 (2) | Dec-88 | 30.7 | 405 | 81 | | 109000 | 3080 | 544 | 96 | 57 | 0.6 | 302 |
| CH65 | May-90 | 31.5 | 208 | 21 | | 12400 | 560 | 103 | 13 | 4 | 0.1 | 39 |
| CH69 | Aug-90 | 32.4 | 107 | 2 | | 550 | 28 | 6 | 1 | < 1 | 0.0 | 2 |
| CH99 | Dec-92 | 28.5 | 640 | 38 | 72000 | 35900 | 2060 | 336 | 63 | 23 | 5.6 | 283 |
| Total Input | | | | | | | | | | | | |
| | 1985-89 ^a | | | | | 175000 ^b | | 2670 | 420 | | 16.6 | 350 |
| | 1990 ^c | | | | | | | 2140 | 275 | | 6.1 | 215 |
| | 1991 ^d | | | | | | | 2050 | 225 | | 7.9 | 540 |
| | 1992 ^d | | | | | 118000 ^e | | 2020 | 205 | | 9.7 | 258 |

a: NRA, 1993a; b: Newell *et al.*, 1984; c: PARCOM, 1991; d: NRA, 1993b; e: Tioxide, 1993;

† Flow calculated as the residual flow, based on the method outlined by Wood,(1993).

Table 3.9. collates information from a variety of sources regarding the flux of trace metals into and from the Humber Estuary. The input data has been primarily obtained using metal data from acidified river water and measured flowrates. The output data was obtained from acid digested SPM from this study and previous similar studies, calculations used the residual flow data at the Humber mouth modelled using salinity as a conservative end member. Despite the desired for compatible methods of calculations these flux data provide a useful comparison of flux magnitudes. From the average particulate trace metal concentrations obtained at the Humber mouth estimates of particulate trace metal fluxes can be made (Table 3.9.). The significance of the dissolved component compared with the particulate component is dependent on season and the trace metal under examination (Glegg and Millward, 1995). For metals such as Fe and Pb >95% was associated with particles throughout the year, whereas although Co, Zn and Cu were predominantly particle associated in the winter (~70%) the dissolved phase became more dominant during the summer. Cadmium was primarily in the dissolved phase (>50%) throughout the year (Glegg and Millward, 1995). Hence, for the majority of the metals examined during winter the dissolved flux did not contribute significantly to the calculated flux. A comparison of the total inputs with the outputs of trace metals (Table 3.9.) suggested that the Humber Estuary may be accumulating trace metals (Fe, Zn, Cu and possibly Cd). The estuary will act as a depository of these metals and would continue to slowly release them over time even if no further inputs were made. Lead was the only metal which appeared not to be retained and this may be due to its affinity for fine grain material (Section 5.1.). These slow settling particles would have the potential for long range transport.

3.4. Conclusion.

Trace metals in the Irish Sea originated from relatively few sources and contamination occurred by advection of material into different regions of the Irish Sea. High concentrations of trace metals in Liverpool Bay sediment were resuspended and transported into less contaminated sediments along the Cumbrian coastline, this movement was exemplified by the change in surface sediment $^{206}/^{207}\text{Pb}$ isotopic ratio. The current system caused a high degree of mixing, with an underlying northward transport. In contrast along the north east coast of Britain, contamination of the coastal waters appeared

to occur via three estuaries, the Humber, Tees and Tyne. Each estuary being enriched with a selection of different trace metals. The trace metals were advected from the estuary and settled into the coastal waters. The current regime transports the SPM southward towards more contaminating estuaries, resulting in higher trace metal concentrations in the coastal waters of the North Sea compared with the Irish Sea (compare Tables 3.3. and 3.7.).

Chapter 4 - Stable Lead Isotopes.

Chapter 4 - Stable Lead Isotopes.

4.1. Introduction.

Four stable isotopes of Pb exist in the environment - ^{204}Pb (~1.5 %), ^{206}Pb (~23.6 %), ^{207}Pb (~22.6 %) and ^{208}Pb (~52.3 %) (Faure, 1986). The isotopes ^{206}Pb , ^{207}Pb and ^{208}Pb are produced by the natural radioactive decay of U and Th (Figure 4.1.), while the ^{204}Pb isotope is not. Hence, primordial Pb, which contained all four stable isotopes, has been constantly supplemented by additions of ^{206}Pb , ^{207}Pb and ^{208}Pb at known rates (from ^{238}U , ^{235}U and ^{232}Th , respectively) during the Earth's history to produce 'modern' lead. The ratios of these isotopes to the non-radiogenic ^{204}Pb isotope can provide a chronometric measure of age (e.g. Peitit *et al*, 1984). A growth curve, using either $^{207}/^{204}\text{Pb}$ vs $^{206}/^{204}\text{Pb}$ or $^{208}/^{204}\text{Pb}$ vs $^{206}/^{204}\text{Pb}$, can be produced to determine an age for the mineral under examination (Doe, 1970; Doe and Stacey, 1974; Kersten *et al*, 1992). However, other processes can perturb the estimation of the geological age. Additions and removal of U or Pb due to geological and geochemical processes can perturb the Pb isotope growth curve. One of the decay products is Rn (Figure 4.1.), a gaseous element which has the potential to escape from the parent mineral, thereby causing ages which are anomalous to the predicted growth curve. These open systems cause the Pb isotopic growth curve to become linear (Faure, 1986).

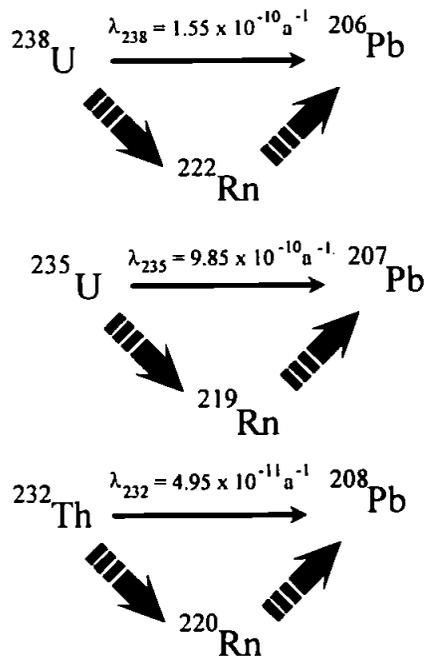


Figure 4.1. Production of Pb isotopes from their natural decay series. λ = decay constant

4.2. Variation in Stable Pb Isotopic Ratio's due to Mixing.

The Pb isotopic data for sediment and SPM of the Irish and North Sea are plotted in Figure 4.2. The non-radiogenic ^{204}Pb isotope allows the isotopic data to be normalised. Shown in Figure 4.2. are isotopic ratios indicative of pure anthropogenic Pb (NIST 981, Broken Hill and Associated Pb), and uncontaminated Pb (Holderness boulder clays) which was typified by a ratio of crustal Pb (Faure, 1986). The Irish and North Sea sediments and North Sea SPM have ratios which cluster close to that expected for the crustal average. The sediment and SPM ratios lie close to a line joining the primordial Pb and typical crustal Pb. Of particular interest were certain samples of Irish Sea SPM which had ratios close to primordial Pb and may suggest low concentrations of the ^{206}Pb and ^{207}Pb isotopes and thus low U contents. Yet, other Irish Sea samples had ratios greater than the average crustal ratio, suggesting enrichment of U. No discernible spatial pattern was observed to explain these observations. Anomalous Pb ratios are not uncommon and are often the result of the mixing of two different radiogenic Pb's (Faure, 1986). The Albright and Wilson effluent is derived from the processing of apatite which is known to be enriched in U. The effluent has an exceptionally high $^{206}/^{204}\text{Pb}$ ratio suggesting ^{238}U enrichment. Further work examining the abundances of Pb and U isotopes is required to gain a better understanding of the complex behaviour of these particles, particularly for Irish Sea suspended particles.

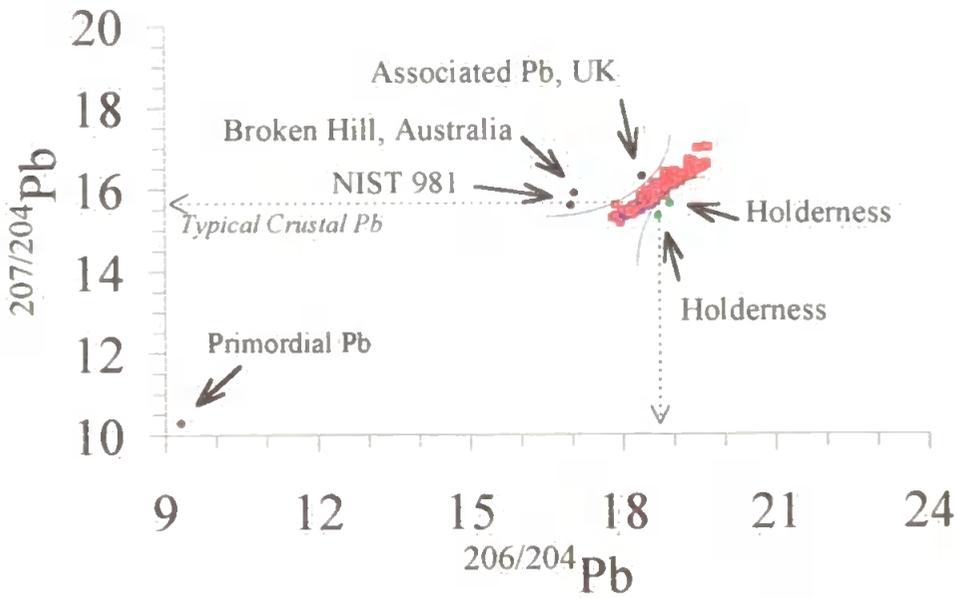
Quantitative use of the $^{206}/^{207}\text{Pb}$ isotopic ratio (Section 1.4.3.), requires the mixing of natural and anthropogenic sources of Pb to be understood. The abundance of each isotope can be determined from Equation 4.1. The variation of the $^{206}/^{207}\text{Pb}$ isotopic ratio may be due to changes in the abundance of either ^{206}Pb or ^{207}Pb .

$$\% \text{ abundance of isotope } i = \frac{\frac{i}{206}}{\frac{204}{206} + \frac{207}{206} + \frac{208}{206} + 1} \times 100 \quad 4.1.$$

where i is either 204, 206, 207 or 208.

It can be seen that the % abundance for each isotope gives a linear relationship with the $^{206}/^{207}\text{Pb}$ isotopic ratio (Figure 4.3.). The $^{206}/^{207}\text{Pb}$ isotopic ratio correlated (95%

a)



b)

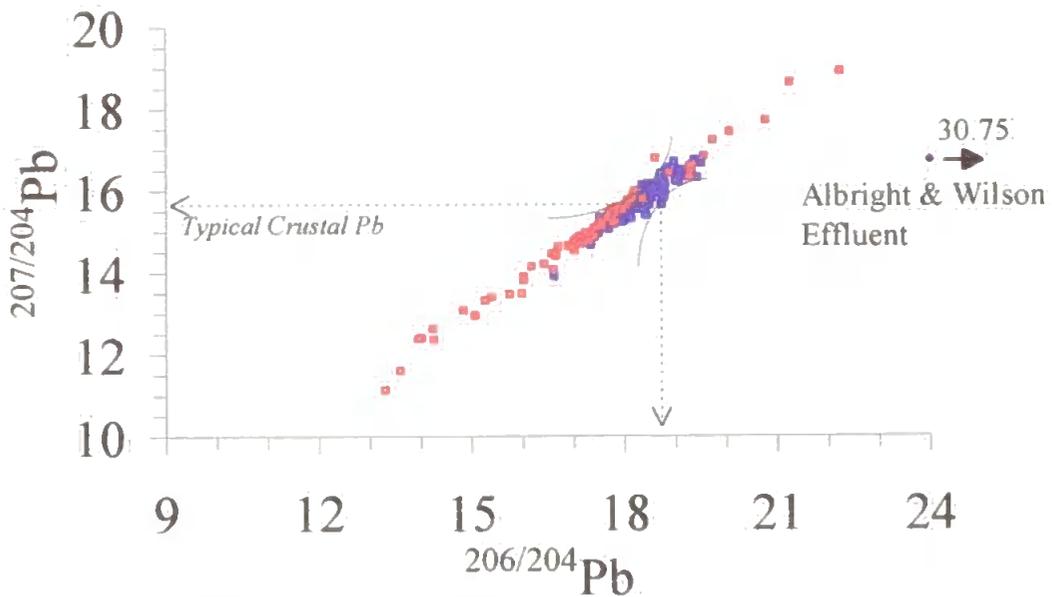


Figure 4.2. Stable Pb Isotopic ratios for a number of samples of a) sediment and b) SPM in the Irish Sea (CH88 - ■) and the North Sea (CH99 - ■), indicated in the diagrams are a number of key ratios (primordial Pb, Holderness boulder clay, UK Pb sources) and the typical ratio for crustal Pb (-----).

confidence) with both the ^{206}Pb and ^{207}Pb % abundance's, but the ^{208}Pb showed no significant correlation (this was similar to the ^{204}Pb trend, not illustrated). Thus the $^{206}/^{207}\text{Pb}$ isotopic ratio was dependent on the % abundance of ^{206}Pb and ^{207}Pb whose inverse covariation resulted in the uniform % abundance of ^{208}Pb . Therefore, a prediction of the % abundance of the stable isotopes, based on the $^{206}/^{207}\text{Pb}$ isotopic ratio, can be made. It should be noted, Figure 4.3. represents a mixing of the stable isotopes of natural (1.21) and anthropogenic lead (1.07). Thus, ^{206}Pb and ^{207}Pb isotopes mixed conservatively but the gradients for each were different e.g. ^{206}Pb : +9.24 and ^{207}Pb : -10.66 (Figure 4.3.), suggesting the $^{206}/^{207}\text{Pb}$ isotopic ratio will not behave conservatively during the mixing of natural and anthropogenic Pb.

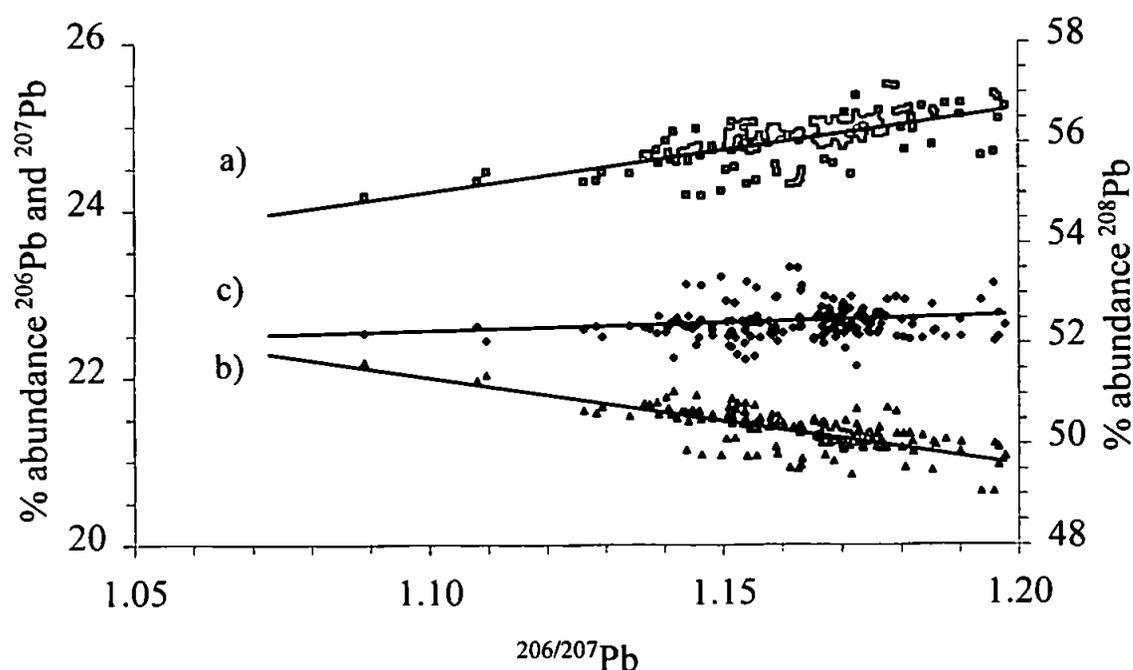
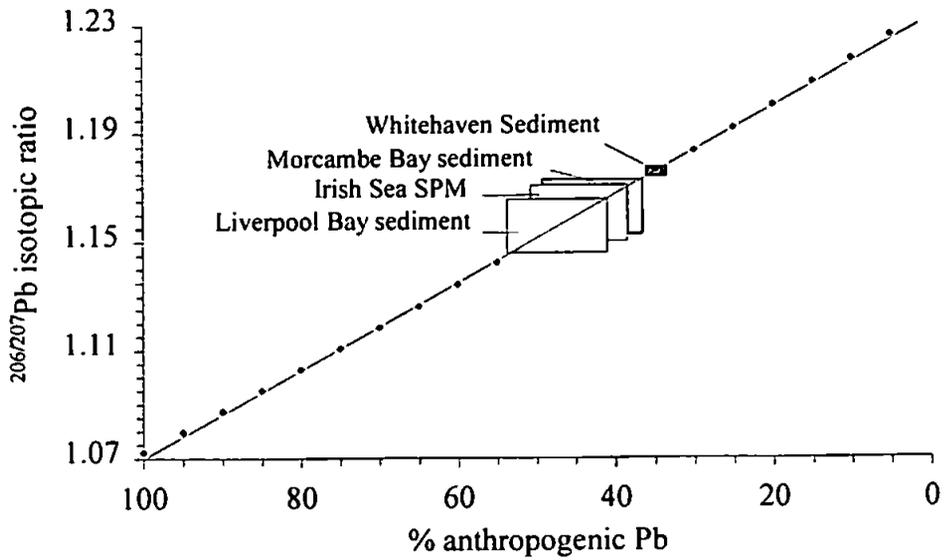


Figure 4.3. Variation of the isotopic abundances of Pb with the $^{206}/^{207}\text{Pb}$ isotopic ratio
a) ^{206}Pb : $y = 9.9 x + 13.4$, $r^2 = 0.43$, $p \leq 0.05$; b) ^{207}Pb : $y = -10.4 x + 33.4$, $r^2 = 0.28$,
 $p \leq 0.05$ and c) ^{208}Pb : $y = 3.0 x + 49.0$, $r^2 = 0.01$, $p > 0.05$.

4.3. Application of Pb Isotope Studies.

Given the relationships in Figure 4.3. a theoretical mixing model, based on combining different proportions of anthropogenic and natural lead, can be devised. By hypothetically mixing natural and anthropogenic Pb in known proportions, the % abundance of ^{206}Pb and ^{207}Pb isotopes for this natural and anthropogenic Pb can be calculated. Combining the % abundances for each proportion of the natural and anthropogenic Pb, produces a hypothetical value of the $^{206}/^{207}\text{Pb}$ isotopic ratio. The results are given in Figure 4.4., though as expected the $^{206}/^{207}\text{Pb}$ isotopic ratio does not mix conservatively ($r \neq 1$), but for practical purposes it should be considered to mix conservatively (Shirahata *et al*, 1980). Thus a value for the % mixing, assuming conservative mixing of natural and anthropogenic Pb, for a given $^{206}/^{207}\text{Pb}$ isotopic ratio can be calculated using the equation of the line (Figure 4.4.). Indicated in Figure 4.4. are the isotopic data from the Irish and North Sea particulate samples. The SPM samples tended to have a higher anthropogenic content compared with sediment from the same area, this was probably due to the preference of anthropogenic Pb for slower settling particles (Chapter 5). The slower settling particles will have a larger water residence time, allowing a longer time for adsorption in the water column (Brügmann *et al*, 1985). Typically, the Irish Sea samples were composed of 50 - 40 % anthropogenic Pb, while the North Sea samples were composed of 40 - 20% anthropogenic Pb. Within the Humber region the pristine Holderness Cliffs contribute 10^6 t a⁻¹ of particulate matter compared with 10^5 t a⁻¹ of anthropogenically modified riverine particles (McCave, 1987), this difference was reflected in the lower % anthropogenic content of the North Sea samples. The mixing and transport of material in the Humber region is illustrated in Figure 4.4b., the progressive increase in $^{206}/^{207}\text{Pb}$ isotopic ratio due to the mixing of Humber and Holderness material was shown by samples from the Humber Estuary, Humber Mouth, Humber Plume and Holderness material.

a)



b)

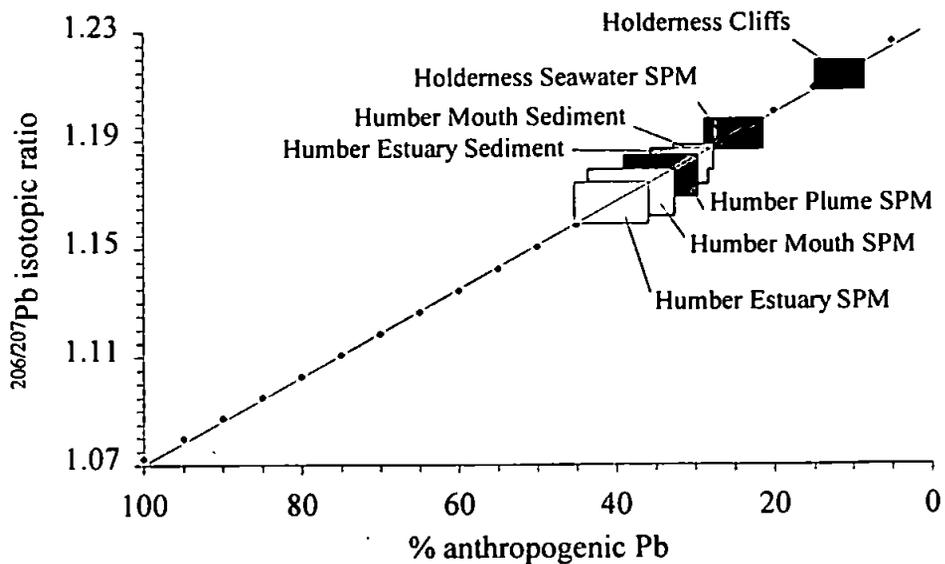


Figure 4.4. Relationship between $^{206}/^{207}\text{Pb}$ isotopic ratio and anthropogenic content. Equation of the mixing line : $y = 0.0016 x + 1.0704$; $r^2 = 0.9996$. Indicated are $^{206}/^{207}\text{Pb}$ isotopic ratios from British coastal waters, the boxes indicate the area enclosed by the mean \pm standard deviation of the $^{206}/^{207}\text{Pb}$ isotopic ratio, a) Irish Sea sediment and SPM and b) North Sea sediment and SPM.

4.4. Conclusion.

All the stable isotopes of Pb can provide valuable information about the transport and mixing of marine particulates. The majority of this type of work has been performed by geological scientists which has hindered the adoption of these techniques by marine chemists. This chapter has examined some of the applications of stable isotopes with respect to marine geochemical applications and has shown the need to develop a clearer understanding of applying stable Pb isotope data to naturally and anthropogenically modified marine particulates. However, as the use of unleaded petrol in the UK increases the applicability of this method will be reduced.

Chapter 5 - Particle Settling Experiments.

Chapter 5. Settling Velocity Experiments.

5.1. Introduction.

In an attempt to investigate the effect of gravitational settling of particles on the long range transport of particulate metals, a number of experiments were performed using a settling velocity tube, referred to as an SVT (Section 2.1.3.). This technique allows estimation of essential values of median settling velocity (w_{50}^0) for the improvement of transport models, such as NORPOL (Murphy and Odd, 1993). The SVT is a modified (length 1m, volume 5l) bottom withdrawal tube of the type described by Owen (1976), with the capability of *in situ* sampling. The tube was designed to remove a horizontal section of the water column, containing typical estuarine and/or coastal SPM, including particles with a wide range of densities and sizes, together with any flocculated material. Essentially, settling experiments of this kind are representative of particle deposition under calm hydrodynamic conditions, such as those encountered at slack water.

Some methods of settling velocity determination require sample manipulation e.g. the pipette method whilst others do not require the collection of a large sample (Kineke *et al*, 1989), however the SVT allows the collection of enough unaltered material for chemical analysis. A number of problems are inherent in the normal use of settling tubes (Syvitski *et al*, 1991), including :-

- i) hindered settling; caused by the fluid counter flow resulting from the settling particles.
- ii) settling convection; where pressure gradients and vortices induced in the falling particles interfere with the quiescent conditions of the tube.
- iii) mass settling; whereby small particles are dragged down by the wake of larger settling particles.
- iv) concentration effect; also referred to as differential or hindered settling, high concentrations of settling particles increases the number of collisions, which will affect the flocculation processes and perturb the expected settling behaviour.

These processes, though referred to as problems for laboratory applications of size fraction determinations, are indicative of the processes affecting natural particles settling through the

water column and can be considered as realistic features when examining settling velocities of *in-situ* samples. However, there are other processes which need to be accounted for when applying this technique:-

- i) thermal convection, resulting from the temperature difference of the ambient air temperature and the sample temperature, and temperature difference between the top and bottom of the SVT (minimised by the use of an insulating jacket fitted around the SVT during each experiment);
- ii) accumulation of particles on the surface of the sampling cone above the tap; this effect has been minimised by the design of the cone to inhibit accumulation;
- iii) wall effects; changes in the fluid flow along the tube wall will reduce settling velocities. However the length to diameter ratio of the SVT was designed to reduce this effect on the overall settling velocity determined;
- iv) turbulence induced by the vibration and motion of the ship after sampling.

Artefacts arising from the above have been minimised as indicated and the first settling velocities of particulate trace metals in estuarine plumes have been determined as part of this study.

Although, a number of authors have examined settling velocities, the vast majority of the work performed has been in highly turbid estuarine environments and has been used to examine sediment transport processes (Owen, 1971; Owen, 1976; Gibbs, 1985; Puls *et al*, 1988; Burban *et al*, 1990; Prochnow *et al*, 1994). The examination of settling velocities in the coastal environment has been less extensively investigated (Kineke and Sternberg, 1989; Kineke *et al*, 1989; Jago *et al*, 1993). This is partly due to the difficulties involved in making measurements in low turbidity conditions, and partly due to less commercial interest compared with siltation of harbour areas. Of the work performed, on the fate of particulate pollutants, only one author has attempted to link the physics of settling with the chemistry of settling particles (Niedergesäß *et al*, 1987; 1994), despite the clear need to characterise the particles which carry most of the trace metal pollutants. The work presented in this thesis is the first attempt to unite the settling characteristics and the chemistry of suspended particles in the coastal environment.

5.2. Sample Collection.

Settling experiments were conducted at site Z in the Irish Sea (see Figure 2.1) during CH88A/92, and within the LOIS RACS study area in the North Sea during cruises CH99/92 and CH108A/93 (see Figures 5.1. and 2.1.).

Irish Sea samples were taken about 1m from the bottom of the water column. These were the first attempts with the method and were intended to examine dense suspensions in strong tidal currents. Hence, these settling experiments represent fluxes of particles to the sediment surface.

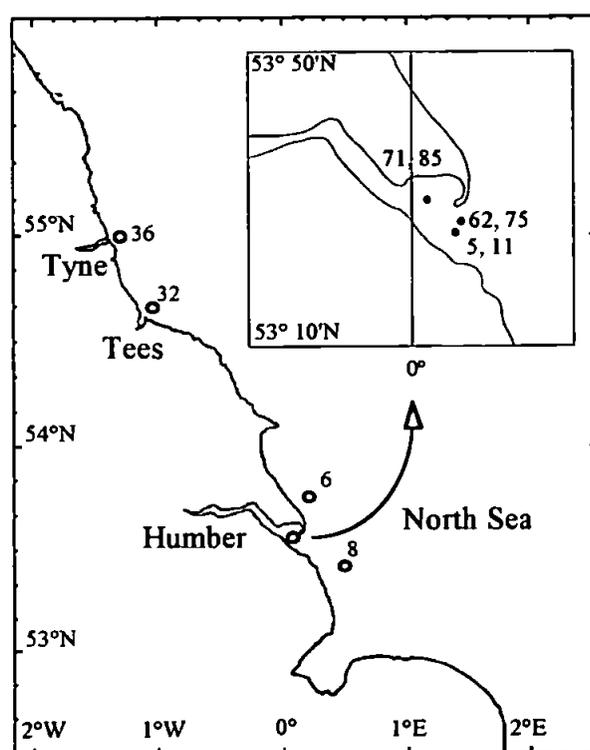


Figure 5.1. Sampling sites for deployment of SVT experiments in the North Sea. Numbers refer to SVT experiments and the associated CTD deployments, see Table 5.2. for further details. The insert shows an expanded area of the Humber mouth to clarify positions of Humber mouth SVT experiments.

The sample sites in coastal waters of the North Sea were selected to give quantitative information on the settling of particles in estuaries and their plumes. The Humber Estuary was a priority, because of high SPM loadings and pollutant inputs, and six experiments were conducted at the mouth of the estuary. One experiment was carried out in the Humber Plume and one off the Holderness coast, which is a potential source region for much of the

plume SPM. Additional experiments were carried out in the plumes of the Tees and the Tyne Estuaries, very low turbidity in the Tweed plume precluded the use of the SVT. All samples were collected from about 1m below the surface.

5.3. Estimation of Settling Velocity.

Estimates of settling velocities from the experimental data were obtained using the method described by Owen (1976). SPM was collected on pre-weighed, acid washed filters (0.4 μ m poresize, \varnothing 147mm, Nuclepore) at selected time intervals (5, 20, 80, 280 minutes and the residual fraction) from the SVT - the weights, time and volume filtered were used to derive a depth factor for the sample in the tube. The depth factor was used to correct the cumulative weight of SPM and time interval for the change in sample volume (i.e. sample height) during the experiment. The corrected % cumulative weight and the corrected time were plotted on a log-linear graph (Figure 5.2.). Plotted on the abscissa were time values which corresponded to known settling velocities at the temperature of the sample, tabulated by Owen (1976).

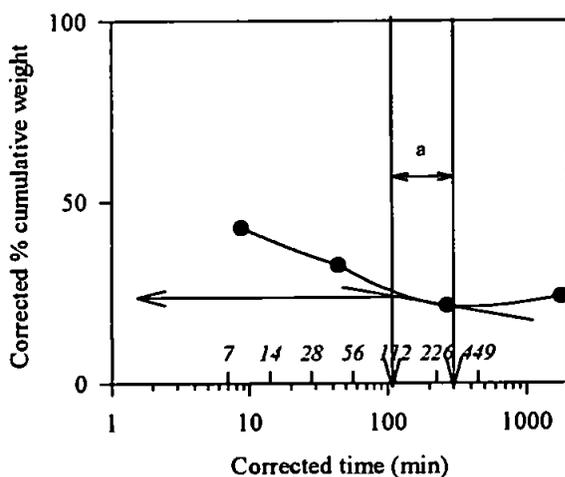


Figure 5.2. Log-linear graph used to estimate the settling velocity distribution of sample CH88A/92/244 taken at site Z, Irish Sea. Plotted on the graph is the template design ($a = \log_{10}e$) and the corresponding tangent used to derived the % cumulative weight. Italic values are times corresponding to known particle settling velocities given by Owen (1976).

On a template, two vertical lines $\log_{10}e$ ($e = \text{exponential}$) apart were drawn, to determine of the intercept of the tangent, on the ordinate. The right hand line was aligned with a predetermined time value e.g. in Figure 5.2. 226 min. A tangent to the curve was drawn

and where the tangent intercepted the left hand line, the % cumulative weight was obtained. This procedure was repeated for each of the plotted time values to give a graph of % cumulative weight versus settling velocity on a log-linear graph (Figure 5.3.). Using this approach the median settling velocity (w_s^{50}) was obtained.

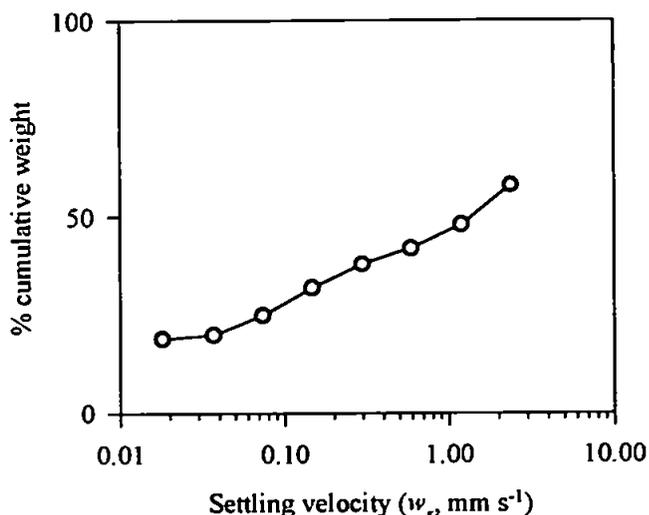


Figure 5.3. Log-linear graph showing the settling velocity distribution for sample CH88/92/244 taken at site Z, Irish Sea. % cumulative weight values were obtained from Figure 5.2. via the time values for known settling velocities (*italic values indicated in Figure 5.2*).

Table 5.1. Comparison between calculation methods of data derived from SVT.

| Sample | Cruise | w_s^{50} (mm s ⁻¹) for SPM | | |
|--------|----------|--|----------------------|-----------------------|
| | | UCNW* | This study | Prochnow [†] |
| 244 | CH88A/92 | 3.11 | 1.41 | 6.7 |
| 366 | CH88A/92 | 1.1×10^{-3} | 0.5×10^{-3} | 0.4 |
| 71 | CH99/92 | 2.0×10^{-2} | 1.0×10^{-2} | 0.27 |

*S. Jones (pers. comm.). [†]Prochnow *et al*, 1994

Alternative mathematical (Prochnow *et al*, 1994; Niedergesäß *et al*, 1994) and computational (Jago *et al*, 1993) methods have been used to derive settling velocity values. Generally, these methods are modifications of the Owen (1976) method. A comparison of the median settling velocities derived from the computational (University of Wales, Bangor - UCNW) and mathematical methods (Prochnow *et al*, 1994) were made with the graphical method described above (Table 5.1.).

Clearly, the method used by Prochnow *et al* (1994) appears to overestimate the settling velocity compared with values obtained by UCNW and from the graphical method applied during this study. The Prochnow procedure does not compensate for temperature effects; it relies on interpolation to derive the median settling velocity and it is unclear whether it compensates for the change in height of the residual volume after a fraction is withdrawn. Consequently, the Prochnow procedure is probably only suitable as a first approximation of the median settling velocity.

Median settling velocities estimated from the method outlined above are given in Table 5.2. and have a typical range of 10^{-1} to 10^{-3} mm s^{-1} , with the exception of CH88A/92/244. For samples taken in the Humber plume, offshore of the Holderness cliffs and at the mouth of the Tees a value of the order of 3×10^{-3} mm s^{-1} was obtained. These values are in reasonable agreement with w_s^{30} values from the North Sea where Jago *et al* (1993) found a background median settling velocity of 10^{-4} mm s^{-1} for samples taken in the eastern North Sea. Fennessy *et al* (1994) observed minimum values in the range 10^{-1} - 10^{-2} mm s^{-1} for the Tamar Estuary and Burban *et al* (1990) gave a typical floc settling rate of 8×10^{-2} mm s^{-1} for settling flocs in an estuarine system. Assuming i) 'Stokesian' behaviour, ii) an average water depth of 25m and iii) no flocculation, particles with a settling velocity of 3×10^{-3} mm s^{-1} would take about 96 days to reach the sediment surface under conditions of low turbulence. Such ideal conditions are unusual in the North Sea, where wind and tidal energy maintain turbulent eddies and these particles can be considered to be permanently suspended. The use of settling velocity values obtained from flocculated material in estuarine systems may not fully reflect flocculated material in coastal waters. Jago *et al* (1993) suggested values in the range 2 to 0.2 mm s^{-1} would be required to allow particles to settle during periods of slack water, yet only sample CH88A/93/244 gave a value close to this. This lends further support to the contention that much of the SPM along the coast of north east England is in long term suspension and could contribute significantly to the long range transport of pollutants. Assuming an average depth of 10m and if the largest flux of SPM from the surface waters were to occur under low turbulence, deposition would take ~4 days, slower settling fractions taking at least ten times longer. These findings suggest that during the period of flood, potential sediment deposition is at a maximum in the Humber Estuary.

The dependence of settling velocity with SPM has been examined by a number of authors (Owen, 1971; van Leussen, 1988; Puls *et al*, 1988; Fennessy *et al*, 1994) to model mass settling to the bed and is related by the following equation:

$$w_s = K.C^m \quad 5.1.$$

where, w_s = settling velocity and C = SPM concentration, K and m are empirical constants.

Plotting values of w_s^{50} versus SPM concentrations from this study (Figure 5.4.), it was found that $m = 0.87$ and $K = 0.014$ with a correlation coefficient (r) of 0.75 ($p = < 0.05$) it was noted that the neap tide data for the Humber mouth gave a high correlation coefficient ($m = 1.96$, $K = 0.045$ for $r = 1.00$, $p = < 0.05$). Values given by van Leussen (1988) for m range between 1.0 and 2.92, while Puls *et al* (1988) gave values between 0.47 and 2.07. The variation in the exponent m suggests a difference between the Humber SPM and the material in LOIS RACS coastal waters. The differences in exponent m have been attributed to a number of causes such as variations in floc density and organic content (Dyer, 1994). The increased gradient for the Humber particles suggest that the particle may have a lower floc density and/or increase in organic matter content.

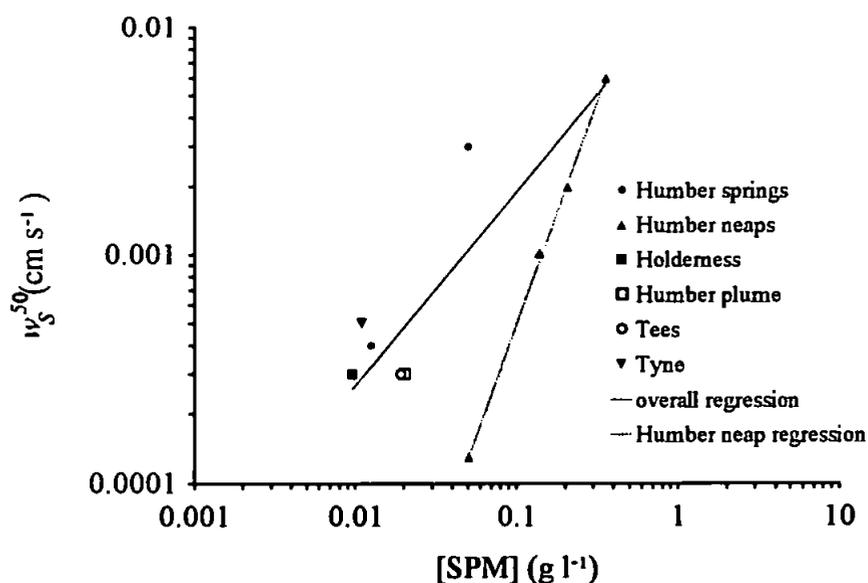


Figure 5.4. The relationship between settling velocity (w_s^{50}) and SPM concentration, using Equation 5.1. from Puls *et al* (1988).

Table 5.2. Details of SVT deployments and settling velocities during cruises CH88A/92, CH99/92 and CH108A/93.

| Cruise/date/SVT | Comments | Tidal conditions | | Salinity | Temperature (°C) | SPM (mg l ⁻¹) | | Median Settling Velocity (w_s^{50}) (x 10 ⁻³ mm s ⁻¹) |
|------------------|-------------------|------------------|---------------------|----------|---------------------|------------------------------|-----------|--|
| | | State | Time (hours ±HW) | | | from SVT† | from CTD‡ | |
| CH88A / 92 / 244 | Site Z, Irish Sea | spring | +3.5 | 32.056 | 6.069 | 105 | | 1410 |
| CH88A / 92 / 366 | Site Z, Irish Sea | neap | +2.9 | 32.580 | 5.924 | 9 | 9 | 0.5 |
| CH99 / 92 / 5 | Humber mouth | spring | +0.8 | 31.798 | 7.047 | 13 | 13 | 4.0 |
| CH99 / 92 / 11 | Humber mouth | spring | -5.6 | 24.217 | 6.469 | 50 | 51 | 30 |
| CH99 / 92 / 85 | Inner Estuary | neap | -3.1 | 26.900 | 6.580 | 357 | 386 | 60 |
| CH108A / 93 / 62 | Humber mouth | neap | -2.3 | 30.950 | 7.097 | 207 | 240* | 20 |
| CH99 / 92 / 71 | Inner Estuary | neap | +2.9 | 29.333 | 6.680 | 139 | 140 | 10 |
| CH108A / 93 / 75 | Humber mouth | neap | +4.4 | 28.616 | 6.377 | 51 | 29* | 1.3 |
| CH108A / 93 / 8 | Humber plume | spring | +0.3 | 34.386 | 9.743 | 19 | 6* | 3.1 |
| CH108A / 93 / 6 | Holderness | spring | -5.2 | 34.536 | 9.917 | 10 | 4* | 3.0 |
| CH108A / 93 / 32 | Tees plume | spring | +3.2 | 34.122 | 9.220 | 19 | 10* | 3.3 |
| CH108A / 93 / 36 | Tyne plume | spring | -0.2 | 34.125 | 9.322 | 11 | 5* | 5.0 |

† SPM values were determined by the ratio of the total cumulative weight of SPM filtered and the total volume filtered.

‡ SPM values were calculated gravimetrically from water samples taken using Go-Flo water sample bottles.

±HW - hours before and after high water; *T. Sands (pers. comm.)

5.4. Particle Sizes and Densities.

From Stokes' Law (Equation 5.2.) it can be seen that w_s is dependent on the square of the particle diameter and density of the settling particle:

$$w_s = \frac{gd^2}{18\mu} (\rho_p - \rho) \quad 5.2.$$

where w_s = settling velocity, g = acceleration due to gravity, d = particle diameter, μ = dynamic viscosity of the fluid, ρ_p = density of the particle and ρ = density of the fluid

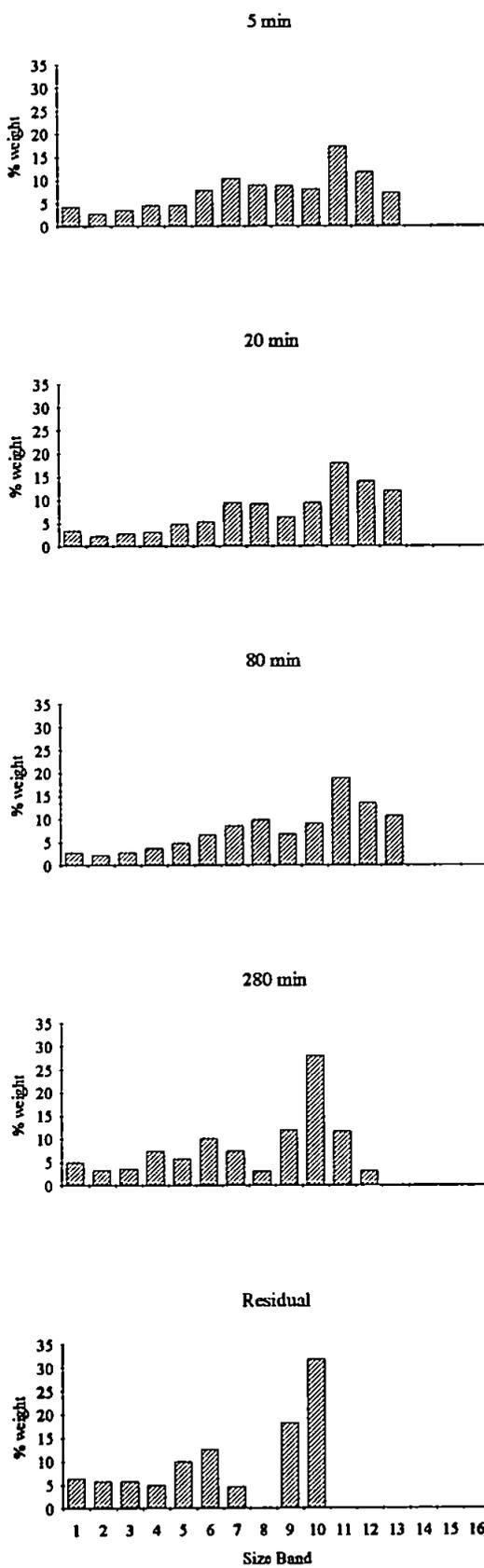
Stoke's Law (Equation 5.2.) is only valid for low Reynolds number (Re), <0.2 is recommended. The Reynolds number can be defined as (Allen, 1987):

$$R_s = \frac{\rho \cdot w_s \cdot d}{\mu} \quad 5.3.$$

Within the marine environment both the particle diameter and the particle density are difficult to determine as particles are often flocculated, with irregular shapes and possibly low densities. During cruises CH88A and CH108A, each time fraction obtained from selected SVTs were examined using a Malvern Laser Particle Sizer (Bale *et al*, 1984). Table 5.3. gives the size band information using a 100mm lens (Section 2.1.5.). Histograms of the % weight in each size band were obtained and representative profiles are shown in Figure 5.5.a and b. The histograms for CH108A/93/75 showed little variation between each time fraction, whereas the histograms for CH88A/92/366 became skewed towards larger particles in the slower settling fractions. This was unexpected and was probably due to either:

- i) a mixture of a rapid settling particle population (high density, small particle diameter) e.g. clay/silicate particles and a slower settling population of flocculated material (low density, large particle diameter)
- or
- ii) the sample contained a wide range of floc diameters, some of which were fragile and were disaggregated by the mechanical agitation of the Malvern Laser Sizer.

a)



b)

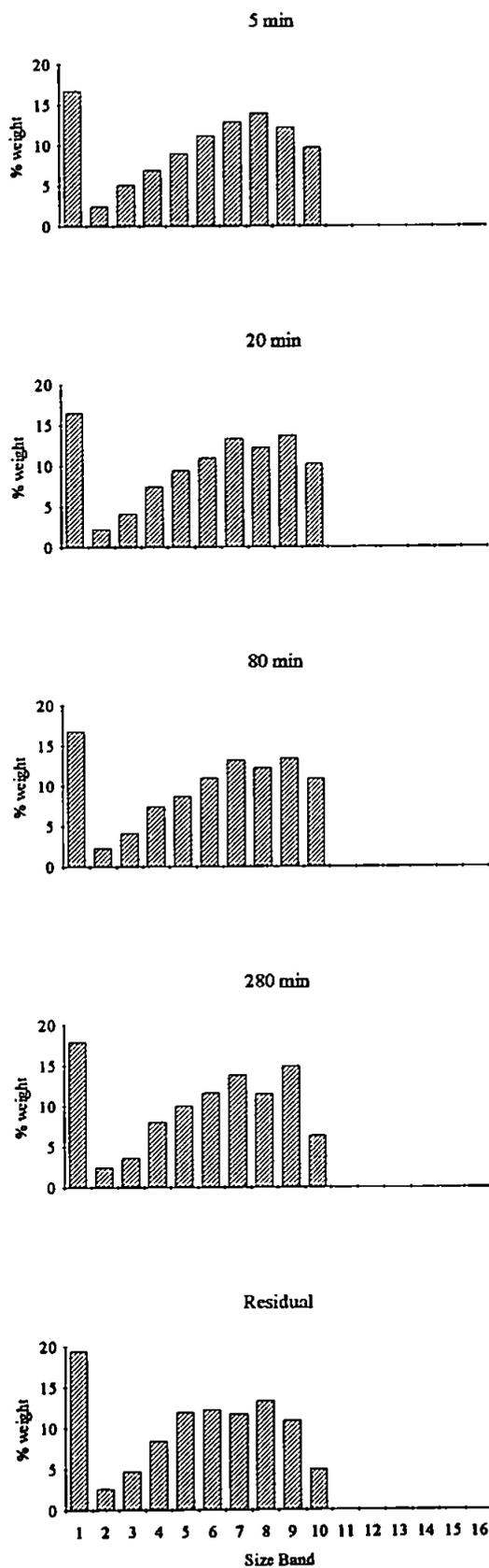


Figure 5.5. Laser particle size distributions from the five SVT settling fractions, a) CH88A/92/366 and b) CH108A/93/75. See Table 5.3. for information relating to size bands.

The latter reason is favoured, as visual observations of sample material did not suggest the presence of two different population types. However, process ii) will occur in all samples irrespective of other processes, though many smaller flocs are relatively stable and are unlikely to disaggregate in the Malvern Laser Sizer. This suggests that particle diameters (d) obtained by a Malvern Particle Sizer may be underestimated (Bale and Morris, 1987). Alternative methods of *in situ* floc sizing do not allow collection of flocs for chemical analysis (Bale *et al*, 1989; Kineke *et al*, 1989; Fennessy *et al*, 1994).

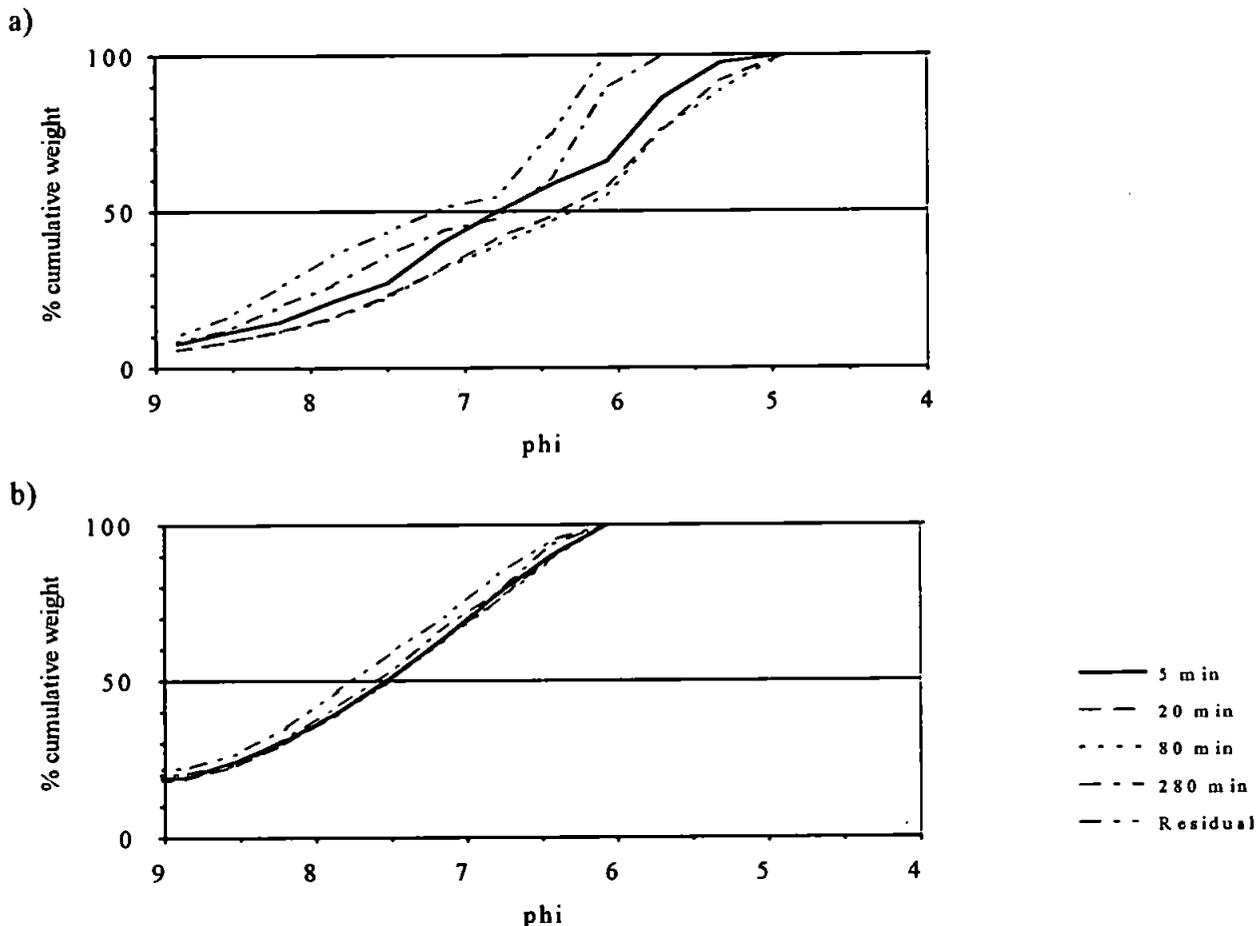


Figure 5.6. % Cumulative weight size distributions derived for each SVT time fraction of samples a) CH88A/92/366 and b) CH108A/93/75.

Quantitative estimates of the particle diameters for the sample population were obtained by plotting the % cumulative weight against the phi value ($\phi = -\log_2(\text{particle diameter in mm})$). Median particle diameters (ϕ^{50} hence d^{50}) for each of the SVT fractions were acquired by estimating the 50% percentile from a cubic spline fit of the data. The values for d^{50} were weight averaged to give a median weight averaged particle diameter, d_w^{50} (see Table 5.4). The estimated diameters correspond to diameters typical of fine to very fine silt.

Table 5.3. Table of size bands used to examine particle size data. Bands represent particle diameters measured as μm and/or units of phi (ϕ).

| Size | Particle diameter | | | | Size | Particle diameter | | | |
|------|-------------------|---------------|---------------|--------|------|-------------------|---------------|---------------|--------|
| Band | max | min | mean | mean | Band | max | min | mean | mean |
| | μm | μm | μm | ϕ | | μm | μm | μm | ϕ |
| 1 | <1.9 | | | | 9 | 13.0 | 10.1 | 11.6 | 6.45 |
| 2 | 2.4 | 1.9 | 2.2 | 8.86 | 10 | 16.7 | 13.0 | 14.9 | 6.09 |
| 3 | 3.0 | 2.4 | 2.7 | 8.56 | 11 | 21.5 | 16.7 | 19.1 | 5.73 |
| 4 | 3.8 | 3.0 | 3.4 | 8.22 | 12 | 28.1 | 21.5 | 24.8 | 5.35 |
| 5 | 4.8 | 3.8 | 4.3 | 7.88 | 13 | 37.6 | 28.1 | 32.9 | 4.94 |
| 6 | 6.2 | 4.8 | 5.5 | 7.53 | 14 | 53.5 | 37.6 | 45.6 | 4.47 |
| 7 | 7.9 | 6.2 | 7.1 | 7.16 | 15 | 87.2 | 53.5 | 70.4 | 3.84 |
| 8 | 10.1 | 7.9 | 9.0 | 6.82 | 16 | 188 | 87.2 | 137.6 | 2.87 |

Table 5.4. Median weight averaged particle diameters (d_w^{50}) SVT experiments.

| Cruise/data/SVT | Location | d_w^{50} (μm) |
|------------------|--------------|---------------------------------|
| <i>Irish Sea</i> | | |
| CH88A/92/244 | Site Z | 16.3 |
| CH88A/92/366 | Site Z | 11.3 |
| <i>North Sea</i> | | |
| CH108A/93/62 | Humber mouth | 5.4 |
| CH108A/93/75 | Humber mouth | 5.3 |
| CH108A/93/8 | Humber plume | 14.2 |
| CH108A/93/6 | Holderness | 20.8* |
| CH108A/93/32 | Tees mouth | 8.5 |
| CH108A/93/36 | Tyne mouth | 9.9* |

* for CH108A/93/6 only the 20 min fraction and for CH108A/93/36 only the 280 min fraction were particle size determinations possible, therefore these samples were not weight averaged.

Substituting the viscosity (μ) and density of sea water (ρ), the particle settling velocity (w_s^{50} for w_s) and diameter (d_w^{50} for d) for each SVT experiment into Equation 5.3., gave Re

numbers between 10^{-2} and 10^{-6} . These values were sufficiently low to warrant the use of Stokes Law.

Using the Stokes' equation (Equation 5.2.) and assuming a viscosity for sea water of $0.001 \text{ kg m}^{-1} \text{ s}^{-1}$, a density of sea water of 1025 kg m^{-3} , and by plotting d_w^{50} vs w_s^{50} , the average density of the settling particle populations from the SVT experiments can be examined (Figure 5.7.). As previously mentioned the Malvern Particle Sizer may underestimate the particle diameter, hence the plots may lay further to the right i.e. lower density. Additionally, the inferred density from each experiment should be considered as an estimate and not an absolute value. The measurements of median settling velocity and median particle diameter may not be coincident with identical median particle populations, and should be treated in a comparative fashion. The results suggest that the settling particles are predominantly of low density (density of mud flocs $1048 - 1367 \text{ kg m}^{-3}$ from Puls *et al* (1988)), the exception is CH108A/93/62 where the density is significantly higher than other SVT experiments (density of clay particles $2000 - 3300 \text{ kg m}^{-3}$, Allen (1985)). CH88A/92/244 is anomalous ($\rho = 11491 \text{ kg m}^{-3}$) and errors could be present either in the value of w_s^{50} or d_w^{50} . Sample CH88A/92/244 was taken on a spring tides with considerable sediment resuspension (Williams *et al*, 1994) and the suspended particles may be characteristic of large aggregates. Disaggregation of the flocs would cause significant alteration in the estimated density since the square of the particle diameter is inversely proportional to the effective density ($\rho_p - \rho$) (Equation 5.2.). An underestimate of w_s^{50} , caused by disaggregation during SVT sampling, would result in a less significant alteration in the estimated density.

The results of experiment CH108A/93/6 may not be representative of eroded material from the Holderness Cliffs but more offshore in nature, as samples taken from beaches along the Holderness coastline were significantly more turbid (600 to 2900 mg l^{-1} , T. Sands pers. comm.) than observed for the Holderness SVT experiment. The eroded Holderness cliff material (10^6 t a^{-1} , McCave (1987)) may be advected by the prevailing currents as a narrow band towards the Humber Estuary. This could be the reason for the higher density observed in sample CH108A/93/62 during the flood tide, resulting from advection of Holderness material into the mouth of the Humber Estuary.

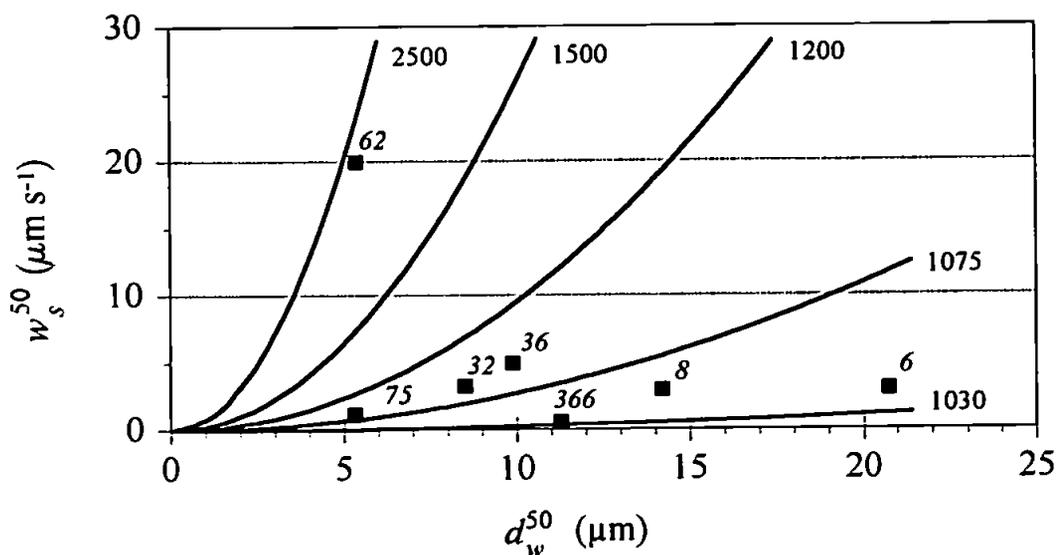


Figure 5.7. Comparison of the densities of each SVT experiment (italic numbers). Plotted are lines of constant density (units: kg m⁻³) for coastal samples (CTD numbers) obeying Stokes' Law (Equation 5.2.).

The Holderness Cliffs are a known source of particulate material in the region of the Humber Estuary (McCave, 1987). Variation in SPM loading may be a product of influxes of Holderness material into the estuary, and resuspension events may be of less significance. Consequently, the reactivity of trace metals within the mixing region of Humber and Holderness particulate material, is of considerable interest (Section 6.4.).

5.5. Trace Metal Analysis of Settling Fractions.

The SVT is ideally suited to examine the association of trace metals with different settling fractions. Unlike other methodologies the SVT allows the filtered particles from each fraction to be analysed (Section 2.3.2.). Measurements of each settling fraction will indicate the significance of each settling fraction to the vertical transport of metals and consequently their advection with settling particles. The particulate associated metal concentrations can also be converted from w/w to w/v for each time fraction (5, 20, 80, 280 min and residual), which allows the values to be treated in the same fashion as the SPM. The derived settling velocity will represent the median settling velocity of the metals associated with the settling SPM. It should be borne in mind that the w/v concentration will be the particulate associated metal loading for a unit volume of water and hence will be dependent on SPM loading. The derived settling patterns for each of the metals will be dependent on the

preferential affinity of each metal with different settling fractions, which may be size or density related, from Stokes' Law (Equation 5.2.).

5.5.1. Chemical Composition of the Settling Fractions.

Assuming that additivity rules apply, the sum of the metal concentrations (for a 1M HCl digest) for each SVT fraction should be the same as that obtained from an analysis of the total particulate sample obtained from the water bottle deployment. Comparison of data from available water bottle values (CH108A (Fe, Mn, Zn) values from T. Sands pers comm.) and SVT experiments gave an average of 101% (with a range of 80 - 140%) of the water bottle values for the more turbid samples. This was considered acceptable, as the values were determined from significantly lower SPM loadings than the water bottle samples and resulted from an accumulation of five fractions. Significant deviations were observed for low turbidity samples and some results should be treated with caution (see Appendix B.). Initial examination of the settling velocity spectra were performed in consultation with University of Wales, Bangor.

Full results are tabulated in Appendix B. Many of the analyses associated with low turbidity samples did not give values above the detection limits of the analysis. To allow easier comparison of the data, histograms of the data are given in Figure 5.8.

Interpretation of the histograms are problematical due to the dynamic nature of the marine environment and possible changes in the adsorptive characteristics of the SPM (see Chapter 6.). These results are complex distributions that reflect the differing geochemistry of each metal with particles originating from dissimilar source regions. The affinity of each metal with the slower or faster settling fractions can be examined from Figure 5.8. Increases in metal concentration from left to right suggest increasing affinity of the metal for the slower settling fractions.

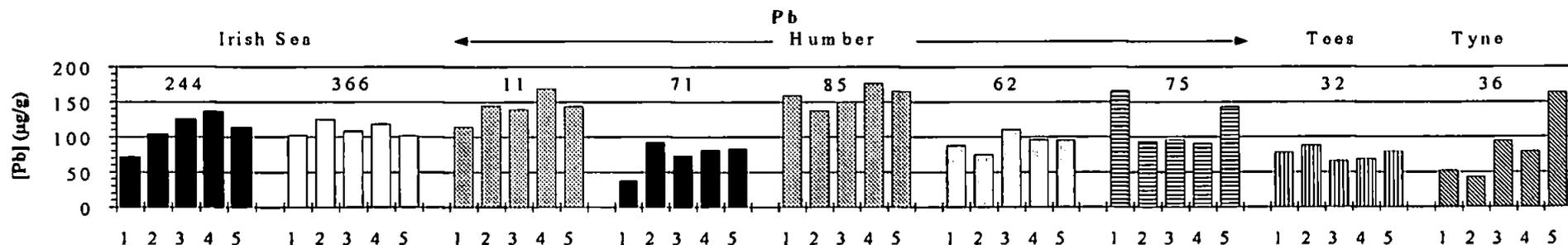
Lead

The $^{206}/^{207}\text{Pb}$ isotopic ratio has been used extensively to examine the degree of anthropogenic contribution to the marine environment (see Chapter 4.). The values obtained from the different settling fractions during the Irish Sea SVT experiment, indicate the preference of anthropogenic lead for the slowest settling fractions (Figure 5.8. CH88A/9244 and 366; Williams *et al*, 1994).

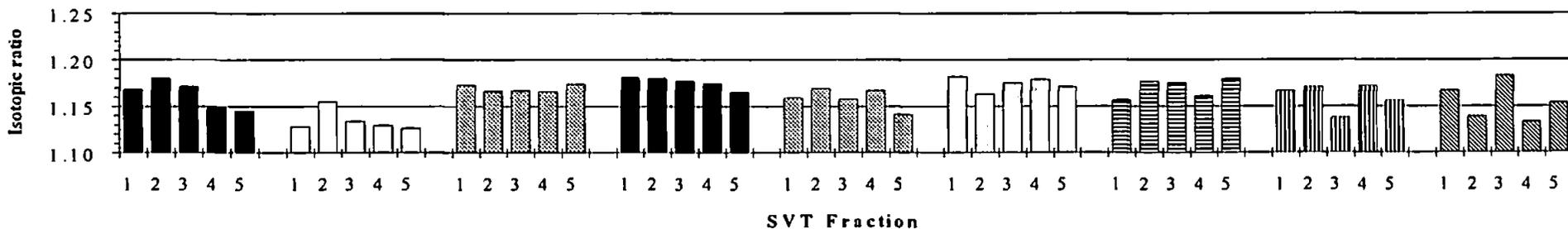
The results for the North Sea are less clear, the tendency was either for the lowest ratio to be associated with the slowest settling fraction (CH99/92/71 and 85) or negligible variation between each fraction (CH99/92/11 and CH108A/93/62). The Humber tended to show higher lead concentrations than the Irish Sea, though the isotopic ratios were higher. The Irish Sea is recipient to industrial waste from Associated Octel (producer of lead additives for petrol, which contains very low $^{206}/^{207}\text{Pb}$ isotopic ratios) and may result in a greater decrease of $^{206}/^{207}\text{Pb}$ isotopic ratios (Bull *et al*, 1983). Both Pb and the $^{206}/^{207}\text{Pb}$ isotopic ratio have the most consistent behaviour; the combination of higher Pb concentrations and lower ratio in the residual SVT fraction strongly suggest the association of anthropogenic lead with the slower settling material.

Iron, Manganese and Cobalt.

The influence of pollutant iron from industry (Newell *et al*, 1984) in the Humber Estuary is clearly seen in Figure 5.8. The Humber Estuary has the highest Fe content of SPM of any North Sea estuary (Turner *et al*, 1991). Generally, Fe concentrations appeared to have little variation between the settling fractions, the exceptions being CH88A/92/244 and CH99/92/71 which showed Fe having a clear preference for the slower settling fractions. The samples CH88A/92/366, CH108A/93/75 and CH108A/93/32 suggested preference towards the faster settling fractions. Mn and Co were inclined to follow the general patterns exhibited by Fe, but more Co samples tended towards the slower settling fractions. The ratio of Fe with Mn will be discussed later.



²⁰⁶/₂₀₇ Pb isotopic ratio



SVT fractions

- 1 - 5 min
- 2 - 20 min
- 3 - 80 min
- 4 - 280 min
- 5 - >280 min

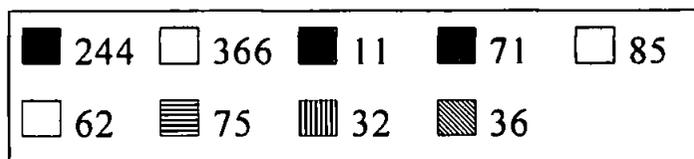


Figure 5.8. Histograms of metal data derived from SVT experiments. Irish Sea data was obtained from site Z, Irish Sea during CH88A. SVT experiments 11, 71, 85 were performed during CH99/92 and 62, 75, 32, 36 were performed during CH108A/93 in the LOIS RACS study area.

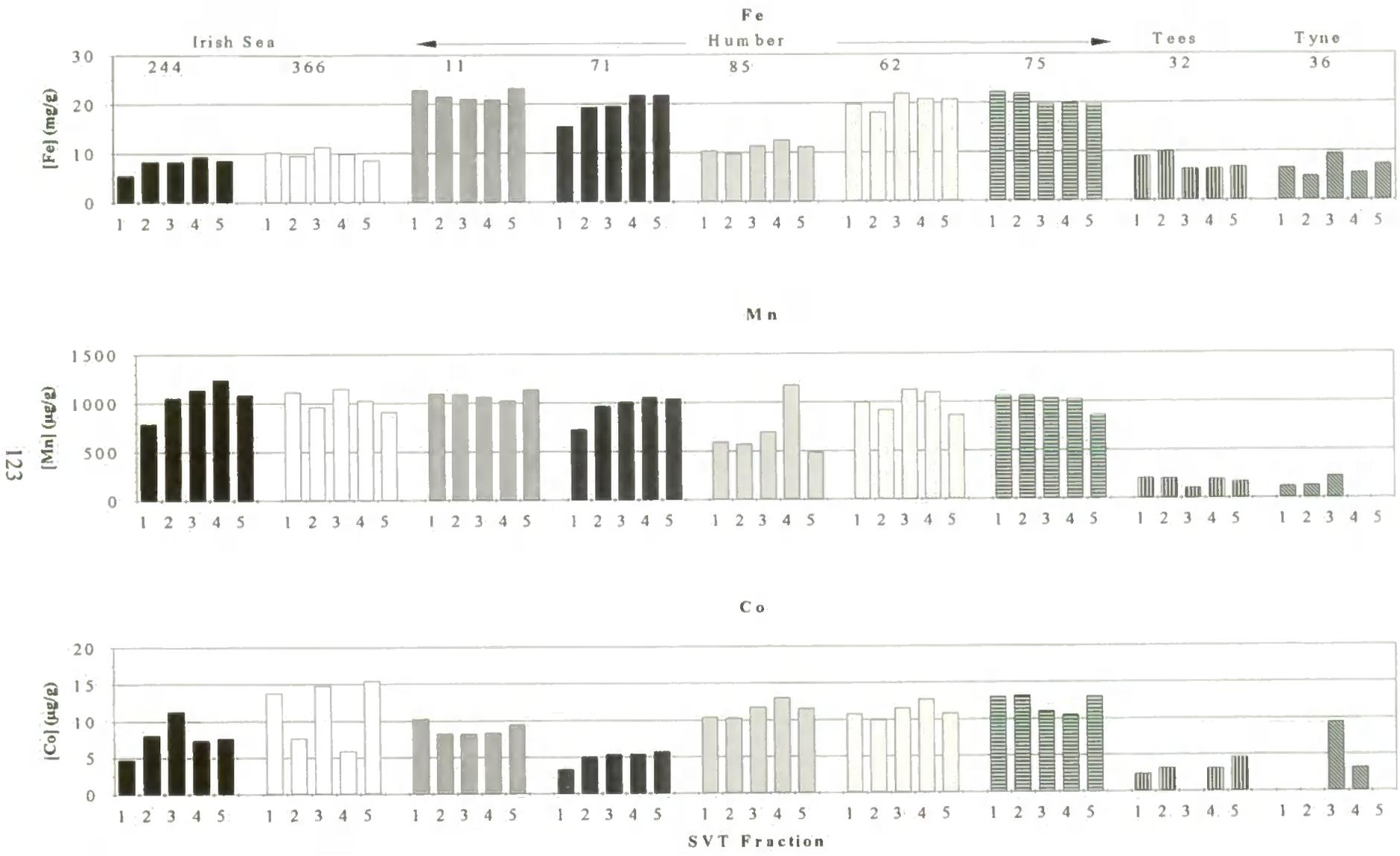


Figure 5.8. continued

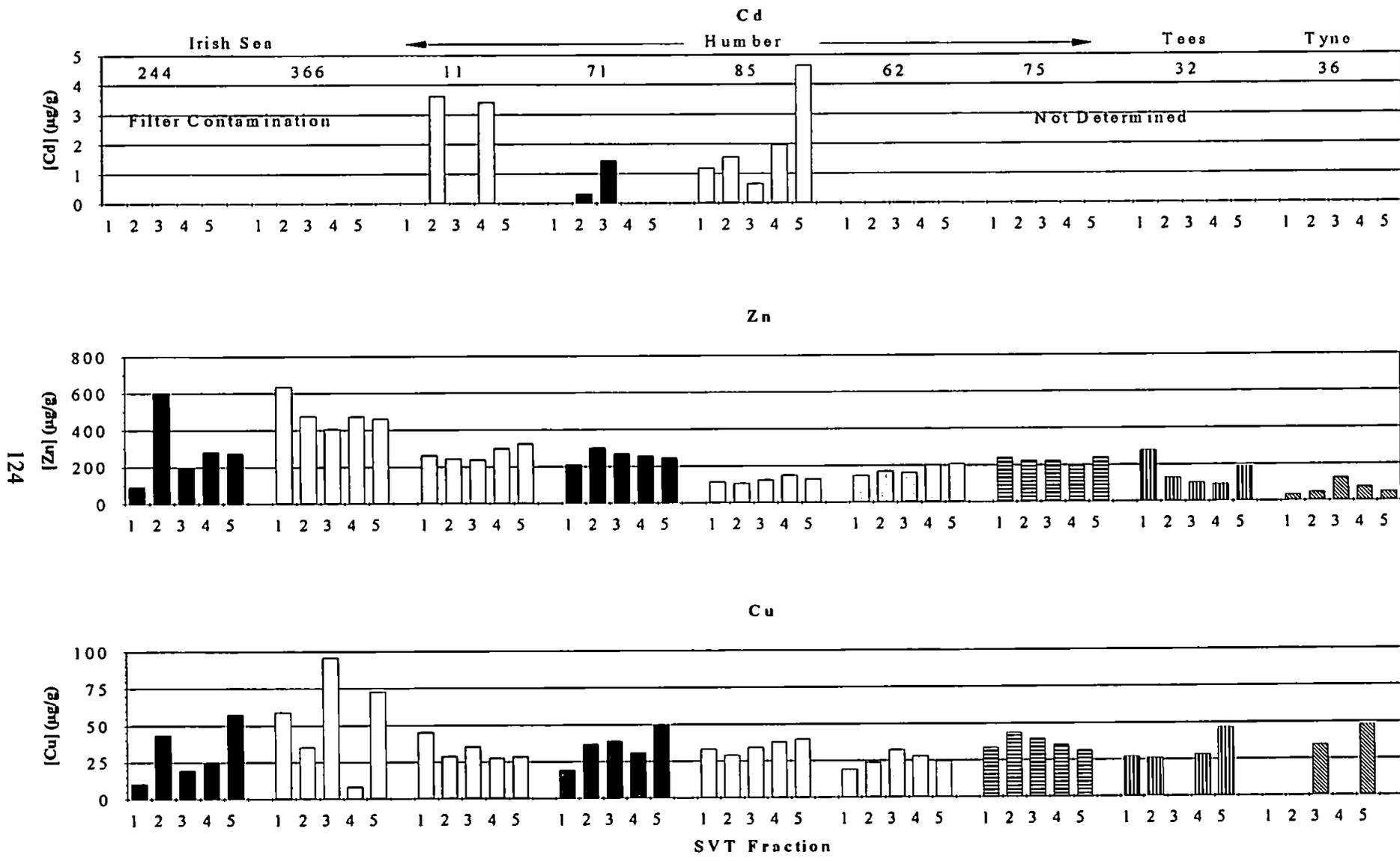


Figure 5.8. continued

All of these metals are known to associate with organic material as well as to varying degrees with ferromanganese coatings on particles, resulting in a complex interaction between different settling fractions and the metals. The low particle affinity of Cd (see Chapter 6) and the difficulties imposed by the SVT technique on its analysis, makes accurate interpretation of the behaviour of Cd problematical. The Cd results showed significant deviation from the water bottle values. Subsequent calculations to determine the settling velocity gave values of >100% for the corrected % cumulative weight (Section 5.2.), which may suggest that Cd is not settling. The affinity of Cd with organic matter (being of low density and hence slow settling) has been observed (Klinkhammer *et al*, 1982; Gendron *et al*, 1986, Gerringa, 1990) and may be, in part, reasons for the unusual settling results. Cd was not determined for CH108A SVT samples. The only full set of results (CH99/92/85) suggests a strong preference of Cd with the slower settling fractions. The behaviours of Zn and Cu showed mixed responses with no dominant associations, although individual experiments appeared to show a consistent preference for either the faster or the slower settling fractions for each metal.

5.5.2. Qualitative Assessment of the Settling Behaviour of Particulate Metals.

Assessment of the general settling behaviour of the metals is a complex task. Particles in the Humber mouth and the Irish Sea originate from a multitude of sources (e.g. eroded Holderness cliffs, fluvial inputs, sewage discharges, dredge spoils dumping, industrial waste inputs) and each SVT fraction will contain in varying degrees material from these sources. The combined effect of these sources on the distribution of trace metals within each settling population is unknown. As a first attempt to examine the metal distribution across the different settling fractions, three types of behaviour were distinguished:

- i) metals associated with faster settling fractions,
- ii) metals showing no apparent preference
- iii) metals associated with slower settling fractions

A qualitative assessment of Figure 5.8. has been given in Table 5.5. The results for the analysis of Ca have not been plotted as no general trend was observed.

Table 5.5. A qualitative assessment of the association of trace metals with settling fractions, derived from the histograms of Figure 5.8. Numbers indicate the occurrence of each type of settling association.

| Metal | Metal Preference for settling fractions | | |
|-------|---|-----------------------|------------------------|
| | (i) Faster Settling | (ii) No Preference | (iii) Slow Settling |
| Fe | 4 | 2 | 3 |
| Mn | 4 | 2 | 3 |
| Co | 1 | 3 | 4 |
| Cd | 0 | 0 | 1 |
| Zn | 4 | 3 | 2 |
| Cu | 2 | 3 | 3 |
| Pb | 0 | 4 | 5 |
| i.r. | 4 | 5 | 0 |

i.r. - ^{206/207}Pb isotopic ratio.

The behaviour of most metals appeared to be dependent on the settling experiment i.e. the particle population, being examined. However some general responses can be postulated, and the metals can be divided in to the three settling groups described previously:

- i) (^{206/207}Pb isotopic ratio - higher values for fast settling fractions)
- ii) Fe, Mn, Zn, Cu, Ca
- iii) Co, (Cd), Pb

The dependence of many metals appeared to be a function of SPM concentration and as previously suggested increases in SPM loading during the flood tide may have resulted from an influx of eroded Holderness cliff. Comparisons of overall concentrations derived from each SVT with mean SPM metal concentrations from Holderness seawater, the mouth of the Humber Estuary and the River Ouse are given in Table 5.6.

The chemical composition of typical Humber mouth material is due to the different heterogeneous reactivities of each trace metal (see Chapter 6). The Fe:Mn ratio has been used to examine the significance of each element to particle surface coating (Turner *et al*, 1991): Humber - 5.5-39.3 (Turner *et al*, 1991); Thames - 4.5-10.0 (Turner *et al*, 1991); Southern North Sea - 1.7-10.0 (Turner *et al*, 1991); Mersey - 4* (Millward *et al*, 1990);

Dee - 3* (Turner *et al*, 1994) (* acetic acid extracts). Using Fe:Mn ratios there is a suggestion that CH99/92/85 is lower than the Fe:Mn ratios of other SVT's (see Figure 5.9). CH99/92/85 and CH108A/93/62 show an increasing tendency towards the Fe:Mn ratio of Holderness material. Both experiments were performed during a flood tide.

Table 5.6. Data comparing the chemical composition of Holderness and Humber SPM with total concentrations found during the SVT experiments.

| Sample | Fe (mg g ⁻¹) | Mn (µg g ⁻¹) | Zn (µg g ⁻¹) | Ca (mg g ⁻¹) | Co (µg g ⁻¹) | Cu (µg g ⁻¹) | Pb (µg g ⁻¹) |
|---------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Holderness | 5 | 355 | 27 | 44 | 3 | 9 | 21 |
| Humber mouth | 17 | 988 | 161 | 34 | 11 | 29 | 126 |
| R. Ouse, Boothferry | 12 | 626 | 130 | 17 | 3 | 49 | 397 |
| 11 | 22 | 1079 | 266 | 33 | 9 | 34 | 138 |
| 71 | 19 | 937 | 256 | 33 | 5 | 34 | 71 |
| 85 | 11 | 673 | 119 | 38 | 11 | 33 | 153 |
| 62 | 20 | 1034 | 162 | 38 | 11 | 25 | 94 |
| 75 | 21 | 1023 | 221 | 32 | 12 | 38 | 110 |

Holderness and Humber mouth values are means of multiple samples (see Chapter 3). Assuming that Holderness material is entering on the flood tide, the Humber mouth means will incorporate this effect.

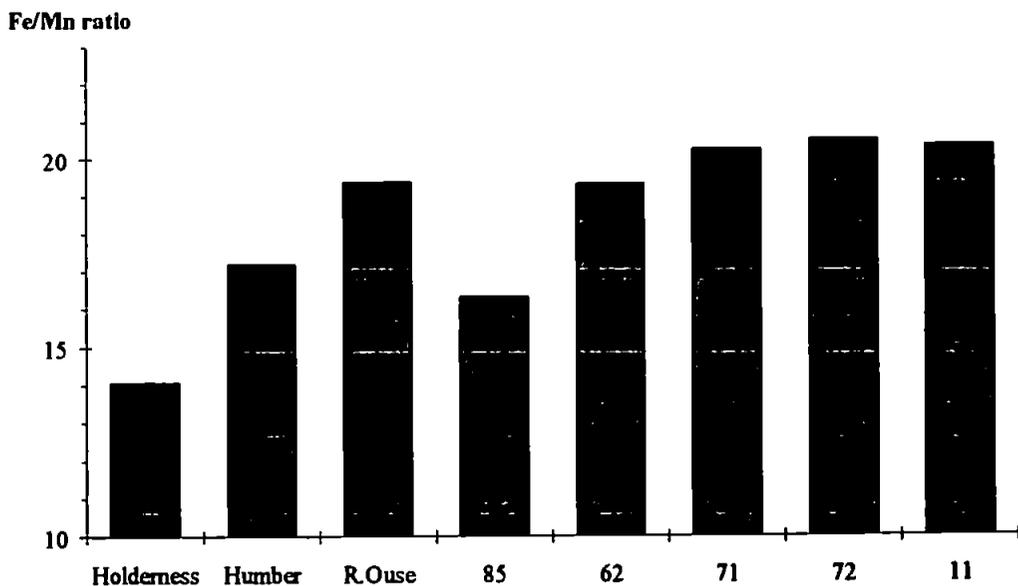


Figure 5.9. Variations of the Fe:Mn ratio from the SVT experiments as a result of mixing Holderness and Humber material. Ratios calculated from the values given in Table 5.6.

5.5.3. *Settling Velocities of Particulate Metals.*

A quantitative approach to the settling behaviour of particulate metals can be applied if a settling velocity spectra for each metal is derived, using the method previously described for SPM. Examples are given in Figure 5.10., where the settling velocity curve for the metals tended to follow the settling velocity curve of the SPM. This was probably because the metal concentrations used to derive the settling velocities, were a function of the SPM loading. However, the position of the curve for each metal relative to the SPM curve is an indication of whether the 'particulate metals' are settling faster or slower than the average SPM, i.e. if the metal is associated primarily with the slow settling fraction, its settling curve will be placed above that of the SPM. As with SPM a median settling velocity for each metal can be derived and will give an indication of which settling fraction the metal is associated with (Table 5.7.).

Table 5.7. Median settling velocities for trace metals.

| | Median settling velocity ($\times 10^{-3}$ mm s^{-1}) | | | | |
|-----|---|-----------------|-----------------|-----------------|-----------------|
| | 11 ^a | 62 ^b | 85 ^a | 71 ^a | 75 ^b |
| SPM | 30 | 20 | 60 | 10 | 1 |
| Fe | 20 | 20 | 40 | 8 | 2 |
| Mn | 20 | 17 | 18 | 11 | 2 |
| Zn | 7 | 8 | 27 | 21 | 1 |
| Ca | 70 | 29 | 71 | 22 | 32 |
| Co | 21 | 18 | 37 | 5 | 4 |
| Cu | 35 | nd | nd | nd | 7 |
| Pb | 8 | 20 | 38 | 2 | 2 |

^a CH99/92, ^b CH108A/93, nd - not determined

Based on the settling velocities, the metals can be divided into three groups (analogous to the groupings described in section 5.5.1.) i) metals which settle faster than the average SPM

(fast), ii) metals that settle at the same rate as the average SPM (medium) and iii) metals that settle slower than the average SPM (slow) (Table 5.8.). The ordering of the metals within each group is a refinement compared with that shown in section 5.5.1.

Table 5.8. Summary of the quantitative approach to trace metal settling behaviour.

| This Study | | Overall assessment of data from Niedergesäß* |
|------------|--|--|
| Fast | Ca (Cu, more data are required to confirm placing) | Ca |
| Medium | Fe, (Mn, tendency towards 'Slow' category) | Zn |
| Slow | Pb, Co, (Zn, mixed response though mainly 'slow') | Fe, Mn, Co |

*Niedergesäß *et al* (1994) - mixed responses were observed for each metal, the dominant behaviour has been used to assign a metal to a group.

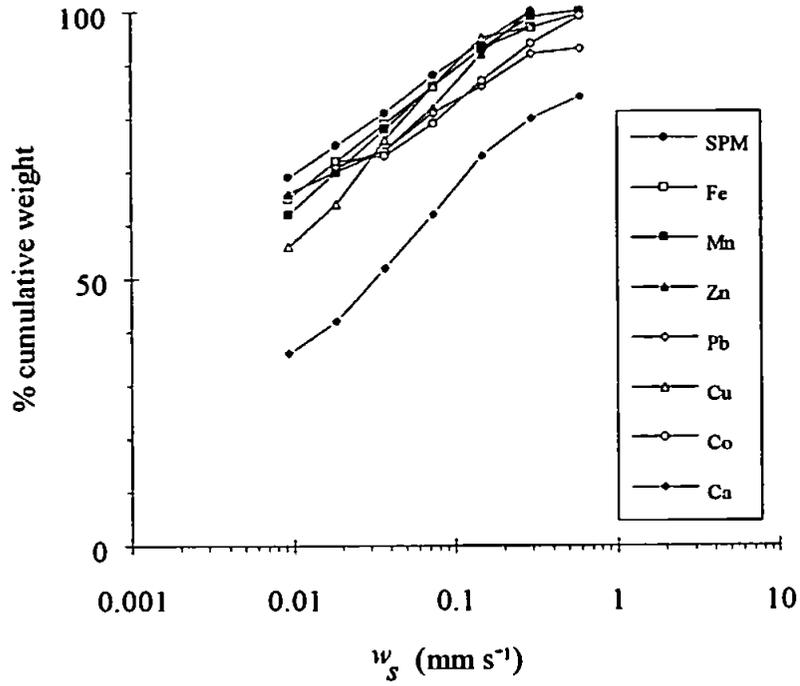
These results suggest preferential long range transport of particular trace metals as a consequence of their association with different settling fraction. Another factor to be considered is the particle reactivity of the metal (Chapter 6) since a particle unreactive metals is not likely to undergo particulate long range transport. Table 5.9. summarises the expected behaviour based on those considerations.

Table 5.9. Summary of expected degree of particulate associated long range transport.

| Metal | Settling Association | Particle reactivity | Degree of Transportation |
|-------|----------------------|---------------------|--|
| Pb | slow fraction | high | long range |
| Co | slow fraction | high | long range |
| Zn | slow/medium fraction | medium | intermediate range |
| Mn | medium/slow fraction | high | intermediate range |
| Fe | medium fraction | high | intermediate range |
| Cu | fast fraction | medium | short range |
| Cd | slow fraction | low | strongly influenced by dissolved phase |

If the metals were to behave as indicated in Table 5.9. then it would be expected that the ratio of Cu to Pb would decrease with distance from the metal source. The particulate

a)



b)

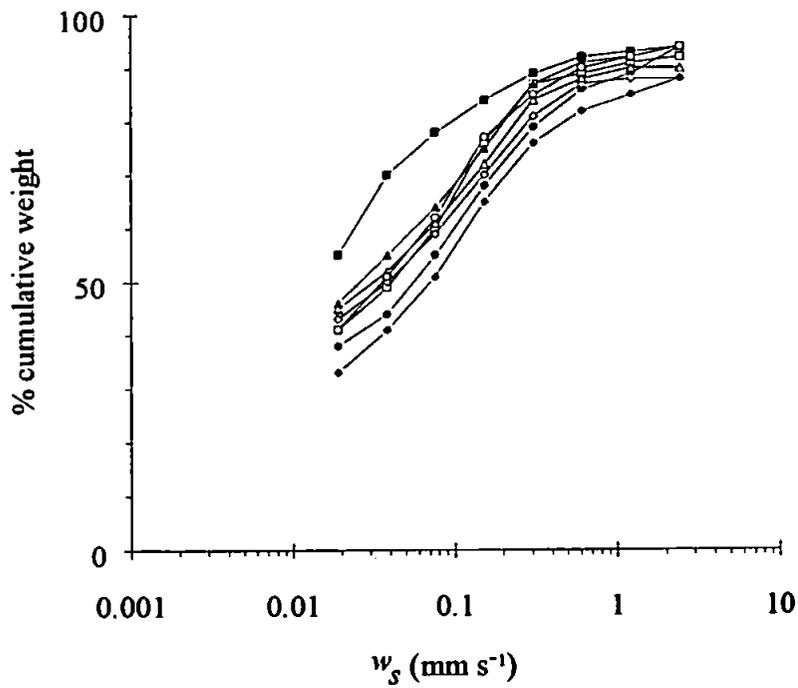


Figure 5.10. Settling velocity distributions for metals analysed during SVT experiments. a) CH108A/93/75 and b) CH99/92/85. Estimation of median settling velocity achieved by extrapolation when necessary.

trace metal data in Chapter 3 provides a limited amount of information to examine this idea. Average particulate metal concentrations were taken from the mouth and plume of the Humber Estuary and their ratios with Pb were normalised to 100. The results in Figure 5.11. suggest that the ratio of Cu to Pb does decrease with distance. Both Co and Cd also appeared to decrease with distance but the other metals do not display a clear trend.

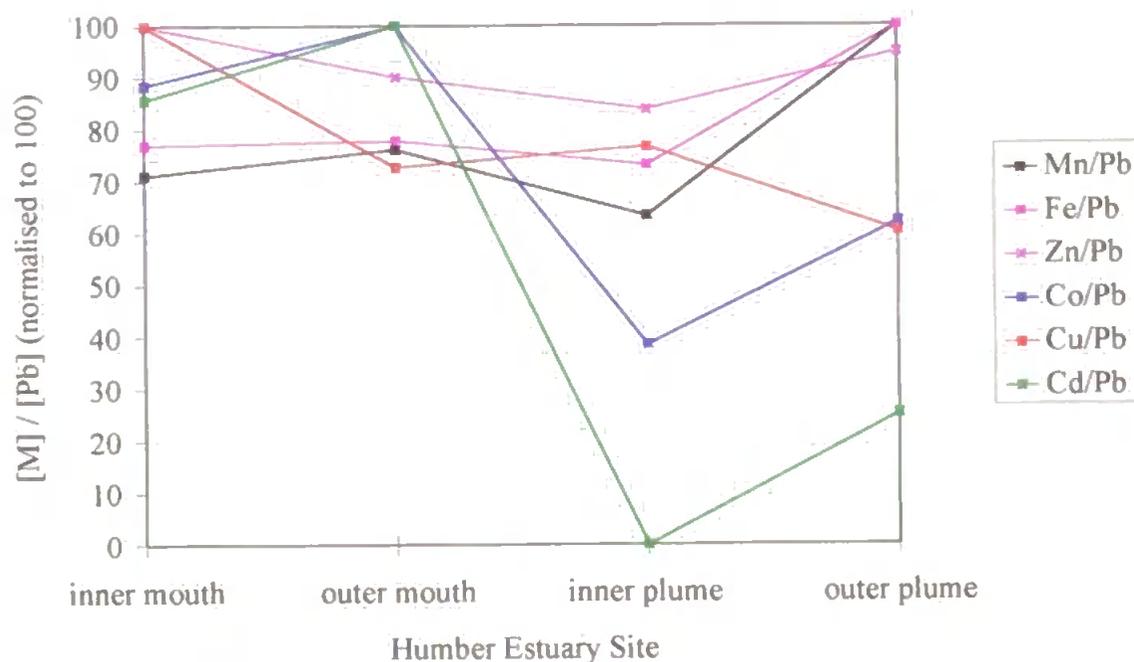


Figure 5.11. Examination of the ratio of concentrations of trace metals to Pb with distance from the Humber Estuary.

5.6. Conclusions.

The relationship between particulate settling and long range transport of particulate trace metals is fundamental to predicting pollutant dispersion. The need to unravel the interdependence of both the chemistry and the physics of settling particles, has resulted in few studies. The complete interpretation of the metals associated with different settling populations, requires an understanding of the complex nature of multi-source particle populations. An investigation of this nature requires considerable work, defining the composition and distribution of each particle type within the settling population. The results presented in this chapter are a first attempt to rectify this problem. The median

settling velocities, typically between 10^{-1} and 10^{-3} mm s⁻¹, can be used in pollutant transport models such as NORPOL (Murphy and Odd, 1993). In addition, it has been shown that the settling of some particulate metals occurs at different rates to the associated SPM. Consideration of these differences is essential in devising realistic models of pollutant dispersion in the marine environment.

The techniques employed during this study have been exploratory in nature and as such potential improvements are desirable. Samples were obtained at specific depths and hence may be only representative of SPM under those settling conditions. Samples obtained in surface waters may be more representative of a slow settling fraction than a sample collected near to the sediment bed. However, to rectify this potential problem SVT samples would need to be collected simultaneously at a variety of depths with the resultant logistical problems of dealing with those extra samples.

The SVT has not been designed to meet the needs of geochemists. The volume of the tube (5 l) is too small to take a large number of time fractions needed for better resolution of the settling velocity spectra, and also have sufficient SPM loadings to analyse for trace metals. Increasing the tube volume would improve metal determinations in low turbidity samples. Any increase in tube volume would have to be balanced against the need to handle the tube during and after deployment. Though the tube, end-stop, cone and tap are plastic, the SVT contains a metal frame and metallic fittings. The metallic components are potential sources of contamination and alternative materials should be used.

The measurement of particle diameters would be best achieved by measuring the particles directly inside the tube, to improve the correlation between settling velocity and particle diameter. One option would be the inclusion of optical windows for the use of non - disruptive sizing techniques. It has been suggested that disruption of the flocs may occur when the tube closes during deployment (Fennessy *et al*, 1994), and hence revision of the closing mechanism may be required. The accurate measurement of particle diameters and settling velocities, with preservation of natural flocs, is crucial to predicting the settling behaviour of particulate metals.

Bearing in mind the considerations already discussed, the use of the SVT has given the first data regarding the settling behaviour of particulate metals in the North Sea. It has proved

to be a valuable tool for understanding the mobilisation and transport of particulate trace metals. It has been shown that the modelling of the long range transport of pollutants, based solely on the settling characteristics of SPM, may not represent the realistic behaviour of the pollutant in the marine environment, and further work using this technique is desirable.

Chapter 6 - Radiochemical Experiments.

Chapter 6 - Radiochemical Experiments.

6.1. Introduction.

An understanding of the mechanisms and kinetics involved in the sorption of dissolved trace metals to SPM is paramount to the accurate modelling of the relative transport of trace metals in the dissolved and particulate phases (Olsen *et al*, 1982; Morris, 1986; Santschi, 1989; Morris, 1990; Förstner, 1994; Millward *et al*, 1994; Turner and Millward, 1994). A measure of the association of trace metals between the dissolved and particulate phase is given by the partition coefficient, K_D (for example Nyffeler *et al*, 1984).

$$K_D = \frac{C_p}{C_s} \quad 6.1.$$

where, C_s is the concentration of metal in the dissolved phase (w/v) and C_p is the concentration of metal in the particulate phase (w/w).

The use of the K_D concept has often assumed instantaneous and reversible equilibrium between the dissolved and particulate phases; homogeneity of particulate surfaces; and the speciation of the dissolved element is not complex (Millward, 1995). Despite these assumptions the K_D concept has been frequently applied to the modelling of trace metal behaviour in estuarine and coastal systems (ECoS, Plymsolve, 1991; Turner *et al*, 1993; Turner and Millward, 1994; Millward *et al*, 1994). Current modelling practises are developing a more realistic appraisal of the variability of K_D values in highly variable natural systems.

Estimation of C_s and C_p can be performed in a number of ways. Traditional methods of dissolved trace metal determinations, e.g. pre-concentration followed by atomic absorption spectroscopy and electrochemical techniques, have been used (Young and Harvey, 1992; Millward *et al*, 1992; Turner *et al*, 1992a; Burton *et al*, 1993; Benoit *et al*, 1994; Valenta *et al*, 1986). However, a major difficulty arises when determining C_p , which is assumed to be the fraction of particulate trace metals exchangeable with trace metals in solution. There are several digests available which are assumed to operationally define an exchangeable fraction (Salomons and Förstner, 1980; Tessier and Campbell, 1987; Förstner, 1993;

Quevauviller *et al*, 1993; Ure *et al*, 1993; Turner *et al*, 1993; Turner *et al*, 1994). Alternatively, radioisotopes may be used as surrogates for stable isotopes (Duursma and Bosch, 1970; Santschi *et al*, 1983a, 1983b; Li *et al*, 1984a, 1984b; Balistrieri and Murray, 1986; Santschi, 1988, 1989; Turner *et al*, 1992b, 1993; Koeppenkastrop and De Carlo, 1993; Turner and Millward, 1994; Millward *et al*, 1994). Implicit in the usage of radioisotopes, is the assumption that the respective stable analogue will behave in the same way as its radioisotopic counterpart (Anderson *et al*, 1987), and that the behaviour of the radioisotope is not affected by either flocculation, wall adsorption or by the presence of the stable element (Beneš *et al*, 1988). However, radioisotopes give a simple, multi-element, contamination free method to sensitively examine the partitioning between the dissolved and solid phases. The results from radioisotope experiments can be used to derive a value for the K_D and to access the percentage of radioisotope in solution (Equations 6.2. and 6.3.).

$$K_D = \frac{A_p}{A_s} \times \frac{V \cdot \rho \cdot 10^3}{mf} \quad 6.2.$$

$$\% \text{ in solution} = \frac{A_s}{A_s + A_p} \cdot 100 \quad 6.3.$$

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 mass of particles in mg; f is the geometric correction factor and ρ is the density of seawater (1.025 g ml⁻¹).

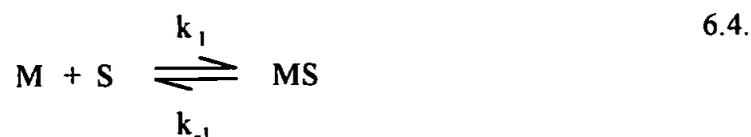
Experiments were performed during cruises in the Irish Sea (CH88/92) and North Sea (CH99/92) examining the reactivity of selected dissolved trace metals (Fe, Mn, Cr, Zn, Cd and Cs) with indigenous particles. Sampling and experimental details are given in Section 2.2.

6.2. Kinetic experiments.

6.2.1. Introduction.

The mechanism of sorption of trace elements onto particle surfaces can be considered to occur principally by either consecutive or parallel reversible reactions (Table 6.1.). Typically porous surfaces could undergo sorption by consecutive reactions in which, after initial sorption of the element on the particle surface, the element migrates into the pore structure. In contrast, the parallel process is represented by adsorption onto a non-porous solid via a series of sites with increasing binding energies. However, the 'parallel' process may allow relatively rapid re-equilibration, whereas, the timescale of the consecutive reaction may be longer because the element becomes trapped inside the pore structure and is less available for exchange with the bulk solution. This will have significant implications for the bioavailability and pollutant transport of that element. In reality, the sorption processes involved with a heterogeneous particle surface will be a more complex situation probably involving both processes and a variety of reaction steps. The aims of the radiochemical studies were two fold, i) to make inferences, from time-dependent experiments about possible mechanisms of surface adsorption in terms of assumed models (Table 6.1.), and ii) to obtain values of rate constants and hence, chemical response times and compare them to timescales for water and particle transport.

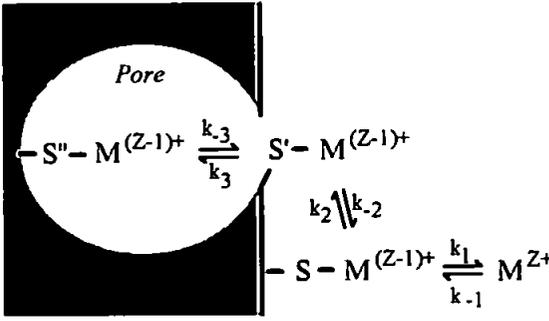
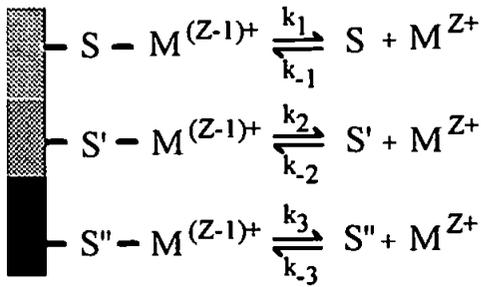
The time dependent uptake experiments (Figure 6.3.) were tested against a model of reversible first order kinetics, based on the work of Jannasch *et al* (1988) and Millward *et al* (1992). The model assumes a reversible first order kinetics and can be represented by the reaction mechanism:



The rate equation for the uptake of trace metal, M , onto particle surface, S , is :-

$$\frac{-d[M]}{dt} = k_1 [M] - k_{-1} [MS] \quad 6.5.$$

Table 6.1. Mechanisms for the surface adsorption of trace metals.

| Mechanism | Model | Description |
|-------------|--|--|
| Consecutive |  | Porous solids with initial reversible surface adsorption and the subsequent complex migration of metal to internal adsorption sites. |
| Parallel |  | Non-porous solid with multiple adsorption sites, of increasing binding energies $S'' > S' > S$ |

$[MS]$ is surface adsorbed metal on the particle at time = 0, $[MS]_{ADS}$, and the amount adsorbed during the experiment (determined as the difference between the dissolved metal concentrations at time = 0 and t, $[M]_0 - [M]_t$). For the radioactive experiments $[MS]_{ADS}$ is zero (Equation 6.6).

$$[MS] = [MS]_{ADS} + [M]_0 - [M]_t = [M]_0 - [M]_t \quad 6.6.$$

The integration of Equation 6.5. gives (Millward *et al*, 1992):

$$([M]_t - [M]_E) = ([M]_0 - [M]_E) \exp[-(k_1 + k_{-1})t] \quad 6.7.$$

Where, $[M]_E$ is the equilibrium concentration of dissolved radiotracer. The conditional equilibrium constant is given by:

$$K = \frac{k_1}{k_{-1}} = \frac{[M]_0 - [M]_E}{[M]_E} \quad 6.8.$$

Thus, k_{-1} can be derived in terms of k_1 :

$$k_{-1} = \frac{k_1 [M]_E}{[M]_o - [M]_E} \quad 6.9.$$

Equation 6.9. can be substituted in the term $(k_1 + k_{-1})$ from Equation 6.7.

$$(k_1 + k_{-1}) = \left(k_1 + \frac{k_1 [M]_E}{[M]_o - [M]_E} \right) = k_1 \frac{[M]_o}{[M]_o - [M]_E} \quad 6.10.$$

This expression can be substituted into Equation 6.7. and after rearrangement yields :-

$$[M]_t = ([M]_o - [M]_E) \exp \left[-t \left(k_1 \frac{[M]_o}{[M]_o - [M]_E} \right) \right] + [M]_E \quad 6.11.$$

$$\frac{([M]_t - [M]_E)}{([M]_o - [M]_E)} = \exp \left[-t \left(k_1 \frac{[M]_o}{[M]_o - [M]_E} \right) \right] \quad 6.12.$$

$[M]_o = 100\%$ of radiotracer in dissolved phase.

$$\log_e \left[\frac{([M]_t - [M]_E)}{([M]_o - [M]_E)} \right] = -k_1 t \left[\frac{[M]_o}{[M]_o - [M]_E} \right] \quad 6.13.$$

$$k_1 t = \left[\frac{[M]_o - [M]_E}{[M]_o} \right] \log_e \left[\frac{[M]_o - [M]_E}{[M]_t - [M]_E} \right] \quad 6.14.$$

Thus, setting $C_s = [M]_t$ and $C_p = 100 - [M]_t$, at time t , K_D' (partition coefficient as a function of time) is given by :-

$$K_D' = \frac{(100 - [M]_t)}{[M]_t} \quad 6.15.$$

From Equation 6.7 and by assuming the five day K_D approximates to equilibrium, k_{-1} can be estimated using Equation 6.16.

$$k_{-1} = \frac{k_1 [M]_E}{[M]_o - [M]_E} \quad 6.16.$$

The forward and reverse rate constants, can then be used to obtain the system response time for each metal using Equation 6.17., which gives the rate to achieve 63% of the new metal solution - solid partitioning equilibrium (Honeyman and Santchi, 1988) after the system has been altered. The system response time can be used in modelling to relate to the flushing time of water segments and hence, be used to examine the transport of pollutants.

$$\tau_{resp} = \frac{I}{k_f + k_{-f}} \quad 6.17.$$

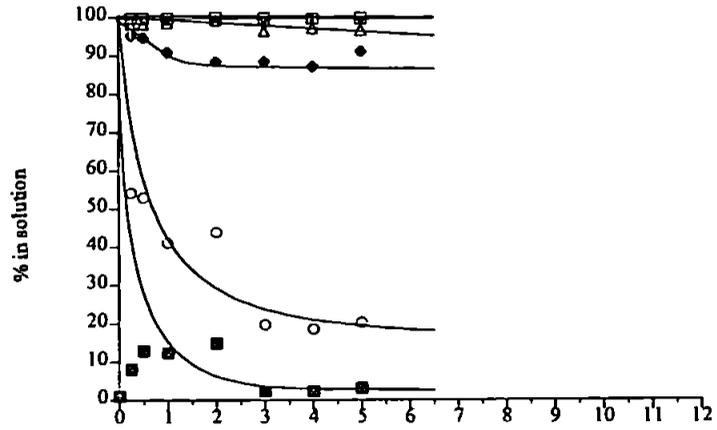
6.2.2. Trace Metal Uptake onto Suspended Particulate Matter.

6.2.2.1. Irish Sea.

The uptake of dissolved radioisotopes by SPM at Y and Z, in the Irish Sea is given in Figure 6.2. The metals, except Mn, behaved in a similar fashion at both sites. Cadmium favours the dissolved phase in seawater because of chloro-complexes (CdCl_4^{2+}), whereas Cs exists as the free ion (Cs^+) in seawater (Turner *et al*, 1981). Both metals showed a low affinity for the particulate phase, with almost no loss from solution. Though Zn did adsorb onto particulate matter >90% was still in solution at the end of both experiments. Initially, Cr and Fe were rapidly adsorbed during the first few days of the experiment, and then appeared to reach a quasi-equilibrium, both of these metals are likely to interact with the container walls and it is difficult to distinguish between wall effects and particle uptake from these results. Uptake of Mn at Site Y, was considerably less than at site Z. The autocatalytic precipitation of Mn onto particulate matter has been well documented (Stumm and Morgan, 1981; Morris and Bale, 1979; Yeats and Strain, 1990), and may suggest a reason for the disparity in the behaviour of Mn, at these two sites. The concentration of particle associated Mn, between the two sites, is similar ($1159 \mu\text{g g}^{-1}$ and $1119 \mu\text{g g}^{-1}$ for sites Y and Z respectively), however the concentration of SPM is more than a magnitude greater at Site Z than site Y (4.1 mg l^{-1} and 71.4 mg l^{-1} , for Site Z and Y respectively). This suggests that the difference in Mn adsorption between the two sites, could be a function of Mn load in suspension, i.e. 5 mg Mn l^{-1} for Site Y compared with 83 mg Mn l^{-1} . Samples from Site Z will have a much greater concentration of particulate Mn available to autocatalyse the precipitation of Mn. Though it would have been desirable to examine the results using the

K_D concept, difficulties were encountered in accurately weighing the samples, which prevented a reliable calculation of K_D 's for the radioisotopes.

a)



b)

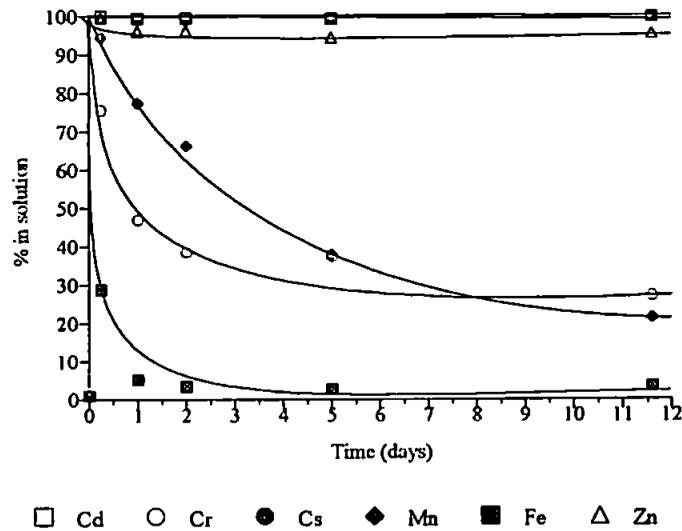


Figure 6.2. Time dependent adsorption studies for a) Site Y and b) Site Z in the Irish Sea (Figure 2.1.), % in solution calculated using Equation 6.3.

6.2.2.2. North Sea.

Kinetic studies were performed on SPM, taken from the Holderness coast, and from the mouth of the Humber Estuary (see Figure 6.4.). The time dependent uptake of radioisotopes were evaluated with Equations 6.11. and 6.15. to derive a value for k_1 . The value of k_1 was used in Equation 6.14. to produce model curves and to obtain values for k_1 and τ_{resp} (Table 6.2.). The sensitivity of this method was examined and it was found that a variation of $\pm 20\%$ in the value of k_1 , was within the scatter of the data whereas a 50% decrease in the value of k_1 was unacceptable (Figure 6.3.).

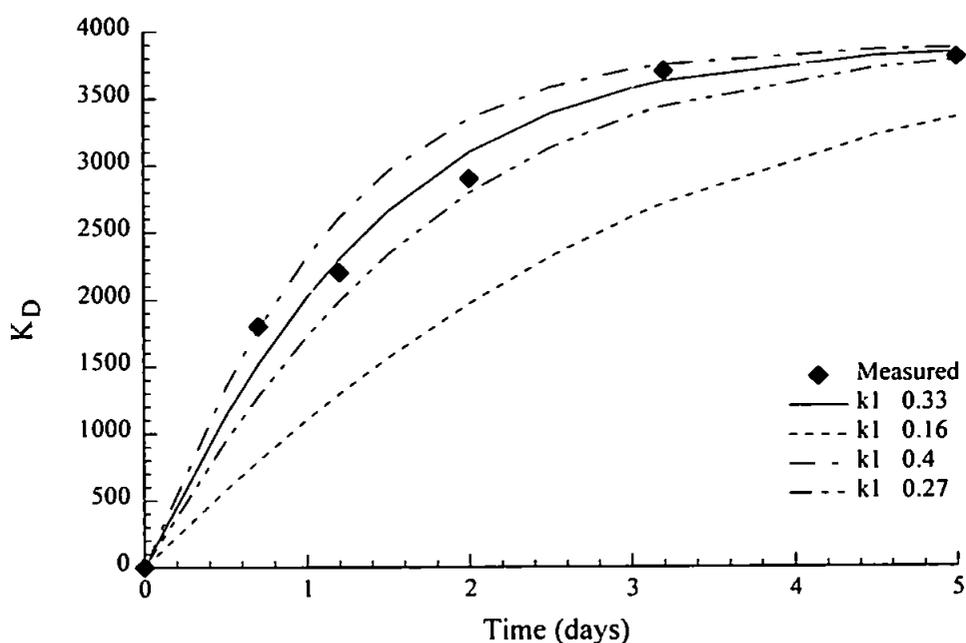


Figure 6.3. Time dependent profile of Zn with Humber particles. Model curves are variations in the value of k_1 corresponding to $\pm 20\%$ and 50% of the optimal value for k_1 (0.33 d^{-1}).

All of the metals, except Cs, had a greater affinity for Humber particles compared with Holderness particles. SPM in the Humber plume is composed of a multiplicity of particle types, which include inputs from i) the estuary, ii) eroded Holderness material, iii) industrial effluent, iv) sewage and v) dredge spoils. Each particle type could have a different reactivity towards trace metals, due to different surface composition, for example SPM from the estuary gave an exceptionally high Fe content of 18 mg g^{-1} compared to $<5 \text{ mg g}^{-1}$

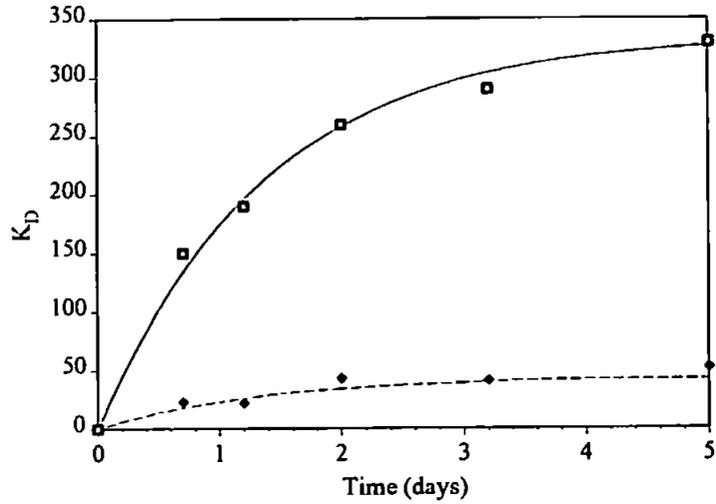
for Holderness SPM (Section 3.3) which could cause an increase in the sorptive capacity of the Humber particles (Millward and Moore, 1982).

Initial uptake of Cd, Cs, Zn and Fe appeared to be rapid, followed by slower uptake after one or two days which may suggest a secondary reaction following the initial uptake of the radiotracer. Anomalous results were obtained for Cr and for the Fe sorption onto Holderness particles where after initial uptake the K_D decreased, which probably indicated adsorption of the radioisotopes onto the container wall.

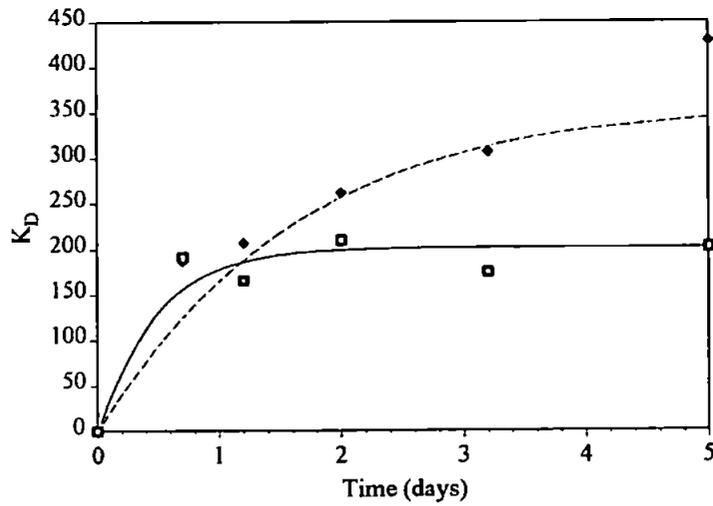
The greater affinity of dissolved Cs for Holderness particles (composed of boulder clay) is believed to be the result of Cs displacing K ion in the clay lattice structure (Nyffeler *et al*, 1984; Turner *et al*, 1992b). This has been described as a two step process, initial surface adsorption precedes transport inside of the clay lattice. The presence of amorphous Fe and organic coatings on Humber material will inhibit the second step of this mechanism because of the blocking of pores, making the internal sites inaccessible for sorption.

Large differences in the Mn partition coefficients were observed between the Humber samples ($K_D^5 = 6 \times 10^4$) and the Holderness samples ($K_D^5 = 8 \times 10^2$). Typical Humber particles have a Mn concentration about $1000 \mu\text{g g}^{-1}$, whereas SPM samples from the Holderness area are $350 \mu\text{g g}^{-1}$. The model curve for reversible first order kinetics for the sorption of Mn onto Humber particles did not fit, indicating a different mechanism. As indicated in Section 6.2.2.1. sorption of Mn is likely to follow an autocatalytic process. The Mn associated with Humber SPM may originate from industrial discharges and therefore, represent freshly precipitated Mn oxides; whereas the Holderness SPM is liable to be weathered and aged, and be less sorptive compared with Humber SPM. The sorption of Mn onto Holderness particles appeared to follow zero order kinetics, similar to that observed by Morris and Bale (1979) for riverine material of low Mn content. Thus, Holderness material is not conducive to Mn adsorption and the subsequent mixing of the end member particles would produce a reduction in the apparent K_D value for the mixed system (see Section 6.4.).

a) Cd



b) Cs



c) Zn

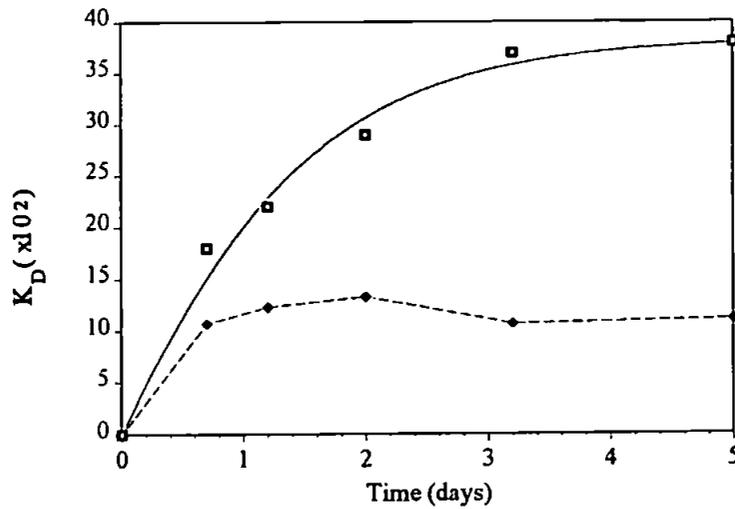
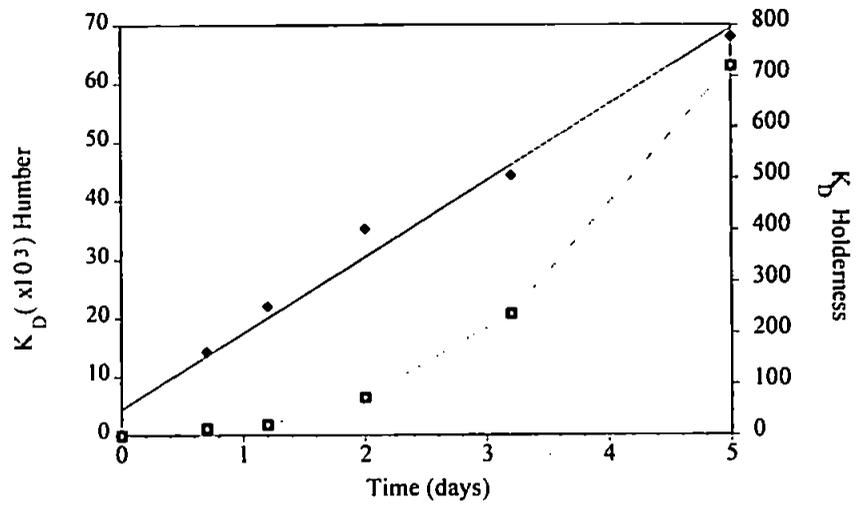
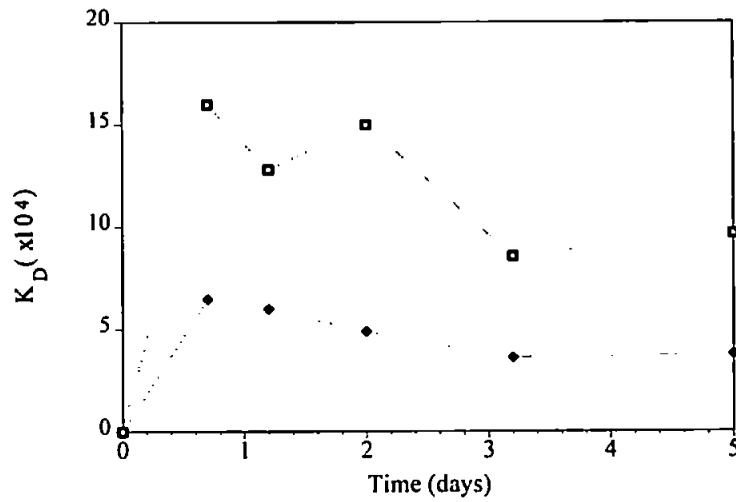


Figure 6.4. Time dependent uptake experiments a) Cd, b) Cs, c) Zn, d) Mn, e) Cr and f) Fe, comparing Humber SPM (—□—) with Holderness SPM (- - ♦ - -). Model curves are indicated based on k_1 values from Table 6.2., the exception is for Mn (Holderness) which shows zero order kinetic and is fitted to the equation $y = 148.5 x + 50.7$ $r^2 = 0.981$ $p < 0.05$ (non-smoothed lines indicate that no values of k_1 were available).

d) Mn



e) Cr



f) Fe

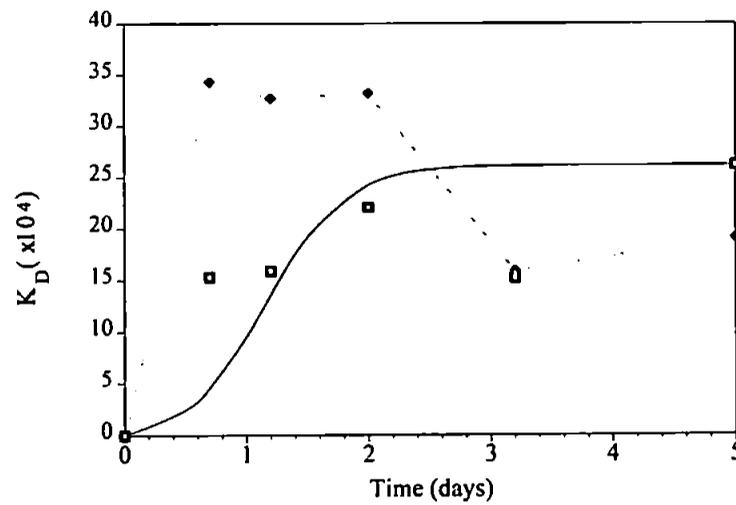


Figure 6.4. continued.

Table 6.2. Derived values of the forward rate constant (k_1) from the time dependent uptake studies using Holderness and Humber SPM. Indicated are the r and p values associated with the derivation of k_1 from Equation 6.14. Also shown are the reverse rate constant (k_{-1}) and the system response time (τ_{resp}) which have been derived using k_1 .

| | k_1 (d^{-1}) | r | p | k_{-1} (d^{-1}) | τ_{resp} (d) |
|-------------------|-----------------------|-------|-------------|--------------------------|--------------------------|
| <i>Holderness</i> | | | | | |
| Zn | - | - | - | - | - |
| Cd | 0.02 | 0.963 | ≤ 0.05 | 0.76 | 1.29 |
| Cs | 0.12 | 0.840 | ≤ 0.10 | 0.60 | 1.42 |
| <i>Humber</i> | | | | | |
| Zn | 0.33 | 0.985 | ≤ 0.05 | 0.65 | 1.03 |
| Cd | 0.03 | 0.987 | ≤ 0.05 | 0.72 | 1.32 |
| Cs | 0.02 | 0.923 | ≤ 0.05 | 2.03 | 0.49 |

For Mn, the results from the Irish and North Sea, both illustrate the apparent importance of pre-existing particulate Mn, in promoting the uptake of dissolved Mn. This lends support to the idea previously proposed that the behaviour of Mn is affected by autocatalytic reaction promoted at the particle surface (Morris and Bale, 1979; Yeats and Strain, 1990). However, Mn adsorption in the Humber is dependent on the reactivity of the Mn surface composition (inferred from the concentration of exchangeable Mn and knowledge of industrial input to the region), compared with the Holderness Mn composition. In the Irish Sea, due to the similarity between the particle composition at Sites Y and Z, the important criterion appears to be the total number of particles present (inferred from the SPM concentration).

As the flushing time of the Humber Estuary is of the order of 40 days and the τ_{resp} for the trace metals are significantly less than this, dissolved trace metals discharged into the estuary are likely to equilibrate with the SPM and enter into the source sink pathway of particulate matter before being advected into the adjacent coastal waters. Thus, modelling of the behaviour of trace metals in the Humber mouth should consider trace metal inputs to behave as equilibrated species.

6.3. Partitioning of Trace metals with Marine Particles over Five Days.

K_D^5 's have been used, as a representative time scale, for modelling interchanges of trace metals in salinity defined hydrodynamic segments, of a macrotidal estuary (Morris, 1990, Turner *et al*, 1993). Five day K_D s have been widely used, to provide quasi equilibrium K_D values (Turner *et al*, 1992b, Turner *et al*, 1993, Turner and Millward, 1994), allowing inter-comparisons of trace metal behaviour in different environments, to be made (Table 6.3.).

Table 6.3. Comparison of K_D^5 values from this study with data from the literature.

| Reference | Location | K_D^5 s (x 10 ³)* | | | | | |
|-----------------|---------------------|---------------------------------|------|------|-----|----|------|
| | | Cd | Cs | Zn | Mn | Cr | Fe |
| This Study† | Irish Sea | 0.20 | 0.18 | 1.2 | 30 | 19 | 97 |
| | 1 Dee Estuary | 0.55 | 0.25 | 10.0 | 675 | 12 | 1360 |
| This Study‡ | Humber Mouth | 0.33 | 0.20 | 3.8 | 63 | 97 | 260 |
| This Study‡ | Holderness seawater | 0.05 | 0.43 | 1.1 | 0.8 | 38 | 190 |
| | 2 Humber Estuary | 0.75 | 0.62 | 11.0 | 108 | | |
| | 3 Humber Plume | 0.40 | 0.51 | 5.4 | 53 | | |
| | 3 Thames Plume | 0.53 | 0.31 | 3.7 | 33 | | |
| | 4 Tamar Estuary | 0.28 | 0.17 | 13.0 | | | |
| 5 Rhine Estuary | 0.53 | | 14.0 | | | | |

1 Turner and Millward, 1994; 2 Turner *et al*, 1993; 3 Turner *et al*, 1992b; 4 Bale, 1987; 5 Salomons and Förstner, 1980. * pH 8 ± 0.5. † Average of K_D^5 's from CH88/92. ‡ K_D^5 's taken from kinetic experiments during CH99 (see Section 6.3.).

It can be seen from Table 6.2., that each metal is typified by a K_D range, e.g. Cs has a K_D between 10¹ to 10², whereas Fe ranges between 10⁵ and 10⁶. Generally, the particle affinity, as measured by the K_D^5 , showed an increasing metal affinity for particles, as shown below :

$$\text{Fe} > \text{Cr} > \text{Mn} > \text{Zn} > \text{Cs} \approx \text{Cd}$$

This ordering was similar to that found by Turner *et al*, 1992 (Mn, Zn, Cs, Cd), in the southern North Sea. With the exception of cadmium in the Hudson Estuary, this ordering was found in the other marine waters identified in Table 6.3.

Comparison of the five day K_D s from this study, indicate a number of conclusions. The Irish Sea K_D s for Zn, Mn, Cr and Fe tend to be lower than those observed in the Humber mouth. The Irish Sea samples were obtained from an offshore site (site Z, see Figure 2.1.), whereas the Humber mouth samples are likely to be more influenced by anthropogenic inputs. Of particular geochemical importance, among other waste inputs, is the iron rich industrial waste discharge from a titanium dioxide factory (Grant and Middleton, 1990, Greenpeace, 1992) near Immingham. The iron from the discharge could be rapidly hydrolysed, forming fresh iron precipitates, giving rise to new sorptive surfaces and thereby increasing the K_D (Millward and Moore, 1982). The differences between Irish Sea and Humber mouth K_D s, for Cd and Cs, are small. Both elements exhibit low particle affinity. The influence of changes in particle characteristics, will therefore be less pronounced, and in this case almost negligible.

The K_D 's from the Humber mouth and Holderness show that metals have a greater particle affinity for Humber particles compared with those of the Holderness region, the exception is Cs. Cs is known to replace interstitial K^+ in clay lattices (Li *et al*, 1984b), and hence, the relatively pristine particles from the eroded Holderness cliffs, allow easier passage of Cs into the lattice, than coated Humber particles (previously discussed in Section 6.2.2.2.). Humber mouth K_D s compare with the values obtained from the Humber plume (Turner *et al*, 1992), and are not too dissimilar to the values observed in New York coastal water (Li *et al*, 1984b). These similarities suggest that the Humber mouth samples, taken during CH99/92, are more representative of coastal SPM than estuarine SPM. This was unexpected, as the samples were taken during an ebb tide (HW +4 hours), which suggests a dynamic mixing and entrainment of multiple particulate sources in the Humber mouth region.

6.4. Particle Mixing Experiments.

Radioisotopes can be used to examine multi-component systems, where partitioning occurs between a variety of dissolved and particulate phases. These experiments have been loosely termed as 'mixing series', and can be used to elucidate the behaviour of trace metals in populations of mixed particle origin, as illustrated in the Humber Plume region. In simplistic terms, within the Humber Plume; fluvial, offshore and eroded Holderness Cliff material combine together. Repartitioning of trace metals between particles of different origin can occur and hence, information about these processes is important in terms of the long range transport of pollutants into the North Sea.

If a body of water is considered in the plume region of the Humber Estuary it will contain particulate trace metals originating from the Humber and Holderness regions in addition to dissolved metals.

Let: C = concentration of particulate metals

S = concentration of dissolved metals

and subscripts p = plume region; Ho = Holderness origin; Hu = Humber origin.

Thus, the mixing of the particulate trace metals can be described by Equation 6.18.

$$C_p = \frac{SPM_{Ho} C_{Ho} + SPM_{Hu} C_{Hu}}{SPM_{Ho} + SPM_{Hu}} \quad 6.18.$$

Let P = proportion of Humber material to the total material in the plume

$$P = \frac{SPM_{Hu}}{SPM_{Ho} + SPM_{Hu}} \quad 6.19.$$

and

$$1 - P = \frac{SPM_{Ho}}{SPM_{Ho} + SPM_{Hu}} \quad 6.20.$$

Equation 6.18 can be rewritten by substituting Equations 6.19 and 6.20 into Equation 6.18.

$$C_p = (1 - P) C_{Ho} + P C_{Hu} \quad 6.21.$$

The concentration of particulate metal from each region can be described in terms of the K_D for each particle type and the concentration of the dissolved metal.

$$C_p = K_{D_p} S \quad 6.22.$$

$$C_{Ho} = K_{D_{Ho}} S \quad 6.23.$$

$$C_{Hu} = K_{D_{Hu}} S \quad 6.24.$$

Equations 6.22.; 6.23. and 6.24. can be substituted into Equation 6.21.

$$K_{D_p} S = (1 - P) K_{D_{Ho}} S + P K_{D_{Hu}} S \quad 6.25.$$

$$K_{D_p} = (1 - P) K_{D_{Ho}} + P K_{D_{Hu}} \quad 6.26.$$

$$K_{D_p} = K_{D_{Ho}} + P (K_{D_{Hu}} - K_{D_{Ho}}) \quad 6.27.$$

The value P assumes additivity, i.e. that the Humber and Holderness particles present are available for interaction with dissolved metals as independent particles. However, this may not be valid as the presence of each material may affect the other. For example organic material introduced from the Humber Estuary may affect Holderness particles and flocculation of Holderness material (containing low ferromanganese) with Humber material may affect the interaction of the Humber particles. It was found that to account for non-additive behaviour P was required to be raised to the power A , where A = additivity constant and P was rewritten as -

$$P^A = \left(\frac{SPM_{Hu}}{SPM_{Hu} + SPM_{Ho}} \right)^A \quad 6.33.$$

Thus Equation 6.32. becomes a Mixing Equation describing the behaviour of particulate trace metals in the plume region of the Humber Estuary (Millward *et al*, 1994).

$$K_{D_p} = K_{D_{Ho}} + (K_{D_{Hu}} - K_{D_{Ho}}) P^A \quad 6.34.$$

The extent of non-additivity is measured by the value of A (Equation 6.18). If $A = 1$ the two end members mix in a linear fashion, whereas if $A > 1$ (concave curve) or $A < 1$ (convex

curve) the two end members will be mixing in a simple fashion with additional processes causing curvature of the line away from the linear situation (Davies-Colley *et al*, 1984).

Rearrangement and taking logarithms of Equation 6.34. gives Equation 6.35. Equation 6.35. can be used to give an estimate of the A (see Figure 6.6).

$$\log[K_{D_p} - K_{D_{Ho}}] = \log[K_{D_{Hn}} - K_{D_{Ho}}] + A \cdot \log P \quad 6.35.$$

$$y = c + mx$$

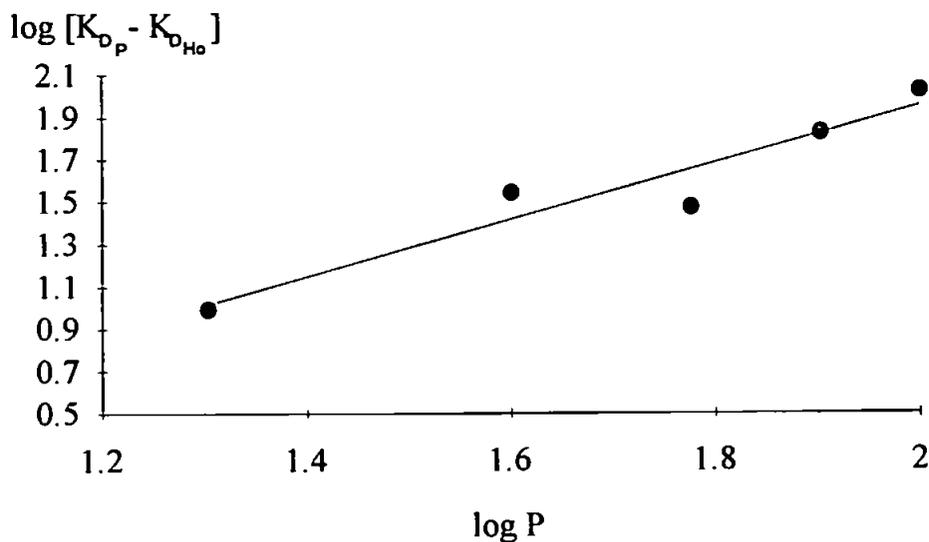


Figure 6.5. Plot of $\log[K_{D_p} - K_{D_{Ho}}]$ versus $\log P$ to find the additivity factor (A) for Cs ($A = 1.3$, $r = 0.91$)

Holderness and Humber seawater were mixed in varying proportions to give a mixing series (Section 2.2.5.). From Figure 6.6., the behaviour of Zn and Fe during mixing of Humber and Holderness SPM appears to be additive (Honeyman and Santschi, 1988). Zn is strongly bound by Fe oxyhydroxide coatings (Millward and Moore, 1982) and consequently the behaviour of both Fe and Zn are similar (Figures 6.6i. and ii.). Of the six metals examined (Cd, Cr, Cs, Fe, Mn and Zn) during this experiment only Cs exhibited a higher K_D for Holderness SPM compared with Humber SPM. While the remaining metals show a clear preference for Humber SPM (Table 6.2.). The behaviour of Cs is less clear cut due to the scatter of the points and could be considered to be additive (Figure 6.6c.). As previously mentioned (Section 6.2.2.) Cs is initially adsorbed onto the surface of the

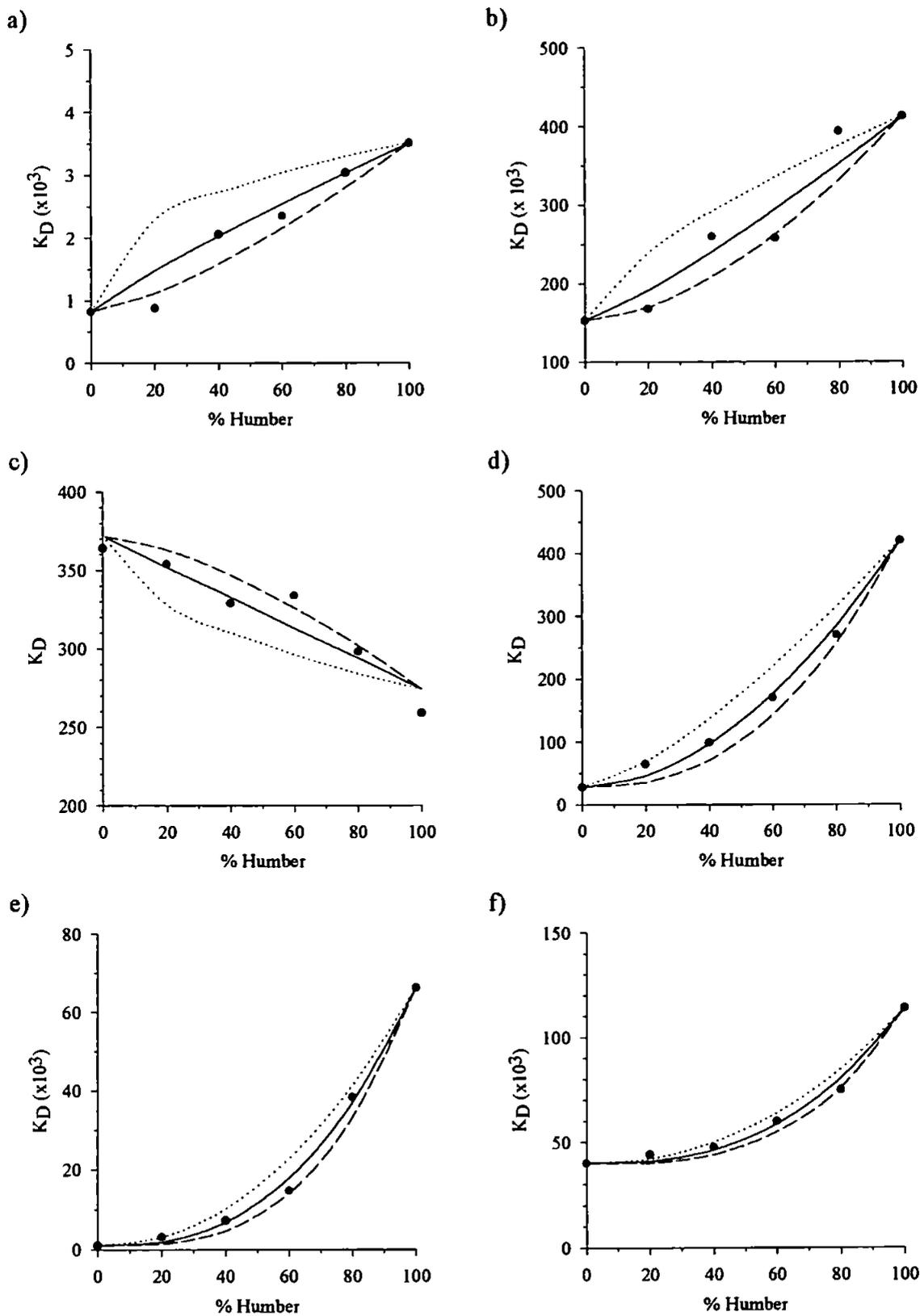


Figure 6.6. Equation 6.34. fitted to a mixing series experiment using Humber and Holderness SPM, lines indicate A (—), $A + 0.5$ (- - - -) and $A - 0.5$ (· · · · ·). a) Zn ($A = 0.8$), b) Fe ($A = 1.2$), c) Cs ($A = 1.0$), d) Cd ($A = 1.9$), e) Mn ($A = 2.64$), f) Cr ($A = 2.7$).

particle and then migrates into the particle matrix, by displacement of K ions in the clay lattice (Turner *et al*, 1993). Holderness particles are relatively pristine and hence, will not exhibit either fresh Fe precipitates or organic coatings, these would inhibit the migration of Cs into the lattice of the Holderness particles. However, Cd, Mn and Cr are clearly non-additive. The speciation of Cd favours a low K_D and shows an increase in particle affinity once 40% of Humber material is present. This may be a reflection of the near pristine condition of the Holderness particles compared with Humber particles whose coatings allow more adsorption sites for Cd. Mn interacts with particles by an autocatalytic precipitation (Morris and Bale, 1979). Holderness particles have a much lower Mn content than Humber particles, hence the autocatalytic effect will be reduced in the presence of Holderness SPM, and an increasing affinity for particles was observed during the addition of Humber SPM (Figure 6.6v.). The dissolved speciation of Cr in the marine environment is as an oxy anion (CrO_4^{2-} , NaCrO_4^-) (Turner *et al*, 1981; Pettine *et al*, 1991; Turner and Millward, 1994). The Cr was added in this experiment as the more particle reactive reduced species (Cr III), the oxidative residence time is 17 to 100d (Santschi, 1988), hence during the five day incubations of the mixing series the Cr will be predominately in the reduced state. However, oxidation of Cr is enhanced at the surface of Mn oxides (Eary and Rai, 1987; Johnson and Xyla, 1991) and photoreduction occurs in the presence of dissolved organic carbon (Santschi, 1988). Clearly, the adsorption of Cr onto marine particles is a complex process, and Humber SPM is enriched in both Mn coatings and organic matter, compared with Holderness SPM.

Equation 6.19. did not always give the best solution for A , and it was necessary to use iterative methods to find A . A comparison between the calculation and the iterative methods is shown in Table 6.3. The use of Equation 6.34. as a tool for modelling long range transport of trace metals requires knowledge of the value P . The value of the $^{206}/^{207}\text{Pb}$ isotopic ratio (see Section 1.6.) could be developed to give an indication of the contribution of the relative proportions of Holderness and Humber particles (Section 4.3.). This information may provide an estimate of the % of uncontaminated Holderness material with contaminated Humber material.

Table 6.3. A comparison of the methods for determining the additivity constant from the Humber/Holderness mixing series.

| Metal | Additivity Constant | |
|-------|---------------------|-----------|
| | calculated | Iterative |
| Fe | 1.7 | 1.2 |
| Zn | 0.9 | 0.8 |
| Cs | 1.3 | 1.0 |
| Cd | 1.5 | 1.9 |
| Mn | 2.1 | 2.6 |
| Cr | 1.8 | 2.7 |

6.5. Uptake of Trace Metals by Particles with Different Settling Velocities.

Samples of *in situ* SPM were taken and allowed to settle under gravity using a settling velocity tube (Chapter 5.). From some of these experiments, the trace metal reactivity of each settling fraction was examined using radioisotopes (see Section 2.2.4. and Table 6.4.).

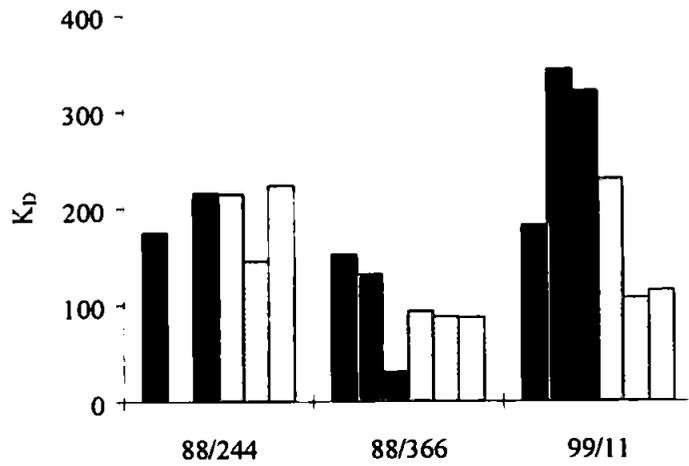
Table 6.4. Details of samples used in SVT-Radiotracer experiments.

| Cruise | CTD No | Description | Tidal Conditions | | Salinity | SPM (mg l ⁻¹) | Temp. (°C) |
|--------|--------|--------------|------------------|-----|----------|---------------------------|------------|
| | | | | | | | |
| CH88A | 244 | Site Z | Sp | ebb | 32.056 | 105 | 6.069 |
| CH88A | 366 | Site Z | Np | ebb | 32.580 | 9 | 5.924 |
| CH99 | 11 | Humber Mouth | Sp | LW | 24.217 | 50 | 6.469 |

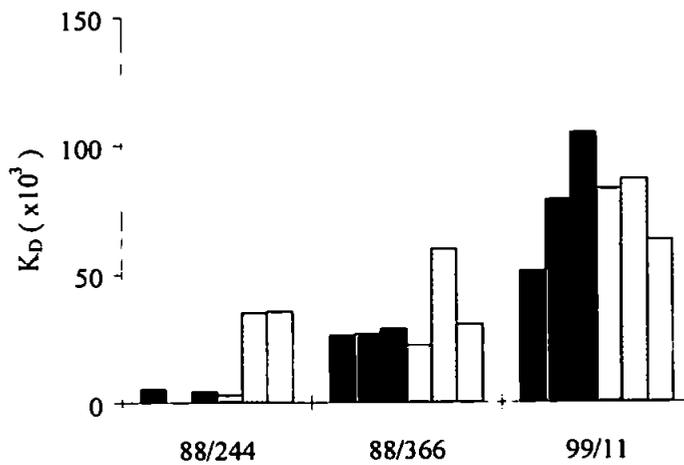
Sp - spring tide; Np - neap tide; LW - low water

The results from these studies are given in Figure 6.8. i) - vi). Using the same qualitative approach, which was applied to the metal contents (see Section 5.5.1.), the radioisotopes do not show preferential reactivity towards either the faster settling fractions or the slow settling fractions. The higher K_D 's of Fe and Mn for CH88/244 compared to CH88/366 may be attributable to a higher SPM concentration. Correlation of the radioisotopic K_D with the concentrations of particulate Fe and Mn in each fraction did not show any

i) Cd



ii) Cr



iii) Cs

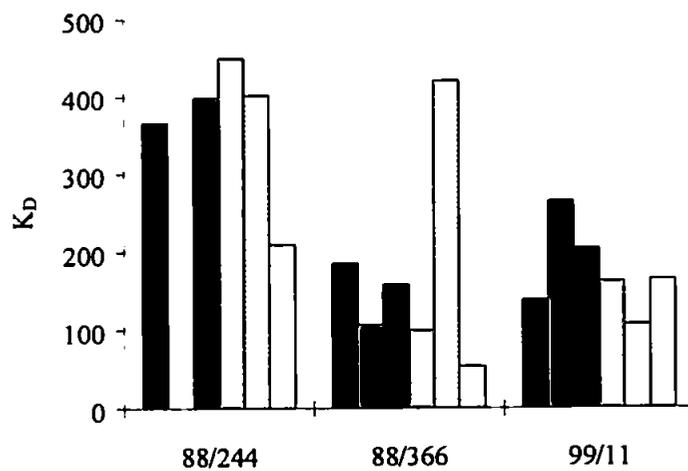
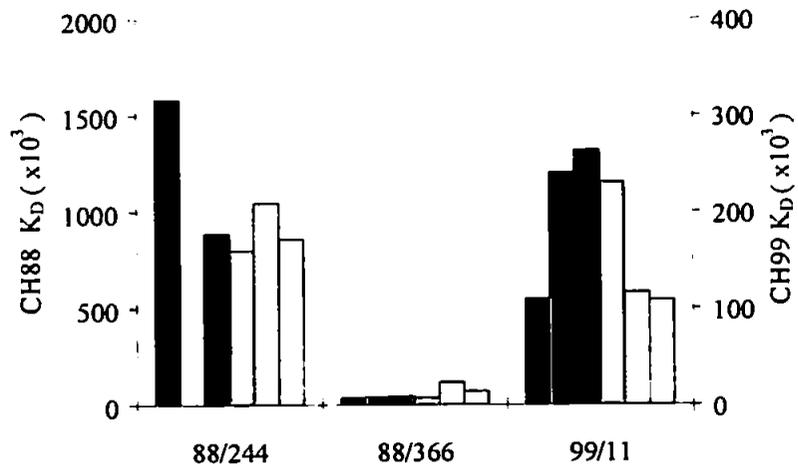
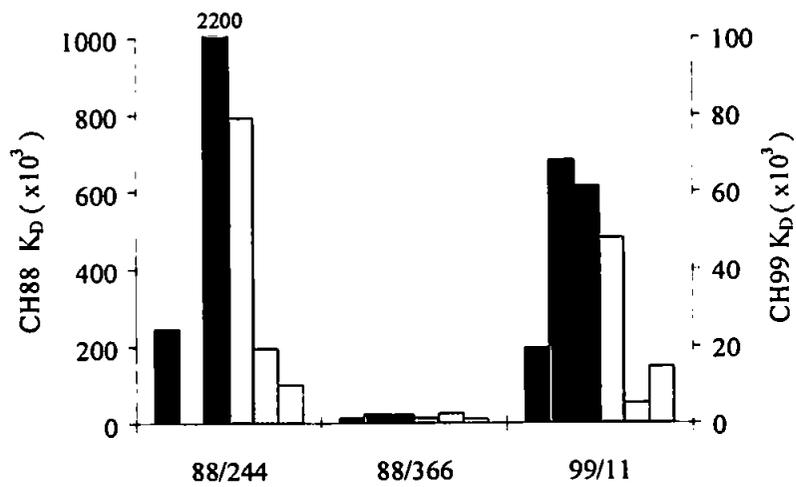


Figure 6.8. Variation of K_D with particle populations differentiated by settling. Legend indicates settling time in minutes. i) Cd ii) Cr iii) Cs iv) Fe v) Mn vi) Zn

iv) Fe



v) Mn



vi) Zn

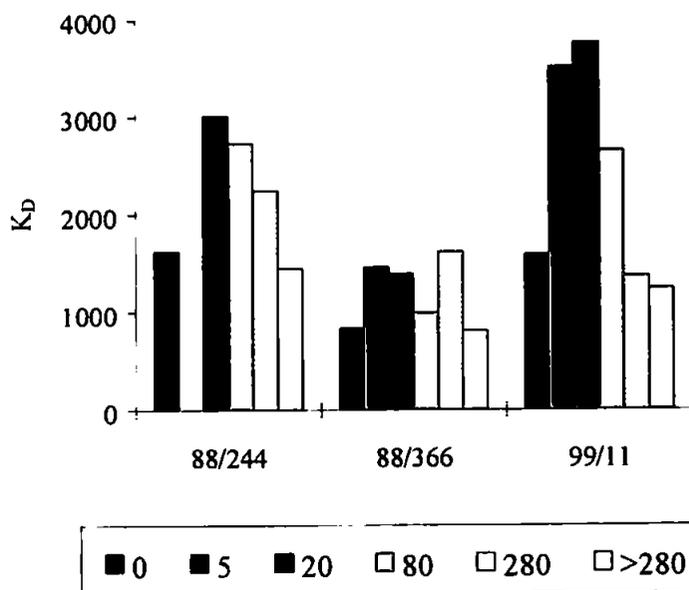


Figure 6.8. cont.

correlations at the 95% confidence interval. Though a significant correlation (95%) was found between the concentration of SPM and some of the radiotracers (Cs, Cd, Zn, Mn) in CH99/11. For the majority of the metals the lowest K_D 's tended to be found in the fast and slow settling fractions, which may be caused by the different nature of each settling fraction. The fast settling fraction (5 min) will contain particles of large diameter and low surface area. Unexpectedly low K_D 's were also observed in the slowest settling fractions. It was originally expected that the slower settling fraction would have smaller particles, with high surface areas, resulting in larger K_D 's. As observed in Section 5.4, these slow settling particles exist as flocculated material. Flocculated material will reduce the available area for metal adsorption by hiding potential adsorption sites within the floc and consequently reduce the observed value of K_D .

6.6. Conclusion.

Though much work has been performed on estuarine mixing processes using radioisotopes, little has been done to examine coastal mixing processes. The work presented in this chapter has attempted to model the behaviour of particle mixing in the plume region of the Humber Estuary and examine a number of the processes involved with homogeneous trace metal reactivity in mixed particle populations. As many models use K_D values to describe trace metal reactivity, general algorithms have been postulated to predict the resultant K_D caused by these mixing processes. Modelling of trace metal particle interactions will contribute to the understanding of the long range transport of trace metals through the coastal boundary zone.

**Chapter 7 -
Conclusions:
Application of the Results for Modelling
the Long Range Transport of Particulate
Trace Metals.**

Chapter 7 - Conclusions: Application of the Results for Modelling the Long Range Transport of Particulate Trace Metals.

7.1. The Objectives and Achievements of this Study.

This study has successfully examined many of the factors affecting the long range transport of particulate trace metals in coastal waters. Of its original aims discussed in Section 1.5. and the modelling consideration given in Section 1.4.4. (summarised below), most have been achieved satisfactorily. Others aims have achieved a greater success and have provided new insights into the processes governing the long range transport of particulate trace metals.

- i. Particulate trace metals were successfully examined both spatially and temporally in coastal waters. These measurements are essential to the understanding of geochemical associations and with the aid of $^{206/207}\text{Pb}$ isotopic ratio provide an overview of the effect of particulate transport processes, in addition to contributing to the available database at the British Oceanographic Data Centre, Bidston.

Surprisingly some of the highest suspended particulate concentrations of Mn were measured adjacent to the Tweed Estuary. High concentrations of Mn have been previously observed (Laslett, 1995) but no conclusive reason has yet been given for this observation. Further study of the Tweed Estuary is expected within the LOIS community which may explain this apparent anomaly.

This dissertation also provides the first comprehensive examination of $^{206/207}\text{Pb}$ isotopic ratios in UK coastal waters and has provided novel applications of $^{206/207}\text{Pb}$ isotopic ratios examining the mixing of disparate particle populations.

- ii. The interaction of dissolved trace metals with particles is of key importance when determining their behaviour and this study has used established methods involving radioisotopes to determine the partition coefficients (K_D). These experiment have been used to examine the kinetics of trace metal uptake and to provide estimates of the system response times (typically 1.5 days) for a number of trace metals (Cd, Cs, Zn). Which suggests rapid equilibration with changes in water conditions relative to

the flushing time of the Humber Estuary (Section 6.2.2.2.).

The mixing of different particle populations was examined in a number of ways. Measurements and novel applications of Pb isotopic ratios (Chapter 4.3.) provided a means of determining the mixing ratio of particle populations containing different anthropogenic Pb contents. These measurements were particularly useful in the North Sea and Irish Sea, but in situations where the particle populations are anthropogenically difficult will arise using Pb isotopic ratios. The increasing use of unleaded petrol may also invalidate this method for determining the mixing ratio between particle populations and future work may be required to enable characterisation of each particle source.

Experiments were also performed using radioisotopes to examine the partitioning of trace metals between different particle populations (i.e. Humber and Holderness particles). These experiments identified non-additivity by some of the metals (Cd, Mn, Cr) when particle populations are mixed (Section 6.4.). The non-additivity appeared to be attributed to the heterogeneous reactivity of the trace metals. For example, the auto-catalysis of Mn was affected when Mn poor particles from Holderness were mixed with Humber particles containing a high concentration of Mn. An algorithm was postulated to predict the mixing behaviour of trace metals based on a knowledge of their K_D values and the mixing ratio of the particle populations (Equation 6.18.).

- iii. The settling of particle populations has been examined extensively by sedimentologists but neglected by marine chemists. One of the key aims of this study was to provide a basis for the understanding and a measure of the importance of trace metal association with particles of differing settling velocities.

Within the plume zone and coastal water particles are continually being removed from the water column by settling. Unique work examining settling particle fractions and their trace metal composition has provided a valuable insight into the factors governing the long range transport of particulate trace metals and has provided data (such as settling velocity, typically $< 0.1 \text{ mm s}^{-1}$) directly relevant to inclusion into a Fine Sediment Transport Model for Metals (FISTRAMM). It was shown that metals preferentially associate with different settling fractions and hence imply different long range transport, exemplified by anthropogenic Pb (low $^{206}/^{207}\text{Pb}$ isotopic ratio) associating with the slow settling particles while Ca associated with the fast settling

particles. As with the stable trace metal isotopes, the uptake of radioisotopes showed different reactivities with different settling fraction, rarely did the highest partition coefficient coincide with the slowest settling fraction.

New data has been provided on the behaviour of particulate trace metals associated with different settling fractions, until now many assumptions have been made by marine chemists and this information will provide valuable data for the prediction of trace metal behaviour in coastal waters.

- iv. Particulate trace metals were significantly affected by tidal processes. Higher particulate trace metal concentrations occurred during the ebb tide in the Irish Sea, caused by the advection of land based particles, while the flood tide advected offshore material. Variations in particulate trace metal concentrations during the neap tide, suggested that fine metal rich surficial sediment may have been resuspended. No evidence confirmed this hypothesis and further work would be required.

Flux calculation of suspended particulate trace metals from the mouth of the Humber Estuary were of a similar magnitude to fluxes observed during the winter, 1988. However, except for Pb, the available information suggests that the Humber receives a larger input than output of trace metals. This may indicate that the Humber Estuary is retaining these metals probably within the sediments, which could result in a continued flux of trace metals from the estuary irrespective of tighter legislation in the future on metal inputs to the estuary.

- v. Porewater flux calculations suggested that inputs from the sediment surface could be the same order of magnitude as inputs into the Mersey Estuary and Morecambe Bay.
- vi. The influence of benthic fauna was a potential artefact in the sedimentary distribution of trace metals, particularly in the Irish Sea cores. However, this topic requires further consideration to determine the influence of bioturbation on suspended particle and the effect of burrowing on porewater fluxes.

The work presented in the dissertation provides useful information (see Section 7.2.) for models simulating trace metal behaviour in coastal waters such as NORPOL (Murphy and

Odd, 1993) and proposed models for the North Sea (Simpson, 1994; Huthnance *et al*, 1993). It has addressed a number of issues not previously examined in particular the settling characteristics of particulate trace metals.

7.2. Implications for Modelling Long Range Transport of Particulate Trace Metals.

Before consideration is given to developing a FISTRAMM an overall appraisal should be given to the processes affecting the spatial distribution of particulate trace metals in coastal waters. These processes have been schematically represented in Figure 7.2. The diagram has been centred on the processes affecting particulate trace metal in the plume region of an estuary. The estuarine inputs enter the coastal region, where upon they mix with a variety of different particle populations, concurrently particles with progressively slower settling velocities will settle to the sediment bed. Various hydrodynamic factors (e.g. tidal currents) will effect the rate of mixing and resuspension of the sediment surface. Each of the particle populations will have a different composition (both in terms of trace metal concentration and bulk character) hence at all stages, different rates of interaction will occur between the particles and the dissolved phase.

The schematic approach though useful in visualising the processes is not very helpful for the mathematical treatment required for modelling purposes. The schematic shown in Figure 7.2. has been used to develop the 3-D conceptual model of the Humber Plume shown in Figure 7.3. The overall driving force behind fine sediment transport is hydrodynamic factors while the driving force behind the prevention of the fine sediment transport is particle settling followed by accretion. The flow diagram within the boxed area represents processes occurring within short time scales and consequently it is envisaged that the area trying to be modelled would be divided into three dimensional segments whose size would be determined by either the residence time of the water mass or perhaps in more practical terms by distance. Each segment would produce a trace metal concentration and particle composition to the adjoining segments, the data given would be dependent on the hydrodynamic factors (e.g. currents passing east to west inside the segment would produce data for segments to the west and not to the east). Each segment would receive the data

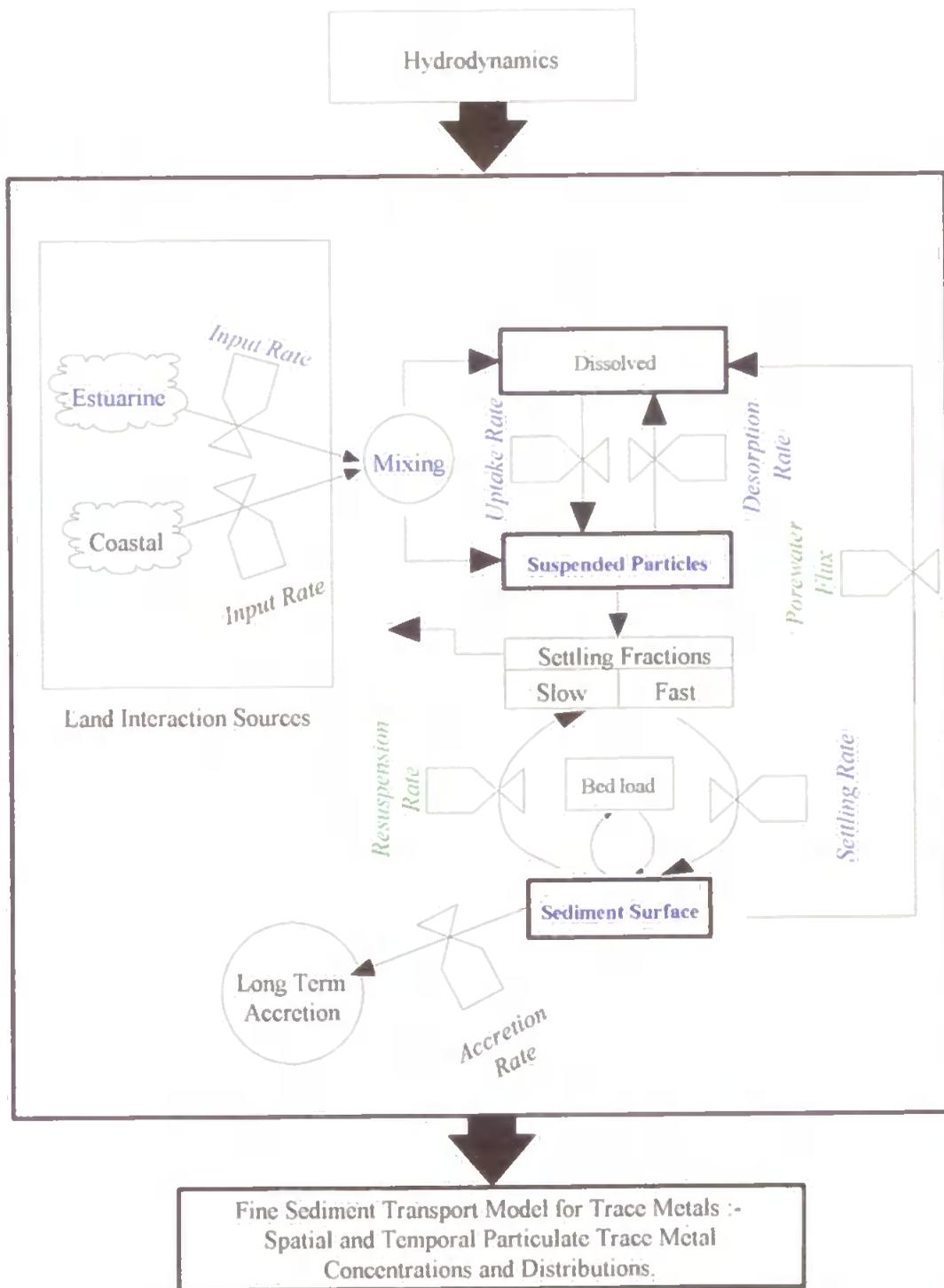
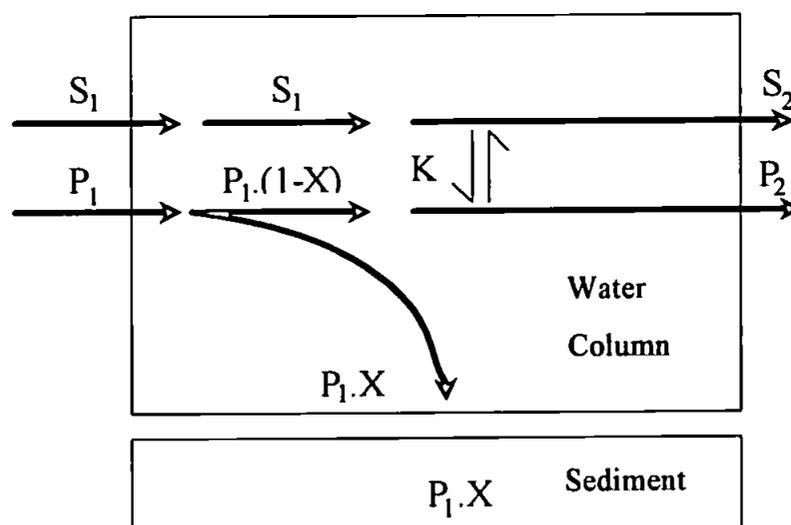


Figure 7.2. Conceptual model of particulate trace metals in the Humber Plume during winter.

During mixing particulate metals are removed from solution by particle settling, yet little information in the literature examines this sink. Novel experiments were performed examining the removal of trace metals by particle settling (Chapter 5.). This work produced differences in the association of particulate trace metals with each 'settling' fraction. The Duinker model produced an overview of the particulate trace metal settling behaviour (Equation 3.1., Table 3.6.). Recent concerns highlight the possible temporary nature of sediment accretion (Kitts *et al*, 1994), changes in sea level, fluvial flow and wave action can cause areas which were historically depositional to become areas of sediment erosion and hence, the accumulation of past particulate trace metal inputs will become released in the water column.

A steady state model can be examined by consideration of the in the mass balance of trace metals changes (due to settling and partitioning) during sediment transport (Figure 7.4.). A number of assumptions have been made to give the following model - no resuspension of bed sediment, the concentration of SPM is constant, re-equilibration is instantaneous and the particle population is homogenous. Further development will occur using this model as a basis.



- Where :
- S = mass of dissolved metal
 - P = mass of particulate metal
 - X = proportion of particulate metal removed due to settling
 - K = equilibrium coefficient between the mass of dissolved and particulate metals ($K = K_D \cdot [SPM]$)

Figure 7.4. Model of trace metal transport with consideration of partitioning and removal by settling.

$$\text{Total initial mass of metal present} = S_1 + P_1 \quad 7.1.$$

$$\text{Total final mass of metal present} = S_1 + P_1 - P_1 X \quad 7.2.$$

The mass of particulate metal after settling = Total final mass of metal - mass of dissolved metal after settling

$$P_2 = (S_1 + P_1 - P_1 X) - S_2 \quad 7.3.$$

The equilibrium coefficient is constant throughout:

$$K = \frac{P_1}{S_1} = \frac{P_2}{S_2} \quad 7.4.$$

$$P_2 = K S_2 \quad 7.5.$$

substitution of 7.5. into 7.3.

$$K S_2 = (S_1 + P_1 - P_1 X) - S_2 \quad 7.6.$$

$$K S_2 + S_2 = (S_1 + P_1 - P_1 X) \quad 7.7.$$

Rearrangement gives the relationship between initial inputs and the final dissolved output:

$$S_2 = \frac{(S_1 + P_1 - P_1 X)}{K + 1} \quad 7.8.$$

Substitution of 7.8. into 7.3.

$$P_2 = S_1 + P_1 - P_1 X - \frac{(S_1 + P_1 - P_1 X)}{K + 1} \quad 7.9.$$

$$S_1 + P_1 - P_2 = P_1 X + \frac{(S_1 + P_1 - P_1 X)}{K + 1} \quad 7.10.$$

$$S_1 + P_1 - P_2 = \frac{S_1 + P_1 + K P_1 X}{K + 1} \quad 7.11.$$

$$S_1 K + S_1 + P_1 K + P_1 - P_2 K - P_2 = S_1 + P_1 + K P_1 X \quad 7.12.$$

$$S_1 K + P_1 K - K P_1 X = P_2 + P_2 K \quad 7.13.$$

Rearrangement gives the relationship between the initial inputs and the final output of particulate metal.

$$P_2 = \frac{S_1 K}{1+K} + \frac{P_1 K (1-X)}{1+K} \quad 7.14.$$

The value of X is the proportion of metal removed by settling, note this is not the same as the proportion of SPM removed by settling, e.g. if 80 % of the metal is associated with the fast settling fraction of SPM and 10% of the SPM is fast settling, then $X = 0.8$ but the proportion of SPM removed by settling is 0.1.

By considering multiples of the box model (Figure 7.4.) connected in series, the transport of a trace metal can be modelled away from a point source (Figure 7.5.). A variation of 1000 fold in the values of K_D show little variation in transport properties. Sensitivity increases more significantly with lower K_D values.

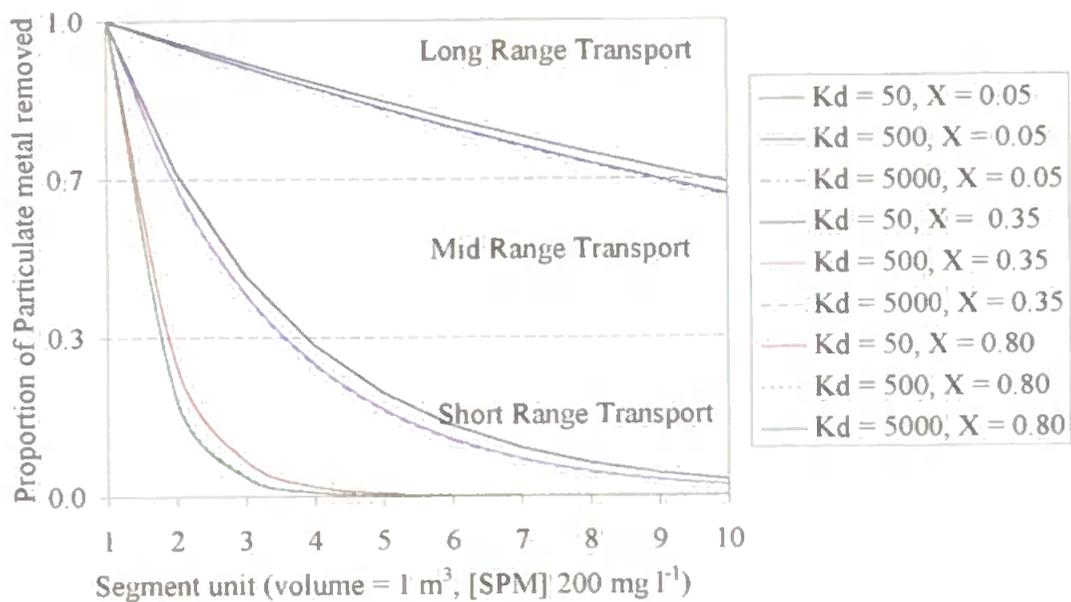


Figure 7.5. Predictions of the transport of particulate trace metals according to the model described in Figure 7.4.

Assuming that the values of X are a function of w_s and are proportional to w_s . Rearrangement of Equation 7.14. illustrates that X is proportional to the reciprocal of K.

The trace metal data can be summarised using a plot of K_D vs the reciprocal of w_s (Figure 7.6.).

$$S_1 + P_1 - P_2 - \frac{P_2}{P_1} \frac{l}{K} = X \quad 7.15.$$

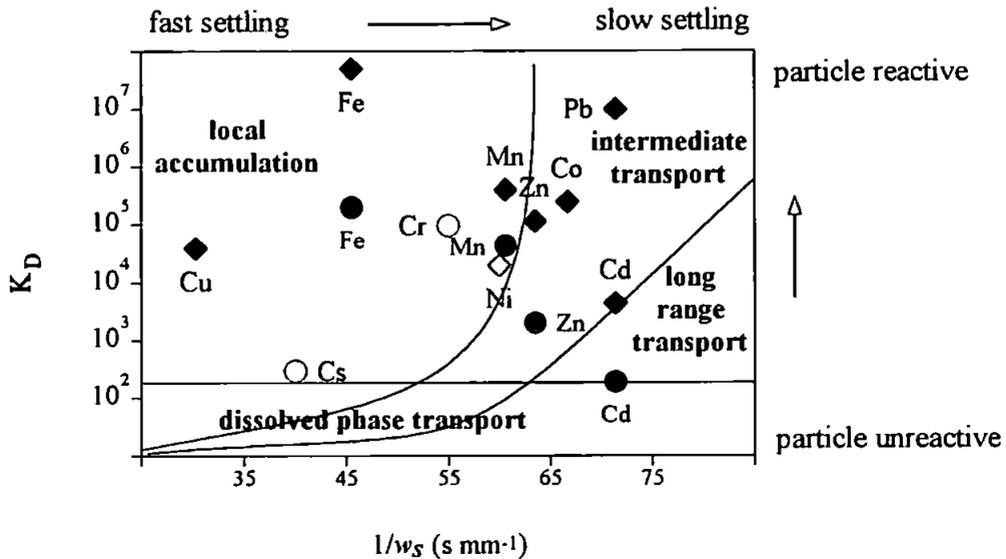


Figure 7.6. Summary of the transport behaviour of particulate trace metals. ● radioisotopic K_D and measured w_s , ○ radioisotopic K_D and estimated w_s , ◆ stable isotopic K_D and measured w_s , ◇ stable isotopic K_D and estimated w_s . (stable isotopic K_D values - Millward *pers. comm.*)

Controlled uptake experiments were performed using radioisotopes to examine the kinetics of dissolved metal interaction with particle surfaces and system response times were found to be about a day (Table 6.2.) for a number of metals. Such information is essential to determine whether particles entering a segment will equilibrate within the particle residence time inside the segment.

The effect of current regimes of 'resuspension' events were examined in the Irish Sea to understand the effect on particulate trace metal concentrations (Section 3.2.3.) and variations in trace metal concentrations were examined during resuspension events (Sections 3.2.3. and 3.3.3.) in the Irish and in the Humber mouth. It was found that within the north eastern Irish Sea a residual current persists through out the tidal cycle causing during the spring tide strong resuspension of sediment, which having a lower trace metal

concentration than the SPM, dilutes the measured particulate trace metal concentration over the tidal cycle.

'Benthic processes' were examined through taking sediment cores and examining the distribution of trace metals resulting from diagenetic alteration and trace metals inputs. This work highlighted the potential of surficial metal rich sediments for selected trace metals (e.g. Mn) contributing to the particulate trace metal burden of the water column caused by resuspension, although large resuspension events often caused a dilution of the suspended particulate trace metal concentration. The importance of considering the impact of porewater fluxes for selected trace metal (Table 3.2.) were shown for the Irish Sea. Most of the variables and processes within a FISTRAMM have been examined during this study and have provided some unique insights into the processes affecting the long range transport of particulate trace metals. In some cases data are now available that is immediately useful to modelling those processes.

7.3. Further Studies.

One of the most significant areas of study requiring further work is an examination of the settling of particulate trace metals. The situations dealt with during this study have been performed during the winter season, the inclusion of planktonic species would probably radically affect the settling characteristics of suspended particulate trace metals and would require clarification. The bulk composition of each settling fraction requires more extensive study to determine the key factors affecting the differential association of trace metals with the settling fractions, in particular, the influence of organic coatings. It would also be useful to see if the particle settling profiles were related to different types of particle populations (e.g. sewage vs riverine SPM) and to try to identify the contribution of different particle populations to each settling fraction.

Quantification of the importance of trace metal desorption processes is needed to investigate the repartitioning of trace metals during the mixing of two or more particle populations.

A more widespread use of $^{206}/^{207}\text{Pb}$ isotopic ratio's may provide a useful tool to examine many processes. However, this technique may have a limited lifetime as more people start using unleaded petrol.

It was postulated that resuspension of metal rich fine surficial sediment may be contributing to the observed particulate trace metals profiles. If this was the case a continuous transport of trace metals may be occurring. Further investigation is needed to clarify, if this is the case and to measure the contribution of bed load transport to the long range transport of trace metals.

The influence of atmospheric inputs upon entering coastal waters requires investigation, particularly for the Irish Sea.

References

References

- Ackermann, F., Bergmann, H. and Schleichert, U., 1983. Monitoring of heavy metals in coastal and estuarine sediments - A question of grain - size: <20 μm versus <60 μm . *Environmental Technology Letters*, **4**, 317 - 328.
- Allen, J.R.L., 1985. *Principles of Physical Sedimentology*. George Allen and Unwin, London, 272pp.
- Allen, T., 1987. Sedimentation techniques of particle size measurements. In: *Particle Size Analysis, 1985* (Ed. P.J. Lloyd), John Wiley and Sons, Chichester, 25 - 45.
- Aller R.C. and Yingst, J. Y., 1985. Effects of the marine deposit-feeders *Heteromastus filiformis* (polychaeta), *Macoma balthica* (bivalvia), and *Tellina texana* (bivalvia) on averaged sedimentary solute transport, reaction rates, and microbial distributions. *Journal of Marine Research*, **43**, 615 - 645.
- Aller, R.C., 1990. Bioturbation and manganese cycling in hemipelagic sediments. *Philosophical Transactions of the Royal Society of London*, **331A**, 51 - 68.
- Aller, R.C., 1994a. Bioturbation and remineralisation of sedimentary organic matter: Effects of redox oscillation. *Chemical Geology*, **114**, 331 - 345.
- Aller, R.C., 1994b. The sedimentary Mn cycle in Long Island Sound: Its role as intermediate oxidant and the influence of bioturbation, O_2 , and C_{org} flux on diagenetic reaction balances. *Journal of Marine Research*, **52**, 259 - 295.
- Anderson, R.F., Santschi, P.H., Nyffeler, U.P. and Shiff, S.L., 1987. Validating the use of radiotracers as analogs of stable metal behaviour in enclosed aquatic ecosystem experiments. *Canadian Journal of Fisheries and Aquatic Science*, **44** (suppl. 1), 251 - 259.

- Bacon, J.R., Berrow, M.L. and Shand, C.A., 1992. Isotopic composition as an indicator of origin of lead accumulations in surface soils. *International Journal of Environmental Analytical Chemistry*, **46**, 71 - 76.
- Bale, A.J., Morris, A.W. and Howland, R.J.M., 1984. Size distributions of suspended material in the surface waters of an estuary as measured by laser Fraunhofer diffraction. In: *Transfer Processes in Cohesive Sediment Systems* (Eds. W.R. Parker and D.J.J. Kinsman), Plenum Press, New York, 75 - 87.
- Bale, A.J. and Morris, A.W., 1987. In situ measurements of particle size in estuarine waters. *Estuarine, Coastal and Shelf Science*, **24**, 253 - 263.
- Bale, A.J., Barrett, C.D., West, J.R. and Oduyemi, K.O.K., 1989. Use of *in-situ* laser diffraction particle sizing for particle transport studies in estuaries. In: *Developments in Estuarine and Coastal Study Techniques* (Eds. J. McManus and M. Elliott), EBSA 17 Symposium: September 1987, Dundee, Olsen and Olsen, Fredensborg, 133 - 138.
- Balistreri, L.S. and Murray, J.W., 1986. The surface chemistry of sediments from the Panama Basin: Influence of Mn oxides on metal adsorption. *Geochimica et Cosmochimica Acta*, **50**, 2235 - 2243.
- Balls, P.W., 1985. Copper, lead and cadmium in coastal waters of the western North Sea. *Marine Chemistry*, **15**, 363 - 378.
- Balls, P.W., 1986. Composition of suspended particulate matter from Scottish coastal waters - Geochemical implications for the transport of trace metal contaminants. *The Science of the Total Environment*, **57**, 171 - 180.
- Barr, R., Watson, P.G., Ashcroft, C.R., Barnett, B.E. and Hilton, C., 1990. Humber Estuary - a case study. *Hydrobiologia*, **195**, 127 - 143.
- Belderson, R.H. and Stride, A.H., 1969. Tidal currents and sand wave profiles in the north-eastern Irish Sea. *Nature*, **222**, 74 - 75.

- Beneš, P., Kuncová, M., Slovák, J. and Lam Ramos, P., 1988. Analysis of the interaction of radionuclides with solid phases in surface waters using laboratory model experiments: Methodical problems. *Journal of Radioanalytical Nuclear Chemistry*, **125**, 295 - 315.
- Benoit, G., Oktay-Marshall, S.D., Cantu, I.I., Hood, E.M., Coleman, C.H., Corapcioglu, M.O. and Santschi, P.H., 1994. Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. *Marine Chemistry*, **45**, 307 - 336.
- Berndt, H., 1981. Comparison of micro-techniques of flame atomic absorption spectrometry (injection method, boat and cup system and platinum loop method). *Analytical Proceedings*, **18**, 353 - 356.
- Berner, R.A., 1981. A new geochemical classification of sedimentary environments. *Journal of Sedimentary Petrology*, **51**, 359 - 365.
- Brügmann, L., Danielsson, L.-G., Magnusson, B. and Westerlund, S., 1985. Lead in the North Sea and the North East Atlantic Ocean. *Marine Chemistry*, **16**, 47 - 60.
- Bull, K.R., Every, W.J., Freestone, P., Hall, J.R. and Osborn, D., 1983. Alkyl lead pollution and bird mortalities on the Mersey Estuary 1979-1981. *Environmental Pollution*, **31A**, 239 - 259.
- Burban, P.-Y., Xu, Y.-J., McNeil, J. and Lick, W., 1990. Settling speeds of flocs in fresh water and seawater. *Journal of Geophysical Research*, **95 (C10)**, 18213 - 18220.
- Burton, J.D., Althaus, M., Millward, G.E., Morris, A.W., Statham, P.J., Tappin, A.D. and Turner, A., 1993. Processes influencing the fate of trace metals in the North Sea. *Philosophical Transactions of the Royal Society of London*, **343A**, 557 - 568.
- Cabaniss, S.E. and Shumann, M.S., 1988a. Copper binding by dissolved organic matter: 1. Suwannee river fulvic acid equilibria. *Geochimica et Cosmochimica Acta*, **52**, 185 - 193.

- Cabaniss, S.E. and Shumann, M.S., 1988b. Copper binding by dissolved organic matter: II. Variation in type and source of organic matter. *Geochimica et Cosmochimica Acta*, **52**, 195 - 200.
- Camacho-Ibar, V.F., Wrench, J.J. and Head, P.C., 1992. Contrasting behaviour of arsenic and mercury in Liverpool Bay sediments. *Estuarine, Coastal and Shelf Science*, **34**, 23 - 36.
- Cauwet, G., 1987. Influence of sedimentological features on the distribution of trace metals in marine sediments. *Marine Chemistry*, **22**, 221 - 234.
- Chapman, P.M., 1992. Pollution status of North Sea sediments - An international integrative study. *Marine Ecology Progress Series*, **91**, 313 - 323.
- Charnock, H., Dyer, K.R., Huthnance, J.M., Liss, P.S., Simpson, J.N. and Tett, P.B., 1994. *Understanding the North Sea System*, Chapman and Hall, London, 222p.
- Chester R. and Hughes, M.J., 1967. A chemical technique for the separation of ferromanganese minerals, carbonate mineral and adsorbed trace metals from pelagic sediments. *Chemical Geology*, **2**, 249 - 262.
- Chester, R., Sharples, E.J., Murphy, K., Saydam, A.C. and Sanders, G.S., 1983. The atmospheric distribution of lead over a number of marine regions. *Marine Chemistry*, **13**, 57-72.
- Chow, T.J. and Patterson, C.C., 1962. The occurrence and significance of lead isotopes in pelagic sediments. *Geochimica et Cosmochimica Acta*, **26**, 263-308.
- Chow, T.J., Snyder, C.B. and Earl, J.L., 1975. Isotopic ratios of lead as pollutant source indicators. In: *Isotopic Ratios of Lead as Pollutant Source and Behaviour Indicators*. International Atomic Energy Agency No IAEA-SM-191/4, Vienna, 95 - 108.

- Ciceri, G., Maran, S., Martinotti, W. and Queirazza, G., 1992. Geochemical cycling of heavy metals in a marine coastal area: benthic flux determination from pore water profiles and in situ measurements using benthic chambers. *Hydrobiologia*, **235/236**, 501 - 517.
- Colley, S., 1992. *R.R.S. Charles Darwin Cruise 63, 02 Oct 1991: Geochemical and Geological Investigations in the Porcupine Abyssal Plain Area*. Institute of Oceanographic Sciences Deacon Laboratory, Cruise Report No 232, Godalming, U.K., 27pp.
- Davies, A.M. and Jones, J.E., 1992. A three dimensional wind driven circulation model of the Celtic and Irish Seas. *Continental Shelf Research*, **12**, 159 - 188.
- Davies-Colley, R.J., Nelson, P.O. and Williamson, K.J., 1984. Copper and cadmium uptake by estuarine sedimentary phases. *Environmental Science and Technology*, **18**, 491 - 499.
- Dehairs, F., Baeyens, W. and Van Gansbeke, D., 1989. Tight coupling between enrichment of iron and manganese in the North Sea suspended particulate matter and sedimentary redox processes: Evidence for seasonal variability. *Estuarine, Coastal and Shelf Science*, **29**, 457 - 471.
- Doe, B.R., 1970. *Lead Isotopes*. Springer-Verlag, Berlin, 140pp.
- Doe, B.R. and Stacey, J.S., 1974. The application of lead isotopes to problems of ore genesis and ore prospect evaluation: A review. *Economic Geology*, **69**, 757 - 776.
- Duchart, P., Calvert, S.E. and Price, N.B., 1973. Distribution of trace metals in the pore waters of shallow water marine sediments. *Limnology and Oceanography*, **18**, 605 - 610.
- Duinker, J.C., 1983. Effects of particle size and density on the transport of metals to the oceans. In: *Trace Metals in Sea Water* (Eds. C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg). Plenum Press, New York, 209 - 278.

- Duursma, E.K. and Bosch, C.J., 1970. Theoretical, experimental and field studies concerning diffusion of radioisotopes in sediments and suspended particles of the sea. Part B: Methods and experiments. *Netherlands Journal of Sea Research*, 4, 395 - 469.
- Dyer, K.R., 1994. Estuarine sediment transport and deposition. In: *Sediment Transport and Depositional Processes* (Ed. K. Pye). Blackwell Scientific Publications, London, 193 - 218.
- Eary, L.E. and Rai, D., 1987. Kinetics of chromium (III) oxidation to chromium (VI) by reaction with manganese dioxide. *Environmental Science and Technology*, 21, 1187 - 1193.
- Eisma, D. and Irion, G., 1988. Suspended matter and sediment transport. In: *Pollution of the North Sea: An Assessment*, (Ed. W. Salomons, B.L. Bayne, E.K. Duursma, U. Förstner). Springer-Verlag, Berlin, 20 - 35.
- Elbaz-Poulichet, F, Holliger, P., Martin, J.M. and Petit, D., 1986. Stable lead isotopes ratios in major French rivers and estuaries. *The Science of the Total Environment*, 54, 61 - 76.
- Faure, G., 1986. *Principles of Isotope Geology*. J.Wiley and Sons, New York, 590pp.
- Fennessy, M., Dyer, K.R. and Huntley, D.A., 1994. INSSEV: An instrument to measure the size and settling velocity of flocs in situ. *Marine Geology*, 117, 107 - 117.
- Foster, P., 1984. Inhibitions to pollutant dissipation in the north east Irish Sea. *Marine Pollution Bulletin*, 15, 222 - 225.
- Förstner, U., 1993. Metal speciation - General concepts and applications. *International Journal of Environmental and Analytical Chemistry*, 51, 5 - 23.

- Förstner, U., 1994. Solutes/solids interactions of metals in estuaries. In: *Particulate Matter in Rivers and Estuaries*, Proceedings of International Symposium: March 21-25 1994, Hamburg, 73 - 90.
- Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D. and Hartman, B., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochimica et Cosmochimica Acta*, 43, 1075 - 1090.
- Gaillard, J.-F., Pauwels, H. and Michard, G., 1989. Chemical diagenesis in coastal marine sediments. *Oceanologica Acta*, 12, 175 - 187.
- Gendron, A., Silverberg, N., Sunby, B. and Lebel, J., 1986. Early diagenesis of cadmium and cobalt in sediments of the Laurentian Trough. *Geochimica et Cosmochimica Acta*, 50, 741 - 747.
- Gerringa, L.J.A., 1990. Aerobic degradation and the mobility of Cu, Cd, Ni, Pb, Zn, Fe, and Mn in marine sediments. *Marine Chemistry*, 29, 355 - 374.
- Gerringa, L.J.A., 1991. Mobility of Cu, Cd, Ni, Pb, Zn, Fe and Mn in marine sediment slurries under anaerobic conditions and at 20% air saturation. *Netherlands Journal of Sea Research*, 27, 145 - 156.
- Gibbs, R.J., 1985. Estuarine flocs: Their size, settling velocities and density. *Journal of Geophysical Research*, 90 (C2), 3249 - 3251.
- Glegg, G.A. and Millward, G.E., 1995. An assessment of trace metal fluxes from the Humber Estuary to the North Sea. *Estuarine, Coastal and Shelf Science*, (Submitted).
- Grant, A. and Middleton, R., 1990. An assessment of metal contamination of sediments in the Humber Estuary, U.K. *Estuarine, Coastal and Shelf Science*, 31, 71 - 85.
- Greenpeace, 1992. *Filthy 50*. Greenpeace, London, 96pp.

- Hamilton, E.I. and Clifton, R.J., 1979. Isotopic abundances of lead in estuarine sediments, Swansea Bay, Bristol Channel. *Estuarine, Coastal and Shelf Science*, **8**, 271 - 278.
- Hart, B.T., 1982. Uptake of trace metals by sediment and suspended particulates: A review. *Hydrobiologia*, **91**, 299 - 313.
- Hem, J.D., 1978. Redox processes at surfaces of manganese oxide and their effect on aqueous metal ions. *Chemical Geology*, **21**, 199 - 218.
- Hem, J.D., Lind, C.J. and Roberson, C.E., 1989. Coprecipitation and redox reactions of manganese oxides with copper and nickel. *Geochimica et Cosmochimica Acta*, **53**, 2811 - 2822.
- Hinners, T.A., Heithmar, E.M., Spittler, T.M. and Henshaw, J.M., 1987. Inductively coupled plasma mass spectrometric determination of lead isotopes. *Analytical Chemistry*, **59**, 2658 - 2662.
- Holligan, P.M., Aarup, T. and Groom, S.B., 1989. The North Sea: Satellite colour Atlas. *Continental Shelf Research*, **9**, 667 - 765.
- Honeyman, B.D. and Santschi, P.H., 1988. Metals in the aquatic system. *Environmental Science and Technology*, **22**, 862 - 871.
- Hopper, J.F., Ross, H.B., Sturges, W.T. and Barrie, L.A., 1991. Regional source discrimination of atmospheric aerosols in Europe using the isotopic composition of lead. *Tellus*, **43B**, 45-60.
- Huthnance, J.M., Allen, J.I., Davies, A.M., Hydes, D.J., James, I.D., Jones, J.E., Millward, G.E., Prandle, D., Proctor, R., Purdie, D.A., Statham, P.J., Tett, P.B., Thomson, S. and Wood, R.G., 1993. Towards water quality models. *Philosophical Transactions of the Royal Society of London*, **343A**, 569 - 584.
- Institute of Hydrology, 1988. Hydrological Data United Kingdom: Hydrometric Register and Statistics 1981-85. NERC Institute of Hydrology, Wallingford. 143pp.

- Irion, G. and Müller, G., 1990. Lateral distribution and sources of sediment associated heavy metals in the North Sea. In: *Facets of Modern Biogeochemistry*, (Eds. V. Ittekkot, S. Kempe, W. Michaelis, A. Spirtzy). Springer-Verlag, Berlin, 175 - 201.
- Jago, C.F., Jones, S.E. and Boon, D. Quasi *in situ* settling velocity of suspended particulate matter in the North Sea, (In preparation).
- Jago, C.F, Bale, A.J., Green, M.O., Howarth, M.J., Jones, S.E., McCave, I.N., Millward, G.E., Morris, A.W., Rowden, A.A. and Williams, J.J., 1993. Resuspension processes and seston dynamics, southern North Sea. *Philosophical Transactions of the Royal Society of London*, **343A**, 475 - 491.
- Jannasch, H.W., Honeyman, B.D., Balistrieri, L.S. and Murray, J.W., 1988. Kinetics of trace element uptake by marine particles. *Geochimica et Cosmochimica Acta*, **52**, 567 - 577.
- Johnson, C.A. and Xyla, A.G., 1991. The oxidation of chromium (III) to chromium (VI) on the surface of manganite (γ - MnOOH). *Geochimica et Cosmochimica Acta*, **55**, 2861 - 2866.
- Jones, P.G.W. and Jefferies, D.F., 1983. The distribution of selected trace metals in United Kingdom shelf waters and the North Atlantic. *Canadian Journal of Fisheries and Aquatic Sciences*, **40**, 111 - 123.
- Kershaw, P.J., Pentreath, R.J., Woodhead, D.S. and Hunt, G.J., 1992. A review of radioactivity in the Irish Sea: A report prepared for the Marine Pollution Monitoring Management Group. *Aquatic Environmental Monitoring Report*. MAFF Directorate Fisheries Research, Lowestoft, **32**, 65pp.
- Kersten M. and Förstner, U., 1986. Chemical fractionation of heavy metals in anoxic estuarine and coastal sediments. *Water Science and Technology*, **18**, 121 - 130.

- Kersten, M., Kriews, M and Förstner, U., 1991a. Partitioning of trace metals released from polluted marine aerosols in coastal seawater. *Marine Chemistry*, **36**, 165 - 182.
- Kersten, M., Irion, G. and Förstner, U., 1991b. Particulate trace metals in surface waters of the North Sea. In: *Heavy Metals in the Environment* (Ed. J.-P. Vernet), Elsevier, London, 137 - 159.
- Kersten, M., Förstner, U., Krause, P., Kriews, M., Dannecker, W., Garbe-Schönberg, C.-D., Höck, M., Terzenbach, U. and Graßl, H., 1992. Pollution source reconnaissance using lead isotope ratios ($^{206}/^{207}\text{Pb}$). In: *Heavy Metals in the Environment*, Vol 2, (Ed. J.-P. Vernet). Elsevier, Amsterdam, 311 - 325.
- Kineke, G.C., Sternberg, R.W. and Johnson, R., 1989. A new instrument for measuring settling velocities in situ. *Marine Geology*, **90**, 149-158.
- Kineke, G.C. and Sternberg, R.W., 1989. The effect of particle settling velocity on computed suspended sediment concentration profiles. *Marine Geology*, **90**, 159-174.
- Kitts, H.J., Millward, G.E., Morris, A.W. and Ebdon, L., 1994. Arsenic biogeochemistry in the Humber Estuary, UK. *Estuarine, Coastal and Shelf Science*, **39**, 157 - 172.
- Klinkhammer, G., Heggie, D.T. and Graham, D.W., 1982. Metal diagenesis in oxic marine sediments. *Earth and Planetary Science Letters*, **61**, 211 - 219.
- Koeppenkastrop, D. and De Carlo, E.H., 1993. Uptake of rare earth elements from solution by metal oxides. *Environmental Science and Technology*, **27**, 1796 - 1802.
- Krumgalz, B.S., 1989. Unusual grain size effect on trace metals and organic matter in contaminated sediments. *Marine Pollution Bulletin*, **20**, 608 - 611.
- Laslett, R.E., 1995. Concentrations of dissolved and suspended particulate Cd, Cu, Mn, Ni, Pb and Zn in surface waters around the coasts of England and Wales and in adjacent seas. *Estuarine, Coastal and Shelf Science*, **40**, 67 - 85.

- Law, R.J., Fileman, T.W., Fileman, C.F. and Limpenny, D.S., 1989. The distribution of hydrocarbon and metals in the north eastern Irish Sea prior to development of the Morecambe Bay gas field. *Oil and Chemical Pollution*, 5, 285 - 320.
- Li, Y.-H. and Gregory, S., 1974. Diffusion of ions in sea water and in deep-sea sediments. *Geochimica et Cosmochimica Acta*, 38, 703 - 714.
- Li, Y.-H., Burkhardt, L. and Teraoka, H., 1984a. Desorption and coagulation of trace elements during estuarine mixing. *Geochimica et Cosmochimica Acta*, 48, 1879 - 1884.
- Li, Y.-H., Burkhardt, L., Buchholtz, M., O'Hara, P. and Santschi, P.H., 1984b. Partition of radiotracers between suspended particles and seawater. *Geochimica et Cosmochimica Acta*, 48, 2011 - 2019.
- Loring, D.H., 1990. Lithium - A new approach for granulometric normalisation of trace metal data. *Marine Chemistry*, 29, 155 - 168.
- Loring, D.H., 1991. Normalization of heavy-metal data from estuarine and coastal sediments. *ICES Journal of Marine Science*, 48, 101 - 115.
- Lowry, R.K., Cramer, R.N. and Rickards, L.J., 1992. *North Sea Project CD-ROM Users Guide*. BODC, Birkenhead, 168pp.
- Luoma, S.N., 1983. Bioavailability of trace metals to aquatic organisms - A review. *The Science of the Total Environment*, 28, 1 - 22.
- Luoma, S.N. and Bryan, G.W., 1981. A statistical assessment of the form of trace metals in oxidised estuarine sediments employing chemical extractants. *The Science of the Total Environment*, 17, 165 - 196.
- Lynn, D. C. and Bonatti, E., 1965. Mobility of manganese in diagenesis of deep sea sediments. *Marine Geology*, 3, 457 - 474.

- MAFF, 1991. Monitoring and surveillance of non-radioactive contaminants in the aquatic environment and activities regulating the disposal of wastes at sea, 1988-89. *Aquatic Environment Monitoring Report*, Lowestoft, 26, 90pp.
- MAFF, 1992. Monitoring and surveillance of non-radioactive contaminants in the aquatic environment and activities regulating the disposal of wastes at sea, 1990. *Aquatic Environment Monitoring Report*, Lowestoft, 30, 66pp.
- MAFF, 1993. Fifth report of the group co-ordinating sea disposal monitoring. *Aquatic Environment Monitoring Report*, Lowestoft, 39, 35pp.
- Malcom, S.J., Kershaw, P.J., Cromar, N.J. and Botham, L., 1990. Iron and manganese geochemistry and the distribution of $^{239,240}\text{Pu}$ and ^{241}Am in the sediments of the north east Irish Sea. *The Science of the Total Environment*, 95, 69 - 87.
- Maring, H.B. and Duce, R.A., 1990. The impact of atmospheric aerosols on trace metal chemistry in open ocean surface seawater. 3. Lead. *Journal of Geophysical Research*, 95 (C4), 5341 - 5347.
- Martin, J.M., Nirel, P. and Thomas, A.J., 1987. Sequential extraction techniques: Promises and problems. *Marine Chemistry*, 22, 313 - 341.
- McCartney, M., Kershaw, P.J., Allington, D.J., Young, A.K. and Turner, D., 1992. Industrial sources of naturally occurring radionuclides in the Eastern Irish Sea. *Radiation Protection Dosimetry*, 45, 711 - 714.
- McCave, 1987. Fine sediment sources and sinks around the east Anglian coast. *Journal of the Geological Society of London*, 144, 149 - 152.
- Millero, F.J., 1990. Marine solution chemistry and ionic interactions. *Marine Chemistry*, 30, 205 - 229.
- Millward, G.E. and Moore, R.M., 1982. The adsorption of Cu, Mn and Zn by iron oxyhydroxides in model estuarine systems. *Water Research*, 16, 981 - 985.

- Millward, G.E., Turner, A., Glasson, D.R. and Glegg, G.A., 1990. Intra- and inter-estuarine variability of particle microstructure. *The Science of the Total Environment*, 97/98, 289 - 300.
- Millward, G.E., Glegg, G.A. and Morris, A.W., 1992. Zn and Cu removal kinetics in estuarine waters. *Estuarine, Coastal and Shelf Science*, 35, 37 - 54.
- Millward, G.E., Williams, M.R. and Clifton, R.J., 1994. Particle sources and trace element reactivity in the Humber plume. *Netherlands Journal of Aquatic Ecology*, 28, 359 - 364.
- Millward, G.E., 1995. Processes affecting trace element speciation in estuaries: A review. *Analyst*, 120, 609 - 614.
- Millward, G.E., Allen, A.J., Morris, A.W. and Turner, A., 1996. Distributions and fluxes of particulate Fe, Mn, Cu, Zn in the Humber coastal zone, UK. *Continental Shelf Research*, (In press).
- Miyazaki, A. and Reimer, R.A., 1993. Determination of lead isotope ratios and concentrations in sea-water by inductively coupled plasma mass spectrometry after preconcentration using Chelex-100. *Journal of Analytical Atomic Spectrometry*, 8, 449 - 452.
- Morley, N.H., Fay, C.W. and Statham, P.J., 1988. Design and use of a clean shipboard handling system for seawater samples. *Advances in Underwater Technology, Ocean Science and Offshore Engineering*, 16, 283 - 289.
- Morris, A.W. and Bale, A.J., 1979. Effect of rapid precipitation of dissolved Mn in river water on estuarine Mn distributions. *Nature*, 279, 318 - 319.
- Morris, A.W., 1986. Removal of trace metals in the low salinity region of the Tamar Estuary, England. *The Science of the Total Environment*, 49, 297 - 304.

- Morris, A.W., 1988. The estuaries of the Humber and Thames. In: *Pollution of the North Sea* (Eds. W. Salomons, B.L. Bayne, Duursma, E.K., U. Förstner). Springer-Verlag, London, 213 - 224.
- Morris, A.W., 1990. Kinetic and equilibrium approaches to estuarine chemistry. *The Science of the Total Environment*, 97/98, 253 - 266.
- Morrisey, D.J., Underwood, A.J., Stark, J.S. and Howitt, L., 1994. Temporal variation in concentrations of heavy metals in marine sediments. *Estuarine, Coastal and Shelf Science*, 38, 271 - 282.
- Mouvet, C. and Bourg, A.C.M., 1983. Speciation (including adsorbed species) of copper, lead, nickel and zinc in the Meuse River. *Water Research*, 17, 641 - 649.
- Murphy, D.G. and Odd, N.V., 1993. NORPOL - A 3D North Sea Policy Model for Heavy Metal Discharges: Simulation of Cadmium and Lead in 1988/89. Based on Estimated Loads. *Hydraulics Research Report*, Wallingford, SR304, 18pp.
- Murray, L.A., Norton, M.G., Nunny, R.S. and Rolfe, M.S., 1980. The field assessment of effects of dumping wastes at sea: 6. The disposal of sewage sludge and industrial waste off the river Humber. *MAFF Fisheries Research, Technical Report*, No 55.
- Neubecker, T.A. and Allen, H.E., 1983. The measurement of complexation capacity and conditional stability constants for ligands in natural waters. *Water Research*, 13, 1 - 14.
- Newell, R.C., Newell, P.F. and Trett, M.W., 1984. *Benthic Communities in the Lower Humber Estuary in the Vicinity of the Tioxide U.K. Outfall at Grimsby*. Tioxide Environmental Services Group, 46pp.
- Ng, A and Patterson, C.C., 1982. Changes of lead and barium with time in California off-shore sediments. *Geochimica et Cosmochimica Acta*, 46, 2307-2321.

- Niedergesäß, R., Racky, B. and Schnier, C., 1987. Instrumental neutron activation of Elbe River suspended particulate matter separated according to the settling velocities. *Journal of Radioanalytical and Nuclear Chemistry*, **114**, 57 - 68.
- Niedergesäß, R., Eden, H. and Schnier, C., 1994. Trace element concentration in suspended matter fractionated according to the settling velocity. In: *Particulate Matter in Rivers and Estuaries*, Proceedings of International Symposium: March 21-25 1994. Hamburg, 172 - 181.
- Nolting R.F. and Eisma, D., 1988. Elementary composition of suspended matter in the North Sea. *The Netherlands Journal of Sea Research*, **22**, 219 - 236.
- Norton, M.G., Jones, P.G.W., Franklin, A. and Rowlatt, S.M., 1984. Water quality studies around the sewage sludge dumping site in Liverpool Bay. *Estuarine, Coastal and Shelf Science*, **19**, 53 - 67.
- NRA, 1991. Water Act 1989 Consent to Discharge No 017490110, NRA North West Region, 5pp.
- NRA, 1993a. *The Quality of the Humber Estuary, 1980-1990*. Water Quality Series No 12. National Rivers Authority, 35pp.
- NRA, 1993b. *The Water Quality of the Humber Estuary - 1992*. Report of the Humber Estuary Committee of the National Rivers Authority, 35pp.
- NSTF, 1993. *North Sea Subregion 3b Assessment Report*. North Sea Task Force, MAFF, Ruislip, 154pp.
- Nyffeler, U.P., Li, Y.-H. and Santschi, P.H., 1984. A kinetic approach to describe trace-element distribution between particles and solution in natural aquatic systems. *Geochimica et Cosmochimica Acta*, **48**, 1513 - 1522.
- O'Connor, B.A., 1987. Short and long term changes in estuary capacity. *Journal of the Geological Society, London*, **144**, 187 - 195.

- Olsen, C.R., Cutshall, N.H. and Larsen, I.L., 1982. Pollutant-particle associations and dynamics in coastal marine environments: A review. *Marine Chemistry*, **11**, 501 - 533.
- Owen, M.W., 1971. The effect of turbulence on the settling velocities of silt flocs. In: *Proceedings 14th Congress, International Association for Hydraulic Research*. Paris, 27 - 32.
- Owen, M.W., 1976. Determination of Settling Velocities of Cohesive Muds. *Hydraulics Research Report*, Wallingford, IT161, 8pp.
- PARCOM, 1991. *The Paris Commission 1990 Survey: Report of the National Rivers Authority for England and Wales*. Paris Commission, 4pp.
- Perkin Elmer, 1991. *Recommended Conditions for THGA Furnaces*. Publication No. B3110.06, Beaconsfield, U.K., 1pp.
- Petit, D., Mennessier, J.P. and Lamberts, L., 1984. Stable lead isotopes in pond sediments as tracers of past and present atmospheric lead pollution in Belgium. *Atmospheric Environment*, **18**, 1189 - 1193.
- Pettine, M., Millero, F.J. and La Noce, T., 1991. Chromium (III) interactions in seawater through its oxidation kinetics. *Marine Chemistry*, **34**, 29 - 46.
- Plavšić, M. and Cosovic, B., 1994. Influence of surface-active substances on the redox processes of metal ions: A contribution to the speciation analysis of metals in aquatic systems. *Analytica Chimica Acta*, **284**, 539 - 545.
- Plymsolve, 1991. *An Estuarine Contaminant Simulator. User Manual*. Natural Environment Research Council, Swindon, 91pp.

- Prandle, D., Jago, C.F., Jones, S.E., Purdie, D.A. and Tappin, A., 1993. The influence of horizontal circulation on the supply and distribution of tracers. In: *Understanding the North Sea System* (Eds. H. Charnock, K.R. Dyer, J.M. Huthance, P.S. Liss, J.H. Simpson, P.B. Tett). Chapman and Hall, London, 27 - 43.
- Preston, A., 1973. Heavy metals in British Waters. *Nature*, **242**, 95 - 97.
- Prochnow, D., Engelhardt, C. and Bungartz, H., 1994. On the settling velocity distribution of suspended sediments in the Spree River. In: *Particulate Matter in Rivers and Estuaries*, Proceedings of International Symposium: March 21-25 1994, Hamburg, 208 - 219.
- Puls, W., Kuehl, H. and Heymann, K., 1988. Settling velocity of mud flocs: Results of field measurements in the Elbe and the Weser Estuary. In: *Physical Processes in Estuaries* (Eds J. Dronkers and W. van Leussen). Springer-Verlag, Heidelberg, 404 - 424.
- Quevauviller, PH., Rauret, G. and Griepink, B., 1993. Single and sequential extraction in sediments and soils. *International Journal of Environmental and Analytical Chemistry*, **51**, 231 - 235.
- Ramster, J.W. and Hill, H.W., 1969. Current system in the northern Irish Sea. *Nature*, **224**, 59 - 61.
- Redfield, A.C., 1958. The biological control of chemical factors in the environment. *American Science*, **46**, 206 - 226.
- Ridgeway, I.M. and Price, N.B., 1987. Geochemical associations and post-depositional mobility of heavy metals in coastal sediments: Loch Etive, Scotland. *Marine Chemistry*, **21**, 229 - 248.
- Rosman, K.J.R., Chisholm, W., Boutron, C.F., Candelone, J.P. and Görlach, U., 1993. Isotopic evidence for the source of lead in Greenland snows since the late 1960's. *Nature*, **362**, 333 - 335.

- Ruchay, D., 1995. Living with water - Rhine river basin management. *Water Science and Technology*, **31**, 27 - 32.
- Rule, J.H. and Alden, R.W., 1992. Partitioning of Cd in geochemical fractions of anaerobic estuarine sediments. *Estuarine, Coastal and Shelf Science*, **34**, 487 - 499.
- Salomons, W. and Förstner, U., 1980. Trace metal analysis. Part II: Evaluation of environmental impact. *Environmental Technology Letters*, **1**, 506 - 517.
- Santschi, P.H., Adler, D.M. and Amdurer, M., 1983a. The fate of particles and particle-reactive trace metals in coastal waters: Radioisotope studies in microcosms. In: *Trace Metals in Seawater* (Eds. C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg). Plenum Press, London, 331 - 349.
- Santschi, P.H., Li, Y-H., Adler, D.M., Amdurer, M., Bell, J. and Nyffeler, U.P., 1983b. The relative mobility of natural (Th, Pb and Po) and fallout (Pu, Am, Cs) radionuclides in the coastal marine environment: Results from model ecosystems (MERL) and Narragansett Bay. *Geochimica et Cosmochimica Acta*, **47**, 201 - 210.
- Santschi, P.H., 1988. Factors controlling the biogeochemical cycles of trace elements in fresh and coastal marine waters as revealed by artificial radioisotopes. *Limnology and Oceanography*, **33**, 848 - 866.
- Santschi, P.H., 1989. Use of radionuclides in the study of contaminant cycling processes. *Hydrobiologia*, **176/177**, 307 - 320.
- Santschi, P., Höhener, P., Benoit, G. and Buchholtz-ten-Brink, M., 1990. Chemical processes at the sediment-water interface. *Marine Chemistry*, **30**, 269 - 315.
- Sawlan, J.J. and Murray, J.W., 1983. Trace metal remobilisation in the interstitial waters of red clay and hemipelagic sediments. *Earth and Planetary Science Letters*, **64**, 213 - 230.

- Schlemmer, G. and Welz, B., 1986. Palladium and magnesium nitrates, a more universal matrix modifier for graphite furnace atomic absorption spectrometry. *Spectrochimica Acta*, **41B**, 1 - 9.
- Schmidt, H. and Reimers, C.E., 1991. The recent history of trace metal accumulation in the Santa Barbara Basin, southern California Borderland. *Estuarine, Coastal and Shelf Science*, **33**, 485 - 500.
- Shaw, T.J., Gieskes, J.M. and Jahnke, R.A., 1990. Early diagenesis in differing depositional environments: The response of transition metals in pore water. *Geochimica et Cosmochimica Acta*, **54**, 1233 - 1246.
- Shirahata, H., Elias, R.W. and Patterson, C.C., 1980. Chronological variations in concentrations and isotopic compositions of anthropogenic lead in sediments of a remote subalpine pond. *Geochimica et Cosmochimica Acta*, **44**, 149-162.
- Simpson, 1994. Introduction to the North Sea. In: *Understanding the North Sea System* (Eds. H. Charnock, K.R. Dyer, J.M. Huthance, P.S. Liss, J.H. Simpson, P.B. Tett). Chapman and Hall, London, 1 - 4.
- Sørensen, J. and Jørgensen, B.B., 1987. Early diagenesis in sediments from the Danish coastal waters: Microbial activity and Mn-Fe-S geochemistry. *Geochimica et Cosmochimica Acta*, **51**, 1583 - 1590.
- Statham, P.J., 1983. *Analytical and Environmental Studies of Some Trace Metals in Seawater*, Ph.D. Thesis, University of Southampton, 209pp.
- Stumm and Morgan, 1981. *Aquatic Chemistry : An Introduction Emphasizing Chemical Equilibria in Nature Waters*. 2nd Edition, Wiley-Interscience, London, 780pp.
- Sturgeon, R.E., 1989. Graphite furnace atomic absorption analysis of marine samples for trace metals. *Spectrochimica Acta*, **44B**, 1209 - 1220.

- Sturges, W.T. and Barrie, L.A., 1987. Lead 206/207 isotopic ratios in the atmosphere of north America as tracers of US and Canadian emissions. *Nature*, **329**, 144-146.
- Sturges, W.T. and Barrie, L.A., 1989a. Stable lead isotope ratio in Arctic aerosols: Evidence for the origin of Arctic air pollution. *Atmospheric Environment*, **23**, 2513 - 2519.
- Sturges, W.T. and Barrie, L.A., 1989b. The use of stable lead 206/207 isotopic ratios and elemental composition to discriminate the origin of lead in aerosols at a rural site in eastern Canada. *Atmospheric Environment*, **23**, 1645 - 1657.
- Swift, D.J., 1993. The macrobenthic fauna off Sellafield (north eastern Irish Sea) with special reference to bioturbation. *Journal of the Marine Biological Association, UK.*, **73**, 143 - 162.
- Syvitski, J.P.M., Asprey, K.W. and Clattenburg, D.A., 1991. Principles, design and calibration of settling tubes. In: *Principles, Methods and Application of Particle Size Analysis* (Ed. J.P.M. Syvitski). Cambridge University Press, Cambridge, UK., 54 - 63.
- Tappin, A.D., Millward, G.E., Statham, P.J., Burton, J.D. and Morris, A.W., 1995. Trace metals in the central and southern North Sea. *Estuarine, Coastal and Shelf Science*, **41**, 275 - 323.
- Taylor, D., 1979. The effect of discharges from three industrialised estuaries on the distribution of heavy metals in the coastal sediments of the North Sea. *Estuarine, Coastal and Shelf Science*, **8**, 387 - 393.
- Taylor, P.M. and Parker, J.G., 1993. *The Coast of North Wales and North West England: An Environmental Appraisal*. Hamilton Oil Company, London, 80pp.
- Tessier, A., Campbell, P.G.C. and Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, **51**, 844 - 851.

- Tessier, A. and Campbell, 1987. Partitioning of trace metals in sediments: Relationships with bioavailability. *Hydrobiologia*, 149, 43 - 52.
- Tioxide, 1993. *Environmental Performance Site Report*. Tioxide Group Limited, Grimsby, 6pp.
- Tipping, E., Hetherington, N.B., Hilton, J., Thompson, D.W., Bowles, E. and Hamilton-Taylor, J., 1985. Artifacts in the use of selective chemical extraction to determine distributions of metals between oxides of manganese and iron. *Analytical Chemistry*, 57, 1944 - 1946.
- The Humber Advisory Group, 1979. The Humber Estuary. *NERC Publication Series C*, 20, 36pp.
- The Irish Sea Study Group, 1990a. *The Irish Sea, An Environmental Review: Introduction and Overview*. Liverpool University Press, 12pp.
- The Irish Sea Study Group, 1990b. *The Irish Sea, An Environmental Review: Part 2. Waste Inputs and Pollution*. Liverpool University Press, 166pp.
- Tsalev, D.L., Slaveykova, V.I. and Mandjukov, P.B., 1990. Chemical modification in graphite-furnace atomic absorption spectrometry. *Spectrochimica Acta Reviews*, 13, 225 - 274.
- Turner, A., 1990. *Chemical Dynamics in North Sea Estuaries and Plumes*. Ph.D. Thesis, Polytechnic South West, 237pp.
- Turner, A., Millward, G.E. and Morris, A.W., 1991. Particulate metals in five North Sea estuaries. *Estuarine, Coastal and Shelf Science*, 32, 325 - 346.
- Turner, A., Millward, G.E., Schuchardt, B., Schirmer, M. and Prange, A., 1992a. Trace metal distribution coefficients in the Weser Estuary (Germany). *Continental Shelf Research*, 12, 1277 - 1292.

- Turner, A., Millward, G.E., Bale, A.J. and Morris, A.W., 1992b. The solid-solution partitioning of trace metals in the southern North Sea - *in situ* radiochemical experiments. *Continental Shelf Research*, **12**, 1311 - 1329.
- Turner, A., Millward, G.E., Bale, A.J. and Morris, A.W., 1993. Application of the K_D concept to the study of trace metal removal and desorption during estuarine mixing. *Estuarine, Coastal and Shelf Science*, **36**, 1 - 13.
- Turner, A. and Millward, G.E., 1994. Partitioning of trace metals in a macrotidal estuary. Implications for contaminant transport models. *Estuarine, Coastal and Shelf Science*, **39**, 45 - 58.
- Turner, A., Millward, G.E., and Tyler, A.O., 1994. The distribution and chemical composition of particles in a macro-tidal estuary. *Estuarine, Coastal and Shelf Science*, **37**, 1 - 17.
- Turner, D.R., Whitfield, M. and Dickson, A.G., 1981. The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure. *Geochimica et Cosmochimica Acta*, **45**, 855 - 881.
- Ullman, W.J. and Aller, R.C., 1982. Diffusion coefficients in nearshore sediments. *Limnology and Oceanography*, **27**, 552 - 556.
- Ure, A.M., Quevauviller, P.H., Muntau, H. and Griepink, B., 1993. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonisation of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *International Journal of Environmental and Analytical Chemistry*, **51**, 135 - 151.
- Valenta, P., Duursma, E.K., Merks, A.G.A., Rützel, H. and Nürnberg, H.W., 1986. Distribution of Cd, Pb and Cu between dissolved and particulate phases in the eastern Schelt and western Schelt Estuary. *The Science of the Total Environment*, **53**, 41-76.

- van Leussen, W., 1988. Aggregation of particles, settling velocity of mud flocs: A review. In: *Physical Processes in Estuaries* (Eds. J. Dronkers and W. van Leussen). Springer-Verlag, Heidelberg, 347 - 403.
- van Valin, R. and Morse, J.W., 1982. An investigation of methods commonly used for the selective removal and characterisation of trace metals in sediments. *Marine Chemistry*, **11**, 535 - 564.
- Wallace, G.T., 1982. The association of copper, mercury and lead with surface-active organic matter in coastal seawater. *Marine Chemistry*, **11**, 379 - 394.
- Williams, M.R., Millward, G.E., Hill, S. J. and Morris, A.W., 1994. $^{206}/^{207}\text{Pb}$ isotopic ratios applied to particulate transport processes in the north eastern Irish Sea. *Netherlands Journal of Aquatic Ecology*, **28**, 353 - 358.
- Willmot, R.D. and Collins, M.B., 1981. Contemporary fluvial sediment supply to the Wash. *Special Publication of the International Association of Sedimentology*, **5**, 99 - 110.
- Wilson, T.R.S., Thomson, J., Colley, S., Hydes, D.J., Higgs, N.C. and Sørensen, J., 1985. Early organic diagenesis: the significance of progressive sub surface oxidation fronts in pelagic sediments. *Geochimica et Cosmochimica Acta*, **49**, 811 - 822.
- Wilson, T.R.S., Thomson, J., Hydes, D.J., Colley, S., Culkin, F. and Sørensen, J., 1986. Oxidation fronts in pelagic sediments: Diagenetic formation of metal rich layers. *Science*, **232**, 972 - 975.
- Wood, R.G., 1993. *Water Quality Modelling of Estuarine Plumes*. U.K. Department of the Environment Report, 80pp.
- Yeats, P.A. and Strain, P.M., 1990. The oxidation of manganese in seawater : Rate constants based on field data. *Estuarine, Coastal and Shelf Science*, **31**, 11 - 24.

Young, L.B. and Harvey, H.H., 1992. The relative importance of manganese and iron oxides and organic matter in the sorption of trace metals by surficial lake sediments. *Geochimica et Cosmochimica Acta*, 56, 1175 - 1186.

Zwolsman, J.J.G., 1994. *North Sea Estuaries as Filters for Contaminants*. Delft Hydraulics Report No T1233, Delft, The Netherlands, 128pp.

**Appendix A -
Instrumental Conditions**

Element Parameters for**Ca****Matrix :** *Sediment (1M HCl)
SPM (1M HCl)
(diluted to give
2 mg/ml KCl as an
ionisation buffer)*

| | | | |
|--------------------------------|-----------------------|-----------------------------|------------------------|
| Instrument : | GBC 902 | Technique : | Flame AA with microcup |
| Wavelength (nm) : | 239.9 | Slit : | 0.5 |
| Flame Type : | Nitrous/Acetylene | Flame : | Fuel lean (blue) |
| Background Correction : | - | Beam : | Single |
| Flame Height: | 4.5 (arbitrary units) | Signal Measurement : | Peak Height |
| Replicates : | minimum of 3 | | |

Calibration

| | ID | Conc ($\mu\text{g/l}$) | Volume (μl) |
|----------------|-------|-----------------------------|-----------------------------|
| Standard Blank | blank | 0.00 | 200 |
| Standard 1 | 1 | 30.00 | 200 |
| Standard 2 | 2 | 60.00 | 200 |
| Standard 3 | 3 | 120.00 | 200 |
| Standard 4 | 4 | 250.00 | 200 |
| Sample | - | - | 200 |

Calibration type : Linear passing through zero

Calibration Occurrence : Initial calibration then measurements of the standards throughout the analysis

Element Parameters for Cd Matrix : Sediment (1M HCl)

Analyst : Mark Williams, University of Plymouth

| | | | |
|--------------------------------|-------------------------------|-----------------------------|---------------------------|
| Instrument : | Perkin Elmer 4100ZL | Technique : | THGA |
| Wavelength (nm) : | 228.8 | Slit : | 0.7 low |
| Lamp Current (mA) : | 5 | Lamp Energy : | 63 |
| Background Correction : | Zeeman | Signal Measurement : | Peak Area |
| Read Time (sec) : | 5 | Read Delay (sec) : | 0 |
| BOC Time (sec) : | 2 | Replicates : | 3 (samples and standards) |
| Matrix Modifier : | 2000 ppm PO4 + 10 ppm Mg(NO)3 | | |

Calibration

| | ID | Conc (µg/l) | Location | Volume (µl) | Diluent Volume | Modifier Volume |
|---------------------|---|----------------|----------|----------------|-------------------|--------------------|
| Standard Blank A | acid blank | 0.0 | 0 | 5 | 10 | 5 |
| Standard 1 | 1 | 10.0 | 36 | 5 | 5 | 5 |
| Standard 2 | 2 | 5.0 | 35 | 10 | | 5 |
| Standard 3 | 3 | 2.5 | 35 | 5 | 5 | 5 |
| Sample | - | - | - | 5 | 10 | 5 |
| Diluent location : | 33 | | | | | |
| Modifier location : | 34 | | | | | |
| Calibration type : | Standard Addition with calculated intercept | | | | | |

Furnace Program

| Step | Temp | Ramp | Hold | Gas Flow | Read | Gas Type |
|------|------|------|------|----------|------|----------|
| 1 | 110 | 1 | 10 | 250 | | Ar |
| 2 | 140 | 5 | 45 | 250 | | Ar |
| 3 | 500 | 10 | 15 | 250 | | Ar |
| 4 | 1500 | 0 | 5 | 0 | * | |
| 5 | 2200 | 1 | 2 | 250 | | Ar |

| | | |
|---------------------------------|----------------------|-------------------------|
| Injection temperature (°C) : 20 | Pipette Speed : 100% | Extraction system : Off |
|---------------------------------|----------------------|-------------------------|

Element Parameters for Cd Matrix : SPM (1M HCl)

Analyst : Mark Williams, University of Plymouth

| | | | |
|--------------------------------|-------------------------------|-----------------------------|---------------------------|
| Instrument : | Perkin Elmer 4100ZL | Technique : | THGA |
| Wavelength (nm) : | 228.8 | Slit : | 0.7 low |
| Lamp Current (mA) : | 5 | Lamp Energy : | 63 |
| Background Correction : | Zeeman | Signal Measurement : | Peak Area |
| Read Time (sec) : | 5 | Read Delay (sec) : | 0 |
| BOC Time (sec) : | 2 | Replicates : | 3 (samples and standards) |
| Matrix Modifier : | 2000 ppm PO4 + 10 ppm Mg(NO)3 | | |

Calibration

| | ID | Conc (µg/l) | Location | Volume (µl) | Diluent Volume | Modifier Volume |
|------------------|------------|----------------|----------|----------------|-------------------|--------------------|
| Standard Blank A | acid blank | 0.0 | 0 | 5 | 10 | 5 |
| Standard 1 | 1 | 10.0 | 36 | 5 | 5 | 5 |
| Standard 2 | 2 | 5.0 | 35 | 10 | | 5 |
| Standard 3 | 3 | 2.5 | 35 | 5 | 5 | 5 |

Sample - - - 5 10 5

Diluent location : 33

Modifier location : 34

Calibration type : Standard Addition with calculated intercept

Furnace Program

| Step | Temp | Ramp | Hold | Gas Flow | Read | Gas Type |
|------|------|------|------|----------|------|----------|
| 1 | 110 | 1 | 10 | 250 | | Ar |
| 2 | 140 | 5 | 45 | 250 | | Ar |
| 3 | 400 | 10 | 15 | 250 | | Ar |
| 4 | 1400 | 0 | 5 | 0 | * | |
| 5 | 2200 | 1 | 2 | 250 | | Ar |

Injection temperature (°C) : 20

Pipette Speed : 100%

Extraction system : Off

Element Parameters for Co Matrix : Sediment (1M HCl)

Analyst : Mark Williams, University of Plymouth

| | | | |
|--------------------------------|---|-----------------------------|---------------------------|
| Instrument : | Perkin Elmer 4100ZL | Technique : | THGA |
| Wavelength (nm) : | 242.5 | Slit : | 0.2 low |
| Lamp Current (mA) : | 10 | Lamp Energy : | 53 |
| Background Correction : | Zeeman | Signal Measurement : | Peak Area |
| Read Time (sec) : | 2.5 | Read Delay (sec) : | 0 |
| BOC Time (sec) : | 2 | Replicates : | 3 (samples and standards) |
| Matrix Modifier : | 500 µg/ml Pd + 1% Hydroxylammonium Chloride | | |

Calibration

| | ID | Conc (µg/l) | Location | Volume (µl) | Diluent Volume | Modifier Volume |
|------------------|------------|----------------|----------|----------------|-------------------|--------------------|
| Standard Blank A | acid blank | 0.0 | 0 | 10 | 10 | 5 |
| Standard 1 | 1 | 50.0 | 40 | 10 | | 5 |
| Standard 2 | 2 | 25.0 | 40 | 5 | 5 | 5 |
| Standard 3 | 3 | 12.5 | 39 | 10 | | 5 |

Sample - - - 10 10 5

Diluent location : 33

Modifier location : 34

Calibration type : Standard Addition with calculated intercept

Furnace Program

| Step | Temp | Ramp | Hold | Gas Flow | Read | Gas Type |
|------|------|------|------|----------|------|----------|
| 1 | 110 | 1 | 20 | 250 | | Ar |
| 2 | 130 | 5 | 45 | 250 | | Ar |
| 3 | 1350 | 12 | 20 | 250 | | Ar |
| 4 | 2300 | 0 | 5 | 0 | * | |
| 5 | 2500 | 1 | 2 | 250 | | Ar |

Injection temperature (°C) : 20

Pipette Speed : 100%

Extraction system : Off

Element Parameters for Co Matrix : SPM (1M HCl)

Analyst : Mark Williams, University of Plymouth

| | | | |
|--------------------------------|---|-----------------------------|---------------------------|
| Instrument : | Perkin Elmer 4100ZL | Technique : | THGA |
| Wavelength (nm) : | 242.5 | Slit : | 0.2 low |
| Lamp Current (mA) : | 10 | Lamp Energy : | 53 |
| Background Correction : | Zeeman | Signal Measurement : | Peak Area |
| Read Time (sec) : | 2.5 | Read Delay (sec) : | 0 |
| BOC Time (sec) : | 2 | Replicates : | 3 (samples and standards) |
| Matrix Modifier : | 500 µg/ml Pd + 1% Hydroxylammonium Chloride | | |

Calibration

| | ID | Conc (µg/l) | Location | Volume (µl) | Diluent Volume | Modifier Volume |
|---------------------|---|----------------|----------|----------------|-------------------|--------------------|
| Standard Blank A | acid blank | 0.0 | 0 | 10 | 10 | 5 |
| Standard 1 | 1 | 50.0 | 40 | 10 | | 5 |
| Standard 2 | 2 | 25.0 | 40 | 5 | 5 | 5 |
| Standard 3 | 3 | 12.5 | 39 | 10 | | 5 |
| Sample | - | - | - | 10 | 10 | 5 |
| Diluent location : | 33 | | | | | |
| Modifier location : | 34 | | | | | |
| Calibration type : | Standard Addition with calculated intercept | | | | | |

Furnace Program

| Step | Temp | Ramp | Hold | Gas Flow | Read | Gas Type |
|------|------|------|------|----------|------|----------|
| 1 | 110 | 1 | 20 | 250 | | Ar |
| 2 | 130 | 5 | 45 | 250 | | Ar |
| 3 | 1350 | 12 | 20 | 250 | | Ar |
| 4 | 2300 | 0 | 5 | 0 | * | |
| 5 | 2500 | 1 | 2 | 250 | | Ar |

Injection temperature (°C) : 20

Pipette Speed : 100%

Extraction system : Off

Element Parameters for Cu Matrix : Sediment (1M HCl)

Analyst : Mark Williams, University of Plymouth

| | | | |
|--------------------------------|---|-----------------------------|---------------------------|
| Instrument : | Perkin Elmer 4100ZL | Technique : | THGA |
| Wavelength (nm) : | 324.8 | Slit : | 0.7 low |
| Lamp Current (mA) : | 7 | Lamp Energy : | 75 |
| Background Correction : | Zeeman | Signal Measurement : | Peak Area |
| Read Time (sec) : | 5 | Read Delay (sec) : | 0 |
| BOC Time (sec): | 2 | Replicates : | 3 (samples and standards) |
| Matrix Modifier : | 500 µg/ml Pd + 1% Hydroxylammonium Chloride | | |

Calibration

| | ID | Conc (µg/l) | Location | Volume (µl) | Diluent Volume | Modifier Volume |
|------------------|------------|----------------|----------|----------------|-------------------|--------------------|
| Standard Blank A | acid blank | 0.0 | 0 | 5 | 10 | 5 |
| Standard 1 | 1 | 100.0 | 40 | 5 | 5 | 5 |
| Standard 2 | 2 | 50.0 | 39 | 10 | | 5 |
| Standard 3 | 3 | 25.0 | 39 | 5 | 5 | 5 |

Sample - - - 5 10 5

Diluent location : 37

Modifier location : 38

Calibration type : Standard Addition with calculated intercept

Furnace Program

| Step | Temp | Ramp | Hold | Gas Flow | Read | Gas Type |
|------|------|------|------|----------|------|----------|
| 1 | 110 | 1 | 20 | 250 | | Ar |
| 2 | 140 | 5 | 55 | 250 | | Ar |
| 3 | 1200 | 10 | 25 | 250 | | Ar |
| 4 | 2300 | 0 | 5 | 0 | * | |
| 5 | 2500 | 1 | 2 | 250 | | Ar |

Injection temperature (°C) : 20

Pipette Speed : 100%

Extraction system : Off

Element Parameters for *Cu* Matrix : *SPM (1M HCl)*

Analyst : Mark Williams, University of Plymouth

| | | | |
|--------------------------------|---|-----------------------------|---------------------------|
| Instrument : | Perkin Elmer 4100ZL | Technique : | THGA |
| Wavelength (nm) : | 324.8 | Slit : | 0.7 low |
| Lamp Current (mA) : | 7 | Lamp Energy : | 75 |
| Background Correction : | Zeeman | Signal Measurement : | Peak Area |
| Read Time (sec) : | 5 | Read Delay (sec) : | 0 |
| BOC Time (sec): | 2 | Replicates : | 3 (samples and standards) |
| Matrix Modifier : | 500 µg/ml Pd + 1% Hydroxylammonium Chloride | | |

Calibration

| | ID | Conc (µg/l) | Location | Volume (µl) | Diluent Volume | Modifier Volume |
|------------------|------------|----------------|----------|----------------|-------------------|--------------------|
| Standard Blank A | acid blank | 0.0 | 0 | 5 | 10 | 5 |
| Standard 1 | 1 | 100.0 | 40 | 5 | 5 | 5 |
| Standard 2 | 2 | 50.0 | 39 | 10 | | 5 |
| Standard 3 | 3 | 25.0 | 39 | 5 | 5 | 5 |

Sample - - - 5 10 5

Diluent location : 37

Modifier location : 38

Calibration type : Standard Addition with calculated intercept

Furnace Program

| Step | Temp | Ramp | Hold | Gas Flow | Read | Gas Type |
|------|------|------|------|----------|------|----------|
| 1 | 110 | 1 | 20 | 250 | | Ar |
| 2 | 140 | 5 | 55 | 250 | | Ar |
| 3 | 1200 | 10 | 25 | 250 | | Ar |
| 4 | 2300 | 0 | 5 | 0 | * | |
| 5 | 2500 | 1 | 2 | 250 | | Ar |

Injection temperature (°C) : 20

Pipette Speed : 100%

Extraction system : Off

Element Parameters for **Cu** Matrix : *Porewater*

Analyst : Mark Williams, University of Plymouth

| | | | |
|--------------------------------|---|-----------------------------|---------------------------|
| Instrument : | Perkin Elmer 4100ZL | Technique : | THGA |
| Wavelength (nm) : | 324.8 | Slit : | 0.7 low |
| Lamp Current (mA) : | 7 | Lamp Energy : | 75 |
| Background Correction : | Zeeman | Signal Measurement : | Peak Area |
| Read Time (sec) : | 2.6 | Read Delay (sec) : | 0 |
| BOC Time (sec): | 2 | Replicates : | 3 (samples and standards) |
| Matrix Modifier : | 500 µg/ml Pd + 1% Hydroxylammonium Chloride | | |

Calibration

| | ID | Conc (µg/l) | Location | Volume (µl) | Diluent Volume | Modifier Volume |
|------------------|------------|----------------|----------|----------------|-------------------|--------------------|
| Standard Blank A | acid blank | 0.0 | 0 | 10 | 10 | 5 |
| Standard 1 | 1 | 50.0 | 40 | 10 | | 5 |
| Standard 2 | 2 | 25.0 | 40 | 5 | 5 | 5 |
| Standard 3 | 3 | 10.0 | 39 | 10 | | 5 |

| | | | | | | |
|--------|---|---|---|----|----|---|
| Sample | - | - | - | 10 | 10 | 5 |
|--------|---|---|---|----|----|---|

Diluent location : 37

Modifier location : 38

Calibration type : Standard Addition with calculated intercept

Furnace Program

| Step | Temp | Ramp | Hold | Gas Flow | Read | Gas Type |
|------|------|------|------|----------|------|----------|
| 1 | 110 | 1 | 20 | 250 | | Ar |
| 2 | 130 | 5 | 45 | 250 | | Ar |
| 3 | 1200 | 10 | 25 | 250 | | Ar |
| 4 | 2400 | 0 | 5 | 0 | * | |
| 5 | 2400 | 1 | 2 | 250 | | Ar |

Injection temperature (°C) : 20

Pipette Speed : 100%

Extraction system : On

Element Parameters for *Fe* **Matrix :** *Sediment (1M HCl)*
SPM (1M HCl)

| | | | |
|--------------------------------|-----------------------|-----------------------------|------------------------|
| Instrument : | GBC 902 | Technique : | Flame AA with microcup |
| Wavelength (nm) : | 372.0 | Slit : | 0.2 |
| Flame Type : | Air/Acetylene | Flame : | Fuel lean (blue) |
| Background Correction : | - | Beam : | Single |
| Flame Height: | 4.5 (arbitrary units) | Signal Measurement : | Peak Height |
| Replicates : | minimum of 3 | | |

Calibration

| | ID | Conc ($\mu\text{g/l}$) | Volume (μl) |
|----------------|-------|-----------------------------|-----------------------------|
| Standard Blank | blank | 0.00 | 200 |
| Standard 1 | 1 | 9.38 | 200 |
| Standard 2 | 2 | 18.75 | 200 |
| Standard 3 | 3 | 37.50 | 200 |
| Standard 4 | 4 | 75.00 | 200 |
| Sample | - | - | 200 |

Calibration type : Linear passing through zero
 Calibration Occurrence : Initial calibration then measurements of the standards throughout the analysis

Element Parameters for *Fe* **Matrix :** *Sediment (1M HCl)*
SPM (1M HCl)

| | | | |
|--------------------------------|-----------------------|-----------------------------|------------------------|
| Instrument : | IL 151 | Technique : | Flame AA with microcup |
| Wavelength (nm) : | 386.0 | Slit : | 0.3 |
| Flame Type : | Air/Acetylene | Flame : | Fuel lean (blue) |
| Background Correction : | - | Beam : | Single |
| Flame Height: | 4.5 (arbitrary units) | Signal Measurement : | Peak Height |
| Replicates : | minimum of 3 | | |

Calibration

| | ID | Conc ($\mu\text{g/l}$) | Volume (μl) |
|----------------|-------|-----------------------------|-----------------------------|
| Standard Blank | blank | 0.00 | 200 |
| Standard 1 | 1 | 10.00 | 200 |
| Standard 2 | 2 | 25.00 | 200 |
| Standard 3 | 3 | 50.00 | 200 |
| Standard 4 | 4 | 75.00 | 200 |
| Sample | - | - | 200 |

Calibration type : Linear passing through zero
 Calibration Occurrence : Initial calibration then measurements of the standards throughout the analysis

Element Parameters for *Fe* Matrix : *Porewater*

| | | | |
|--------------------------------|-------------------|-----------------------------|------------------------|
| Instrument : | IL 151 | Technique : | Flame AA with microcup |
| Wavelength (nm) : | 248.3 | Slit : | 0.3 |
| Flame Type : | Nitrous/Acetylene | Flame : | Fuel lean |
| Background Correction : | - | Beam : | Single |
| Flame Height: | 2 mm | Signal Measurement : | Peak Height |
| Replicates : | minimum of 3 | | |

Calibration

| | ID | Conc ($\mu\text{g/l}$) | Volume (μl) |
|----------------|-------|-----------------------------|-----------------------------|
| Standard Blank | blank | 0.00 | 200 |
| Standard 1 | 1 | 0.50 | 200 |
| Standard 2 | 2 | 1.00 | 200 |
| Standard 3 | 3 | 2.00 | 200 |
| Standard 4 | 4 | 4.00 | 200 |
| Sample | - | - | 200 |

Calibration type : Linear passing through zero

Calibration Occurrence : Initial calibration then measurements of the standards throughout the analysis

Element Parameters for**Mn****Matrix :** *Sediment (1M HCl)*
SPM (1M HCl)

| | | | |
|--------------------------------|-----------------------|-----------------------------|------------------------|
| Instrument : | GBC 902 | Technique : | Flame AA with microcup |
| Wavelength (nm) : | 279.8 | Slit : | 0.2 |
| Flame Type : | Air/Acetylene | Flame : | Fuel lean (blue) |
| Background Correction : | - | Beam : | Single |
| Flame Height: | 4.5 (arbitrary units) | Signal Measurement : | Peak Height |
| Replicates : | minimum of 3 | | |

Calibration

| | ID | Conc ($\mu\text{g/l}$) | Volume (μl) |
|----------------|-------|-----------------------------|-----------------------------|
| Standard Blank | blank | 0.00 | 200 |
| Standard 1 | 1 | 1.00 | 200 |
| Standard 2 | 2 | 2.00 | 200 |
| Standard 3 | 3 | 4.00 | 200 |
| Standard 4 | 4 | 8.00 | 200 |
| Sample | - | - | 200 |

Calibration type : Linear passing through zero

Calibration Occurrence : Initial calibration then measurements of the standards throughout the analysis

Element Parameters for *Mn* **Matrix :** *Sediment (1M HCl)*
SPM (1M HCl)

| | | | |
|--------------------------------|-----------------------|-----------------------------|------------------------|
| Instrument : | IL 151 | Technique : | Flame AA with microcup |
| Wavelength (nm) : | 403.1 | Slit : | 0.3 |
| Flame Type : | Air/Acetylene | Flame : | Fuel lean (blue) |
| Background Correction : | - | Beam : | Single |
| Flame Height: | 4.5 (arbitrary units) | Signal Measurement : | Peak Height |
| Replicates : | minimum of 3 | | |

Calibration

| | ID | Conc ($\mu\text{g/l}$) | Volume (μl) |
|----------------|-------|-----------------------------|-----------------------------|
| Standard Blank | blank | 0.00 | 200 |
| Standard 1 | 1 | 1.00 | 200 |
| Standard 2 | 2 | 2.00 | 200 |
| Standard 3 | 3 | 4.00 | 200 |
| Standard 4 | 4 | 8.00 | 200 |
| Sample | - | - | 200 |

Calibration type : Linear passing through zero
Calibration Occurrence : Initial calibration then measurements of the standards throughout the analysis

Element Parameters for *Mn* **Matrix :** *Porewater*

| | | | |
|--------------------------------|-------------------|-----------------------------|------------------------|
| Instrument : | IL 151 | Technique : | Flame AA with microcup |
| Wavelength (nm) : | 279.5 | Slit : | 0.5 |
| Flame Type : | Nitrous/Acetylene | Flame : | Fuel lean |
| Background Correction : | - | Beam : | Single |
| Flame Height: | 3 mm | Signal Measurement : | Peak Height |
| Replicates : | minimum of 3 | | |

Calibration

| | ID | Conc ($\mu\text{g/l}$) | Volume (μl) |
|----------------|-------|-----------------------------|-----------------------------|
| Standard Blank | blank | 0.00 | 200 |
| Standard 1 | 1 | 0.50 | 200 |
| Standard 2 | 2 | 1.00 | 200 |
| Standard 3 | 3 | 2.00 | 200 |
| Standard 4 | 4 | 4.00 | 200 |
| Sample | - | - | 200 |

Calibration type : Linear passing through zero
 Calibration Occurrence : Initial calibration then measurements of the standards throughout the analysis

Element Parameters for *Pb* Matrix : *Sediment (1M HCl)*

Analyst : Mark Williams, University of Plymouth

| | | | |
|--------------------------------|---|-----------------------------|---------------------------|
| Instrument : | Perkin Elmer 4100ZL | Technique : | THGA |
| Wavelength (nm) : | 283.3 | Slit : | 0.7 low |
| Lamp Current (mA) : | 5 | Lamp Energy : | 63 |
| Background Correction : | Zeeman | Signal Measurement : | Peak Area |
| Read Time (sec) : | 5 | Read Delay (sec) : | 0 |
| BOC Time (sec) : | 2 | Replicates : | 3 (samples and standards) |
| Matrix Modifier : | 500 µg/ml Pd + 1% Hydroxylammonium Chloride | | |

Calibration

| | ID | Conc (µg/l) | Location | Volume (µl) | Diluent Volume | Modifier Volume |
|---------------------|---|----------------|----------|----------------|-------------------|--------------------|
| Standard Blank A | acid blank | 0.0 | 0 | 5 | 10 | 5 |
| Standard 1 | 1 | 160.0 | 40 | 5 | 5 | 5 |
| Standard 2 | 2 | 80.0 | 39 | 10 | | 5 |
| Standard 3 | 3 | 40.0 | 39 | 5 | 5 | 5 |
| Sample | - | - | - | 5 | 10 | 5 |
| Diluent location : | 37 | | | | | |
| Modifier location : | 38 | | | | | |
| Calibration type : | Standard Addition with calculated intercept | | | | | |

Furnace Program

| Step | Temp | Ramp | Hold | Gas Flow | Read | Gas Type |
|------|------|------|------|----------|------|----------|
| 1 | 110 | 1 | 20 | 250 | | Ar |
| 2 | 130 | 5 | 40 | 250 | | Ar |
| 3 | 1100 | 10 | 25 | 250 | | Ar |
| 4 | 1900 | 0 | 5 | 0 | * | |
| 5 | 2500 | 1 | 3 | 250 | | Ar |

Injection temperature (°C) : 20

Pipette Speed : 100%

Extraction system : Off

Element Parameters for *Pb* Matrix : *SPM (1M HCl)*

Analyst : Mark Williams, University of Plymouth

| | | | |
|--------------------------------|---|-----------------------------|---------------------------|
| Instrument : | Perkin Elmer 4100ZL | Technique : | THGA |
| Wavelength (nm) : | 283.3 | Slit : | 0.7 low |
| Lamp Current (mA) : | 5 | Lamp Energy : | 63 |
| Background Correction : | Zeeman | Signal Measurement : | Peak Area |
| Read Time (sec) : | 5 | Read Delay (sec) : | 0 |
| BOC Time (sec) : | 2 | Replicates : | 3 (samples and standards) |
| Matrix Modifier : | 500 µg/ml Pd + 1% Hydroxylammonium Chloride | | |

Calibration

| | ID | Conc (µg/l) | Location | Volume (µl) | Diluent Volume | Modifier Volume |
|------------------|------------|----------------|----------|----------------|-------------------|--------------------|
| Standard Blank A | acid blank | 0.0 | 0 | 5 | 10 | 5 |
| Standard 1 | 1 | 160.0 | 40 | 5 | 5 | 5 |
| Standard 2 | 2 | 80.0 | 39 | 10 | | 5 |
| Standard 3 | 3 | 40.0 | 39 | 5 | 5 | 5 |

Sample - - - 5 10 5

Diluent location : 37

Modifier location : 38

Calibration type : Standard Addition with calculated intercept

Furnace Program

| Step | Temp | Ramp | Hold | Gas Flow | Read | Gas Type |
|------|------|------|------|----------|------|----------|
| 1 | 110 | 1 | 20 | 250 | | Ar |
| 2 | 130 | 5 | 40 | 250 | | Ar |
| 3 | 550 | 10 | 25 | 250 | | Ar |
| 4 | 1700 | 0 | 5 | 0 | * | |
| 5 | 2500 | 1 | 3 | 250 | | Ar |

Injection temperature (°C) : 20

Pipette Speed : 100%

Extraction system : Off

Element Parameters for *Pb* Matrix : *Porewater*

Analyst : Mark Williams, University of Plymouth

| | | | |
|--------------------------------|---------------------|-----------------------------|---------------------------|
| Instrument : | Perkin Elmer 4100ZL | Technique : | THGA |
| Wavelength (nm) : | 283.3 | Slit : | 0.7 low |
| Lamp Current (mA) : | 5 | Lamp Energy : | 63 |
| Background Correction : | Zeeman | Signal Measurement : | Peak Area |
| Read Time (sec) : | 4 | Read Delay (sec) : | 0 |
| BOC Time (sec) : | 2 | Replicates : | 3 (samples and standards) |
| Matrix Modifier : | 3% Ammonium Oxalate | | |

Calibration

| | ID | Conc (µg/l) | Location | Volume (µl) | Diluent Volume | Modifier Volume |
|---------------------|---|----------------|----------|----------------|-------------------|--------------------|
| Standard Blank A | acid blank | 0.0 | 0 | 10 | 10 | 10 |
| Standard 1 | 1 | 80.0 | 40 | 10 | | 10 |
| Standard 2 | 2 | 40.0 | 39 | 10 | | 10 |
| Standard 3 | 3 | 20.0 | 39 | 5 | 5 | 10 |
| Sample | - | - | - | 10 | 10 | 10 |
| Diluent location : | 37 | | | | | |
| Modifier location : | 38 | | | | | |
| Calibration type : | Standard Addition with calculated intercept | | | | | |

Furnace Program

| Step | Temp | Ramp | Hold | Gas Flow | Read | Gas Type |
|------|------|------|------|----------|------|----------|
| 1 | 110 | 1 | 20 | 250 | | Ar |
| 2 | 130 | 5 | 40 | 250 | | Ar |
| 3 | 450 | 10 | 25 | 250 | | Ar |
| 4 | 1250 | 0 | 5 | 0 | * | |
| 5 | 2400 | 1 | 3 | 250 | | Ar |
| 6 | 20 | 1 | 2 | 250 | | Ar |
| 7 | 1600 | 1 | 5 | 250 | | Ar |

| | | |
|--|-----------------------------|-------------------------------|
| Injection temperature (°C) : 20 | Pipette Speed : 100% | Extraction system : On |
|--|-----------------------------|-------------------------------|

**Element Parameters for *Zn* Matrix : *Sediment (1M HCl)*
*SPM (1M HCl)***

| | | | |
|--------------------------------|-----------------------|-----------------------------|------------------------|
| Instrument : | GBC 902 | Technique : | Flame AA with microcup |
| Wavelength (nm) : | 213.9 | Slit : | 0.5 |
| Flame Type : | Air/Acetylene | Flame : | Fuel lean (blue) |
| Background Correction : | Continuum | Beam : | Double |
| Flame Height: | 4.5 (arbitrary units) | Signal Measurement : | Peak Height |
| Replicates : | minimum of 3 | | |

Calibration

| | ID | Conc ($\mu\text{g/l}$) | Volume (μl) |
|----------------|-------|-----------------------------|-----------------------------|
| Standard Blank | blank | 0.00 | 200 |
| Standard 1 | 1 | 0.25 | 200 |
| Standard 2 | 2 | 0.50 | 200 |
| Standard 3 | 3 | 1.00 | 200 |
| Standard 4 | 4 | 2.00 | 200 |
| Sample | - | - | 200 |

Calibration type : Linear passing through zero

Calibration Occurrence : Initial calibration then measurements of the standards throughout the analysis

Element Parameters for**Zn****Matrix :** *Sediment (1M HCl)*
SPM (1M HCl)

| | | | |
|--------------------------------|----------------------|-----------------------------|------------------------|
| Instrument : | IL 151 | Technique : | Flame AA with microcup |
| Wavelength (nm) : | 213.9 | Slit : | 1.0 |
| Flame Type : | Air/Acetylene | Flame : | Fuel lean (blue) |
| Background Correction : | Continuum | Beam : | Single |
| Flame Height: | 92 (arbitrary units) | Signal Measurement : | Peak Height |
| Replicates : | minimum of 3 | | |

Calibration

| | ID | Conc ($\mu\text{g/l}$) | Volume (μl) |
|----------------|-------|-----------------------------|-----------------------------|
| Standard Blank | blank | 0.00 | 200 |
| Standard 1 | 1 | 0.25 | 200 |
| Standard 2 | 2 | 0.50 | 200 |
| Standard 3 | 3 | 1.00 | 200 |
| Standard 4 | 4 | 2.00 | 200 |
| Sample | - | - | 200 |

Calibration type : Linear passing through zero

Calibration Occurrence : Initial calibration then measurements of the standards throughout the analysis

**Appendix B -
SVT Trace Metal Concentrations**

| | Time min | SPM mg l ⁻¹ | Fe mg g ⁻¹ | Mn µg g ⁻¹ | Zn µg g ⁻¹ | Ca mg g ⁻¹ | Co µg g ⁻¹ | Cu µg g ⁻¹ | Cd µg g ⁻¹ | Pb µg g ⁻¹ | ^{206/207} Pb i.r. | |
|-----------|-------------|---------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|----------------------------|---------------|
| CH88A/ 92 | | | | | | | | | | | | |
| B2 | 244 | 5 | 521 | 5.5 ± 0.1 | 787 ± 9 | 91 ± 1 | NS | 4.7 ± 0.1 | 10.6 ± 1.3 | 70 ± 0 | 1.169 ± 0.009 | |
| | | 20 | 86 | 8.4 ± 0.1 | 1053 ± 37 | 604 ± 10 | NS | 8.0 ± 0.2 | 43.4 ± 14.6 | 103 ± 2 | 1.181 ± 0.005 | |
| | | 80 | 57 | 8.4 ± 0.1 | 1136 ± 17 | 200 ± 3 | NS | 11.4 ± 0.8 | 19.4 ± 1.6 | 124 ± 1 | 1.172 ± 0.019 | |
| | | 280 | 20 | 9.4 ± 0.1 | 1241 ± 7 | 282 ± 1 | NS | 7.3 ± 0.5 | 25.0 ± 0.1 | 135 ± 1 | 1.148 ± 0.002 | |
| | | >280 | 25 | 8.6 ± 0.1 | 1082 ± 8 | 276 ± 3 | NS | 7.6 ± 0.3 | 58.0 ± 1.0 | 113 ± 3 | 1.145 ± 0.024 | |
| | 366 | 5 | 10 | 10.2 ± 0.1 | 1113 ± 8 | 636 ± 2 | NS | 13.8 ± 1.7 | 59.0 ± 3.4 | 102 ± 1 | 1.128 ± 0.002 | |
| | | 20 | 12 | 9.5 ± 0.1 | 961 ± 8 | 476 ± 7 | NS | 7.6 ± 1.0 | 35.1 ± 3.4 | 125 ± 2 | 1.155 ± 0.004 | |
| | | 80 | 10 | 11.3 ± 0.1 | 1145 ± 0 | 405 ± 0 | NS | 14.8 ± 2.7 | 95.6 ± 0.6 | 108 ± 0 | 1.134 ± 0.002 | |
| | | 280 | 8 | 9.9 ± 0.2 | 1026 ± 17 | 472 ± 3 | NS | 5.8 ± 0.0 | 8.2 ± 0.2 | 118 ± 1 | 1.129 ± 0.009 | |
| | | >280 | 7 | 8.6 ± 0.2 | 908 ± 9 | 459 ± 5 | NS | 15.4 ± 1.3 | 73.0 ± 3.3 | 101 ± 0 | 1.126 ± 0.006 | |
| CH99 / 92 | | | | | | | | | | | | |
| | 5 | 5 | 14 | 8.7 ± 0.1 | 253 ± 19 | 281 ± 6 | 23 ± 2 | 7.9 ± 1.0 | 38.1 ± 0.9 | 10.6 ± 0.1 | 112 ± 2 | 1.163 ± 0.009 |
| | | 20 | 13 | 21.5 ± 0.3 | 1186 ± 20 | 351 ± 6 | 23 ± 8 | 7.0 ± 0.0 | 24.6 ± 1.5 | 13.1 ± 0.1 | 93 ± 4 | 1.163 ± 0.005 |
| | | 80 | 15 | 8.5 ± 0.0 | 291 ± 13 | 158 ± 6 | 44 ± 12 | 9.6 ± 0.5 | 80.4 ± 4.6 | ND | 135 ± 1 | 1.139 ± 0.001 |
| | | 280 | 9 | 9.8 ± 0.2 | 255 ± 11 | 96 ± 11 | 23 ± 3 | 7.7 ± 0.9 | 36.9 ± 0.7 | ND | 125 ± 1 | 1.168 ± 0.025 |
| | | >280 | 12 | 8.1 ± 0.2 | 249 ± 11 | 260 ± 18 | 42 ± 8 | 9.8 ± 0.5 | 116. ± 3.9 | 14.7 ± 0.4 | 150 ± 11 | 1.137 ± 0.010 |

| | Time | SPM | Fe | Mn | Zn | Ca | Co | Cu | Cd | Pb | ^{206/207} Pb i.r. |
|----|------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|----------------------------|
| | min | mg l ⁻¹ | mg g ⁻¹ | μg g ⁻¹ | μg g ⁻¹ | mg g ⁻¹ | μg g ⁻¹ | μg g ⁻¹ | μg g ⁻¹ | μg g ⁻¹ | |
| 11 | 5 | 76 | 22.8 ± 0.3 | 1093 ± 21 | 261 ± 4 | 38 ± 8 | 10.3 ± 0.3 | 45.3 ± 0.3 | ND | 114 ± 1 | 1.173 ± 0.008 |
| | 20 | 63 | 21.4 ± 0.4 | 1081 ± 7 | 242 ± 5 | 34 ± 2 | 8.2 ± 0.3 | 28.8 ± 0.6 | 3.63 ± 0.02 | 144 ± 1 | 1.166 ± 0.005 |
| | 80 | 53 | 21.0 ± 0.1 | 1058 ± 19 | 240 ± 7 | 28 ± 1 | 8.1 ± 0.7 | 35.2 ± 0.7 | ND | 139 ± 1 | 1.167 ± 0.005 |
| | 280 | 28 | 20.8 ± 0.4 | 1020 ± 33 | 298 ± 8 | 28 ± 2 | 8.3 ± 0.5 | 27.6 ± 0.4 | 3.40 ± 0.4 | 169 ± 1 | 1.166 ± 0.009 |
| | >280 | 36 | 23.1 ± 0.2 | 1131 ± 24 | 323 ± 16 | 36 ± 2 | 9.4 ± 0.3 | 28.4 ± 0.4 | ND | 143 ± 1 | 1.174 ± 0.005 |
| 71 | 5 | 245 | 15.5 ± 0.3 | 728 ± 22 | 211 ± 6 | 30 ± 0 | 3.3 ± 0.1 | 19.2 ± 0.9 | | 37 ± 2 | 1.182 ± 0.004 |
| | 20 | 144 | 19.4 ± 0.3 | 968 ± 30 | 302 ± 6 | 34 ± 1 | 4.9 ± 0.1 | 36.7 ± 1.8 | | 92 ± 2 | 1.180 ± 0.002 |
| | 80 | 152 | 19.5 ± 0.4 | 1007 ± 34 | 270 ± 4 | 35 ± 1 | 5.3 ± 0.1 | 38.5 ± 2.4 | 1.45 0.03 | 73 ± 8 | 1.178 ± 0.006 |
| | 280 | 83 | 21.7 ± 0.0 | 1054 ± 33 | 258 ± 3 | 27 ± 0 | 5.4 ± 0.1 | 30.8 ± 1.9 | | 82 ± 3 | 1.174 ± 0.004 |
| | >280 | 103 | 21.7 ± 0.4 | 1041 ± 22 | 247 ± 4 | 36 ± 1 | 5.7 ± 0.2 | 50.1 ± 17.4 | 1.19 ± 0.02 | 83 ± 12 | 1.165 ± 0.006 |
| 85 | 5 | 573 | 10.3 ± 0.2 | 591 ± 2 | 113 ± 1 | 43 ± 1 | 10.4 ± 0.2 | 33.0 ± 0.7 | 1.56 ± 0.06 | 159 ± 1 | 1.159 ± 0.002 |
| | 20 | 487 | 9.8 ± 0.2 | 567 ± 6 | 106 ± 2 | 35 ± 2 | 10.3 ± 0.3 | 29.0 ± 0.5 | 0.66 ± 0.02 | 137 ± 1 | 1.169 ± 0.006 |
| | 80 | 444 | 11.3 ± 0.1 | 689 ± 4 | 124 ± 1 | 36 ± 0 | 11.8 ± 0.0 | 34.1 ± 0.9 | 1.97 ± 0.03 | 150 ± 2 | 1.158 ± 0.003 |
| | 280 | 208 | 12.5 ± 0.0 | 1177 ± 16 | 150 ± 7 | 35 ± 1 | 13.0 ± 0.4 | 37.7 ± 0.6 | 4.64 ± 0.01 | 176 ± 1 | 1.167 ± 0.003 |
| | >280 | 98 | 11.1 ± 0.1 | 487 ± 9 | 128 ± 2 | 34 ± 2 | 11.6 ± 0.3 | 39.5 ± 0.3 | 4.93 ± 0.09 | 165 ± 0 | 1.141 ± 0.005 |

| | Time | SPM | Fe | Mn | Zn | Ca | Co | Cu | Cd | Pb | 206/207Pb i.r. |
|-----------|------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|----------------|
| | min | mg l ⁻¹ | mg g ⁻¹ | μg g ⁻¹ | μg g ⁻¹ | mg g ⁻¹ | μg g ⁻¹ | μg g ⁻¹ | μg g ⁻¹ | μg g ⁻¹ | |
| CH108A/93 | | | | | | | | | | | |
| B4 | 6 | 5 | 11 | 10.3 ± 0.3 | 362 ± 14 | 85 ± 8 | ND | ND | ND | 67 ± 5 | 1.193 ± 0.020 |
| | | 20 | 12 | 10.8 ± 0.2 | 398 ± 50 | 98 ± 3 | ND | 4.9 ± 4.9 | ND | 87 ± 4 | 1.144 ± 0.018 |
| | | 80 | 12 | 9.3 ± 0.8 | 415 ± 33 | 197 ± 6 | 5 ± 8 | ND | ND | 92 ± 4 | 1.170 ± 0.016 |
| | | 280 | 4 | 12.6 ± 1.0 | 208 ± 90 | 96 ± 41 | ND | 6.2 ± 5.6 | 70.1 ± 6.3 | 132 ± 5 | 1.134 ± 0.009 |
| | | >280 | 10 | 6.4 ± 0.3 | 126 ± 26 | 296 ± 28 | 8 ± 13 | ND | ND | 112 ± 6 | 1.160 ± 0.016 |
| | 8 | 5 | 11 | 6.3 ± 0.5 | 164 ± 41 | 224 ± 34 | ND | ND | ND | 53 ± 1 | 1.194 ± 0.015 |
| | | 20 | 28 | 4.0 ± 0.2 | 146 ± 0 | 43 ± 7 | ND | 2.8 ± 1.2 | ND | 36 ± 5 | 1.158 ± 0.021 |
| | | 80 | 30 | 4.3 ± 0.1 | 135 ± 20 | 24 ± 10 | 14 ± 11 | ND | 19.2 ± 1.8 | 28 ± 1 | 1.167 ± 0.007 |
| | | 280 | 21 | 2.6 ± 0.3 | 93 ± 6 | 43 ± 5 | 13 ± 3 | ND | 15.8 ± 1.7 | 40 ± 2 | 1.126 ± 0.011 |
| | | >280 | 9 | 7.6 ± 0.6 | ND | 30 ± 14 | 41 ± 32 | 4.7 ± 8.0 | 34.5 ± 5.4 | 43 ± 1 | 1.181 ± 0.031 |
| | 32 | 5 | 23 | 9.0 ± 0.0 | 209 ± 23 | 277 ± 12 | ND | 2.4 ± 3.7 | 26.9 ± 1.5 | 77 ± 0 | 1.167 ± 0.024 |
| | | 20 | 21 | 10.0 ± 0.4 | 201 ± 16 | 129 ± 10 | ND | 3.2 ± 0.6 | 25.9 ± 3.4 | 87 ± 3 | 1.171 ± 0.008 |
| | | 80 | 28 | 6.4 ± 0.2 | 103 ± 8 | 100 ± 7 | ND | ND | ND | 65 ± 1 | 1.138 ± 0.012 |
| | | 280 | 16 | 6.4 ± 0.4 | 191 ± 23 | 92 ± 7 | 21 ± 3 | 3.1 ± 2.3 | 28.2 ± 0.4 | 68 ± 1 | 1.172 ± 0.007 |
| | | >280 | 12 | 6.8 ± 0.7 | 166 ± 21 | 190 ± 14 | ND | 4.6 ± 0.6 | 46.4 ± 2.8 | 79 ± 5 | 1.156 ± 0.013 |

| | Time min | SPM mg l ⁻¹ | Fe mg g ⁻¹ | Mn µg g ⁻¹ | Zn µg g ⁻¹ | Ca mg g ⁻¹ | Co µg g ⁻¹ | Cu µg g ⁻¹ | Cd µg g ⁻¹ | Pb µg g ⁻¹ | ^{206/207} Pb i.r. |
|----|-------------|---------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|----------------------------|
| 36 | 5 | 13 | 6.5 ± 0.3 | 119 ± 40 | 31 ± 9 | ND | ND | ND | | 52 ± 2 | 1.167 ± 0.020 |
| | 20 | 17 | 4.8 ± 0.4 | 126 ± 17 | 46 ± 12 | 1 ± 8 | ND | ND | | 43 ± 2 | 1.139 ± 0.030 |
| | 80 | 7 | 9.5 ± 0.7 | 228 ± 46 | 123 ± 27 | ND | 9.4 ± 1.5 | 34.5 ± 3.7 | | 94 ± 12 | 1.183 ± 0.021 |
| | 280 | 16 | 5.5 ± 0.5 | ND | 74 ± 10 | ND | 3.1 ± 3.1 | ND | | 79 ± 2 | 1.134 ± 0.009 |
| | >280 | 6 | 7.3 ± 0.6 | ND | 49 ± 5 | 37 ± 13 | ND | 48.2 ± 4.1 | | 163 ± 9 | 1.154 ± 0.015 |
| 62 | 5 | 237 | 19.7 ± 0.5 | 993 ± 43 | 145 ± 2 | 37 ± 1 | 11 ± 1 | 18.9 ± 2.8 | | 88 ± 2 | 1.182 ± 0.004 |
| | 20 | 299 | 18.1 ± 1.0 | 917 ± 21 | 167 ± 5 | 33 ± 1 | 10.0 ± 0.3 | 23.7 ± 1.0 | | 74 ± 3 | 1.163 ± 0.006 |
| | 80 | 317 | 21.9 ± 0.4 | 1128 ± 22 | 160 ± 4 | 42 ± 1 | 11.5 ± 1.5 | 32.4 ± 2.4 | | 110 ± 6 | 1.175 ± 0.003 |
| | 280 | 119 | 20.8 ± 0.2 | 1100 ± 22 | 201 ± 7 | 40 ± 3 | 12.8 ± 1.1 | 27.8 ± 0.6 | | 96 ± 4 | 1.179 ± 0.005 |
| | >280 | 58 | 20.7 ± 0.5 | 865 ± 27 | 206 ± 8 | 25 ± 2 | 10.8 ± 0.6 | 24.4 ± 4.9 | | 95 ± 1 | 1.171 ± 0.003 |
| 75 | 5 | 51 | 22.2 ± 0.2 | 1053 ± 28 | 241 ± 4 | 31 ± 2 | 13.0 ± 0.8 | 33.1 ± 1.6 | | 166 ± 6 | 1.157 ± 0.012 |
| | 20 | 59 | 21.9 ± 0.3 | 1056 ± 36 | 224 ± 9 | 30 ± 3 | 13.2 ± 0.7 | 43.1 ± 0.9 | | 93 ± 2 | 1.176 ± 0.010 |
| | 80 | 65 | 19.6 ± 0.5 | 1028 ± 19 | 222 ± 1 | 32 ± 1 | 11.1 ± 0.7 | 39.0 ± 1.2 | | 95 ± 2 | 1.175 ± 0.010 |
| | 280 | 47 | 19.9 ± 0.3 | 1021 ± 23 | 190 ± 7 | 37 ± 1 | 10.6 ± 0.6 | 35.0 ± 0.8 | | 90 ± 3 | 1.162 ± 0.006 |
| | >280 | 28 | 19.7 ± 0.1 | 860 ± 11 | 241 ± 4 | 28 ± 4 | 13.0 ± 1.1 | 31.1 ± 3.6 | | 143 ± 7 | 1.180 ± 0.008 |

N.D. - Not detected; NS - Not Sampled.; i.r. - isotopic ratio.

**Appendix C -
Published Work**

²⁰⁶/₂₀₇Pb ISOTOPIC RATIOS APPLIED TO PARTICULATE TRANSPORT PROCESSES - NORTH EASTERN IRISH SEA.

M.R. WILLIAMS¹, G.E. MILLWARD¹, S.J. HILL¹ and A.W. MORRIS²

KEYWORDS : Irish Sea; lead isotopic ratio; lead, suspended particulate matter; pollution; transport processes.

ABSTRACT

Samples of suspended particulate matter (SPM) were collected from the north eastern Irish Sea, under different tidal conditions. The SPM was extracted with 1M HCl and concentrations of Pb and stable isotopic ratios of Pb (²⁰⁶/₂₀₇Pb) determined using atomic absorption spectrometry and ICP-MS. Lead concentrations were found to be in the range 49 to 115 µg g⁻¹ for spring tides and 72 to 148 µg g⁻¹ for neap tides. The ²⁰⁶/₂₀₇Pb ratios, which were between 1.140 and 1.194, were used to establish possible sources of SPM during the tidal cycle. Samples of surface sediments from along the coastline showed evidence of anthropogenic Pb contamination in the vicinity of Liverpool Bay, with low ²⁰⁶/₂₀₇Pb ratios of about 1.144, which increased northwards away from the estuary. The results are discussed in terms of the tidally-induced transport of SPM in the coastal boundary zone of the Irish Sea.

INTRODUCTION

Lead is a ubiquitous anthropogenic pollutant which has penetrated many environmental reservoirs (KERSTEN *et al.*, 1992), including the remote polar regions (ROSMAN *et al.*, 1993) and shelf seas (IRION and MILLER, 1990; KAMMANN *et al.*, 1994). The north eastern Irish Sea has been subject to a considerable flux of pollutants (NORTON *et al.*, 1984; THE IRISH SEA STUDY GROUP, 1990) because of inputs from the Mersey Estuary and offshore dumping in Liverpool Bay (see Fig. 1). It has been estimated that approximately 18 x 10³ kg a⁻¹ of Pb are discharged to and/or dumped in the coastal waters near the Mersey Estuary (PARIS COMMISSION, 1990) and particulate Pb has become widely distributed in bottom sediments (LANGSTON, 1986; LAW *et al.*, 1989). Furthermore, high concentrations of Pb, which can be in the form of alkyl leads, have resulted in high mortalities of migratory wildfowl in the Estuary and Liverpool Bay (BULL *et al.*, 1983).

The ²⁰⁶/₂₀₇Pb isotopic ratio has been used a pollution source index for more than three decades (KERSTEN *et al.*, 1992). Differences in the ratio arise because the natural radioactive decay of ²³⁸U (λ=1.55 x 10⁻¹⁰ a⁻¹) and ²³⁵U (λ= 9.81 x 10⁻¹⁰ a⁻¹) produces ²⁰⁶Pb and ²⁰⁷Pb, respectively and the relative occurrence of these isotopes depends on the decay constants for ²³⁸U and ²³⁵U and the age of the ore. For example, the primary Pb used in petrol additives in the UK will have isotopic ratios indicative of the parent ores from Australia, with a ratio of 1.04, and Canada, with a ratio of 1.07. These values compare with a background value of about 1.24 (KERSTEN *et al.*, 1992). The routine determination of Pb isotopic ratios has been facilitated with the advent of inductively coupled plasma-mass spectrometry (ICP-MS). Thus, it is theoretically possible to use determinations of Pb isotope ratios to assess the degree of mixing of SPM from different sources, where one end member originates from a contaminated source and the other from an uncontaminated source.

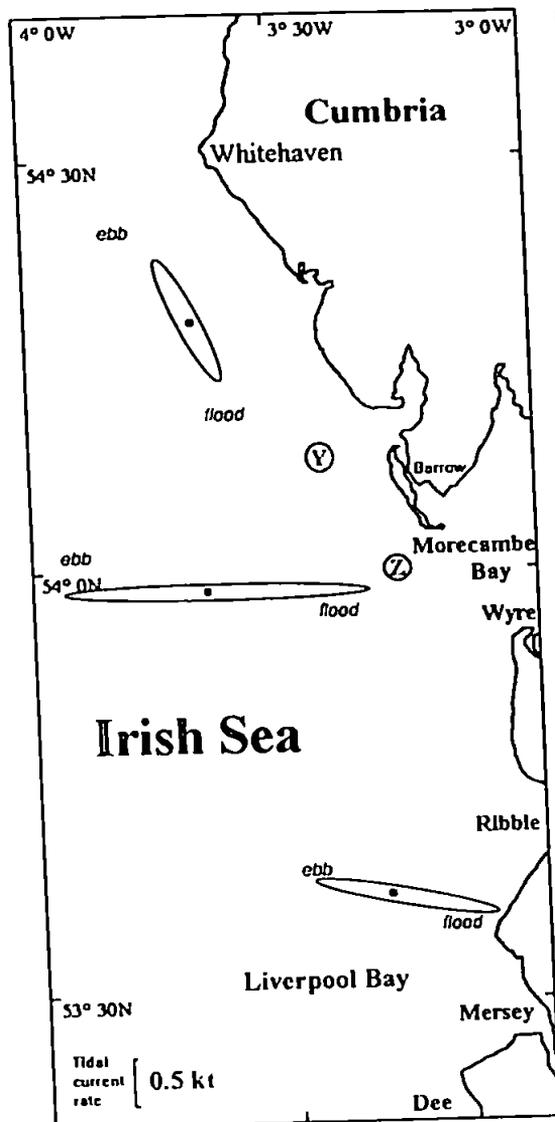


Fig. 1. Map of the north eastern Irish Sea showing the sampling sites Y ($54^{\circ} 57.5' N$ $03^{\circ} 19.5' W$) and Z ($53^{\circ} 75.2' N$ $03^{\circ} 19.5' W$) for cruise CH88A and the tidal current ellipses for the area. The tidal current ellipses based on tidal data from Admiralty chart 1826 (Irish Sea Eastern Part), are a graphical representation of the magnitude and direction of the tidal currents over a tidal cycle.

minated source. The objective of this study was to apply Pb isotopic ratios to the study of SPM transport in the Irish Sea with a view to assessing the dispersion of particle associated Pb from estuarine sources.

METHODS

Samples were collected aboard RRS 'Challenger' in the north eastern Irish Sea (Fig. 1) during cruise CH88A/92 (20 January-4 February 1992) and at a time when phytoplankton activity was at a minimum. SPM samples were collected using a 10 litre acid-cleaned General Oceanics Go-Flo bottles attached to a CTD rosette. Samples were taken over spring and neap tidal cycles at both sites and where possible SPM was retrieved from the top, middle and bottom of the water column. Ultra-clean ship-board procedures were followed throughout (MORLEY *et al.*, 1988) and all sample manipulations were performed in a clean containerised laboratory, fitted with a laminar flow hood. The water samples were pressure filtered through pre-weighed, acid-washed Nucleopore filters (of $0.4 \mu m$ poresize) and the SPM on the filter was washed with <20 ml of Milli-Q water to remove seawater salts. Surface sediment samples were taken using a Day Grab, at coastal locations along the cruise track. All samples were stored at $-18^{\circ}C$ for transport to the laboratory.

At site Z (see Fig. 1) experiments were performed to isolate different fractions of SPM according to their settling velocities. This was achieved using a modified Owen tube (referred to here as a settling velocity tube) which captured 5 litres of water while held horizontally (JAGO *et al.*, 1993). On retrieval the tube was inverted and five water samples retrieved at selected times from 5 minutes to 280 minutes and each fraction was filtered under the conditions described above.

Prior to analysis the SPM samples were returned to room temperature, dried in a laminar flow hood, and the filters re-weighed. The sediment samples were also thawed and wet sieved through an acid-washed plastic mesh of size $63 \mu m$ and allowed to air dry. The dried SPM and sediment samples were extracted with 10 ml of 1M HCl (AristaR) for 24 h at room temperature, following which they were filtered and solutions made up in standard flasks. Additionally, two sediment samples were sequentially digested, using 25% acetic acid, 1M HCl, 1M HNO_3 and conc. HF (with aqua regia as a wetting agent). A VG Plasmaquad PQ2-Turbo ICP-MS (Fisons Instruments Ltd., UK) was used to determine the ratios of the stable Pb isotopes and calibration was achieved using NIST-981 Pb isotopic standard. A relative standard deviation of 0.5% was obtained for the $^{206}Pb/^{207}Pb$ isotopic ratio during multiple determinations over a three day period. Pb in the digest solutions was determined using a Perkin Elmer 4100ZL graphite furnace atomic

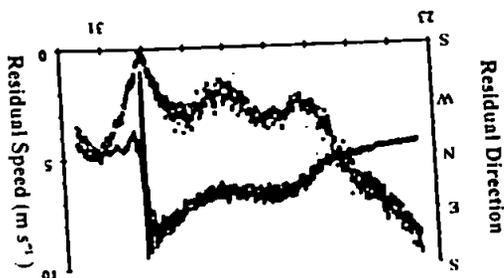


Fig. 2. Current meter data from site Z during CH88A/92 (23-31 January 1992). The data has been manipulated using a Doodson lowpass filter, to remove the diurnal tidal effects, to give residual current direction (—) and speed (---). The residual currents at site Z are predominantly between the north and east.

Table 1. Results from sequential acid extraction (1-4) of 2 samples of surface sediments from the north eastern Irish Sea. The %cum values represent all Pb extracted by that and any previous digest.

| Acid digests used | Sample GW9 | Sample Z 0-2 |
|-----------------------|----------------|----------------|
| | 206/207Pb %cum | 206/207Pb %cum |
| 1 - Acetic acid | 1.171 | 1.155 |
| 2 - Hydrochloric acid | 1.169 | 1.163 |
| 3 - Nitric acid | 1.211 | 1.204 |
| 4 - Hydrofluoric acid | 1.225 | 1.245 |
| | 100 | 100 |

RESULTS AND DISCUSSION

Sequential leaching experiments show that approximately 80% of the total Pb is removed by the HCl leach, which suggests that most of the particulate Pb is surface bound (Table 1). Concentrations of Pb in surface sediments in Liverpool Bay have a range of 130 - 164 µg g⁻¹, which compare with total Pb concentrations of 110 - 160 µg g⁻¹ in the same area by Law *et al.* (1989). The Pb concentrations in sediment samples from this area indicates that the extraction of two surface sediments from Liverpool Bay is confined to the Liverpool region. Sequential extraction of two surface sediment samples from this area indicates that the refractory Pb has an isotopic ratio of 1.225 - 1.245. Removal of approximately 80% of the Pb during hydrochloric acid leaching with the corresponding change in isotopic ratio suggests that a significant fraction of the Pb bound to the surface of the sediment is anthropogenic in origin.

The SPM concentration, particulate Pb and Pb isotopic ratios are given in Table 2 as a function of tidal state. Generally, site Z is more turbid than site Y and the turbidity depends critically on tidal flow was observed (Fig. 2), which would cause offshore sources on the flood and ebb tide during the ebb tide. A northward residual current anti-clockwise circulation with SPM derived from the tidal current ellipses (Fig. 1) suggests a static system perturbed less by tidal fluctuations. The tidal current ellipses (Fig. 1) suggest a static system perturbed less by tidal fluctuations. Conditions during the neap tide result in a more pogenic lead from the coastal region is being advected during the more dynamic spring ebb tide, while location. The implication of these data is that anthropogenic lead from Liverpool Bay and Morecambe Bay could have a significant effect on Pb at this location. Sequential extraction of two surface sediment samples from Liverpool Bay and Morecambe Bay indicates that the extraction of two surface sediment samples from this area indicates that the refractory Pb has an isotopic ratio of 1.225 - 1.245. Removal of approximately 80% of the Pb during hydrochloric acid leaching with the corresponding change in isotopic ratio suggests that a significant fraction of the Pb bound to the surface of the sediment is anthropogenic in origin.

Table 2. Examination of the variation between Pb in suspended particulate matter (SPM), 206/207Pb isotopic ratio and SPM over ebb and flood at spring and neap tide during cruise CH88A at sites Y and Z. Values indicate the mean and standard deviation for >3 samples. These values include samples taken from the top, middle and bottom of the water column.

| Tidal State | Spring Tide | | Neap Tide | | |
|-------------|-----------------------------------|-----------------|-----------------------------------|-----------------|---------------|
| | [Pb] in SPM (µg g ⁻¹) | 206/207Pb ratio | [Pb] in SPM (µg g ⁻¹) | 206/207Pb ratio | |
| Y | Flood | 78 ± 15 | 1.169 ± 0.013 | 104 ± 12 | 1.157 ± 0.008 |
| | Ebb | 98 ± 11 | 1.153 ± 0.013 | 101 ± 22 | 1.153 ± 0.007 |
| Z | Flood | 78 ± 26 | 1.156 ± 0.011 | 100 ± 18 | 1.155 ± 0.004 |
| | Ebb | 90 ± 30 | 1.145 ± 0.003 | 107 ± 23 | 1.150 ± 0.007 |

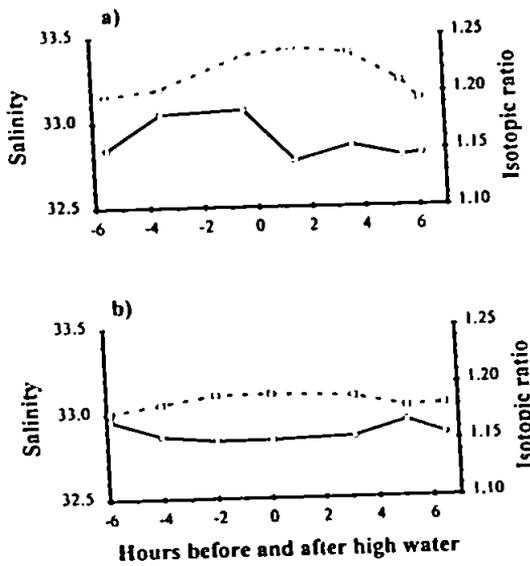


Fig. 3. Variation of the $^{206}/^{207}\text{Pb}$ isotopic ratio in suspended particulate matter (SPM; —○—) and salinity (---□---) over spring (a) and neap (b) tides for site Y.

the SPM to be advected from site Z to site Y. The dominant flow on the flood tide is from the east, transporting offshore dominated SPM; this is reflected by its higher isotopic ratio. The ebb then transports suspended matter from more anthropogenic sources. Thus the sites Y and Z are being influenced by two end members during the spring tidal cycle, one being offshore dominated the other coastal derived. Fig. 3a shows the rise in isotopic ratio with increasing salinity and the subsequent increase in anthropogenic character as fresher water is advected across site Y on the ebb tide. The constant value in isotopic ratio during the neap tide (Fig. 3b) is reflected in the small variation in salinity, indicating that the neap tide represents a system less responsive to tidal fluctuations. The concentration of particulate bound Pb at site Y over the tidal cycles is illustrated in Figs. 4a and b. Insufficient samples were available to examine site Z in such detail. Peaks in Pb concentrations in particulate matter were observed during ebb tides for both spring and neap tides. Pb concentrations in SPM during spring and neap tides at site Y, tends towards lower concentrations during the maximum flood period and higher concentrations during the maximum ebb period, the highest concentration occurred during the neap tide. The difference in Pb concentration during spring and neap cycles results from

the mass dilution effect caused by the increase in SPM in the water column during the more dynamic spring tide (Table 1). The resuspension event observed during the spring flood is not mirrored in the neap flood. Though the pattern in SPM concentrations are dissimilar, the Pb concentrations for the flood and neap period follow the same pattern. Such considerations highlight the dominant influence of the source over particle dilution effects at these sites.

Advection of the SPM is dependent on the settling velocity of the particles. It can be seen from Figs. 5a and b that the residual fraction has the lowest isotopic ratio indicating that anthropogenically derived Pb preferentially binds with the permanently suspended fraction. Both tides show the same pattern in isotopic ratio suggesting that the behaviour of Pb remains the same with the different SPM populations of the spring and neap tides. As the other time fractions derived from the settling velocity tube are an integration of mixed settling fractions detailed interpretation of those results are complex. The least anthropogenic fraction is that which settles within twenty minutes. This experiment, however, provides only a static system whilst the water column turbulence is likely to cause greater amounts to be permanently suspended. What is shown, is that advection favours the transport

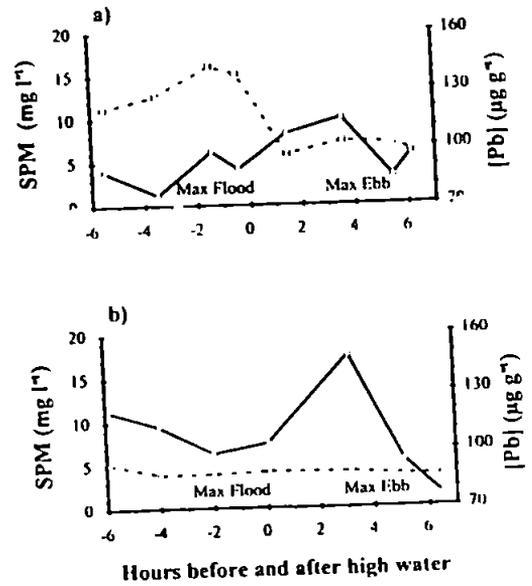


Fig. 4. Variation of suspended particulate matter (SPM; ---) and Pb concentrations in the suspended particulate matter (—) over spring (a) and neap (b) tides for site Y

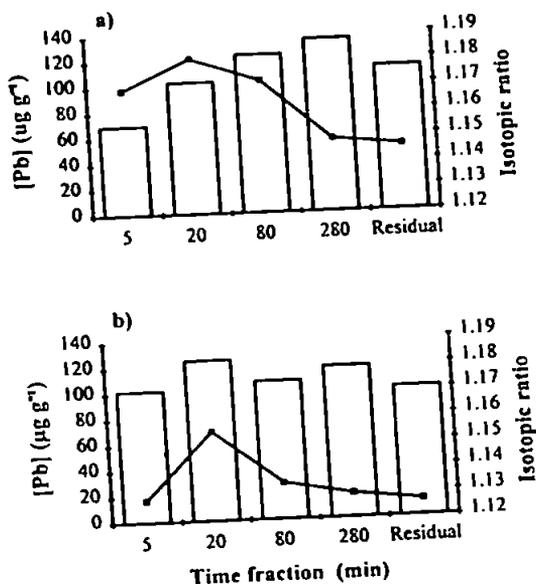


Fig. 5. A comparison between the time fractions taken from the settling velocity tube during maximum ebb current at site Z on spring (a) and neap (b) tides. The $^{206}/^{207}\text{Pb}$ isotopic ratio (—) indicates that the residual fraction contains the greatest percentage of anthropogenic Pb (bars).

of surface bound anthropogenic Pb to the finest particles.

The northward advection of anthropogenic Pb associated with SPM is also apparent in the isotopic ratios of the surface sediments along the Cumbrian coast (Fig. 6). The isotopic ratio trend is towards higher values, although this gradient is not clearly observed in the Pb concentrations in the surface sediments. Perturbation in the isotopic ratio near Whitehaven may be the result of discharges by the Albright and Wilson Marchon plant, which processes phosphate rock. Phosphate rock characteristically has a relatively high uranium content (McCARTNEY *et al.*, 1992) and hence would likely affect Pb isotopic ratios in this area.

CONCLUSION

The use of $^{206}/^{207}\text{Pb}$ isotopic ratios provides a valuable tool to help understand the mixing and transport of Pb within the environment. In this work the isotopic ratio has been used to distinguish between the influence of two particle populations during the spring tidal cycle. The spring flood tide moves marine particles into the nearshore area

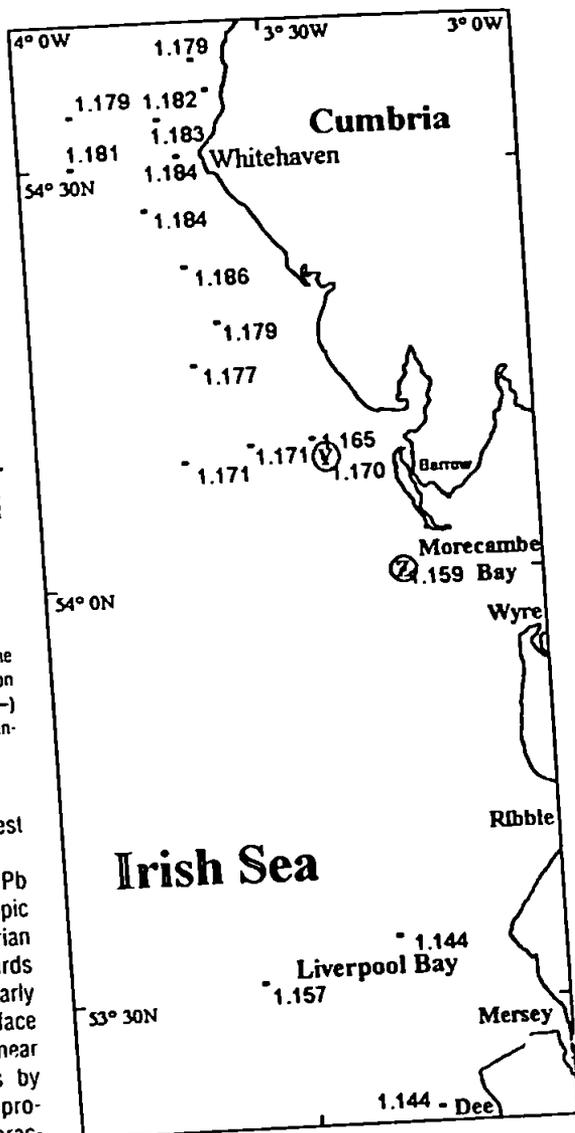


Fig. 6. Geographical variation of $^{206}/^{207}\text{Pb}$ isotopic ratios in the surface sediments along the Cumbrian coastline.

and the spring ebb advects anthropogenic material northwards along the coast. The tidal data implied such a process but the gradual gradient in isotopic ratio from Liverpool Bay (1.144) to Whitehaven (1.184) showed this process to be active and that the influence of Liverpool Bay area extends to Whitehaven a distance of approximately 65 miles. Examination of the Pb concentrations would not be sufficient to draw such conclusions. Indeed in Figs.

5a and b it can be seen that the settling fraction containing the highest concentration of Pb is not the fraction containing the greatest proportion of anthropogenic Pb.

ACKNOWLEDGEMENTS

The authors thank the scientists and crew aboard *R.R.S. Challenger* during cruise CH88A,

Mrs Trish Frickers and Dr Simon Sparks for their assistance in the use of ICP-MS, Dr. Sarah Jones for the loan of the settling velocity tubes and Proudman Oceanographic Laboratory for the raw current meter data. This work was funded by NERC award GT4/91/APPS/44 with contributions from Plymouth Marine Laboratory and British Maritime Technology Ltd. M.R. Williams wishes to mention the Plymouth Marine Fund who assisted in his travel to this conference.

REFERENCES

- BULL, K.R., W.J. EVERY, P. FREESTONE, J.R. HALL and D. OSBORN, 1983. Alkyl lead pollution and bird mortalities on the Mersey Estuary 1979-1981. *Environ. Poll. (Series A)*, 31: 239-259.
- IRION, G. and G. MÜLLER, 1990. Lateral distribution and sources of sediment-associated heavy metals in the North Sea. In: V. Ittekkot, S. Kempe, W. Michaelis and A. Spitz, Eds. *Facets of Modern Biogeochemistry*, Springer-Verlag, Berlin: 175-201.
- JAGO, C.F., A.J. BALE, M.O. GREEN, M.J. HOWARTH, S.E. JONES, I.N. McCAYE, G.E. MILLWARD, A.W. MORRIS, A.A. ROWDEN and J.J. WILLIAMS, 1993. Resuspension processes and seston dynamics, Southern North Sea. *Phil. Trans. Royal Soc. (London) A*, 343, 475-491.
- KAMMANN, U., M. HAARICH, K. HEYER, H. HÜHNERFUSS, L. KARBE, M. KERSTEN, D. SCHMIDT and H. STEINHART, 1994. Large-scale distribution of contaminants in spring 1986 and Winter 1986/87. In: J. Sündermann, Ed., *Circulation and contaminant fluxes in the North Sea*, Springer-Verlag, Berlin, 90-137.
- KERSTEN, M., U. FÖRSTNER, P. KRAUSE, M. KRIEWS, W. DANNECKER, C.-D. GARBE-SCHÖNBERG, M. HÖCK, U. TERZENBACH and H. GRABL, 1992. Pollution source reconnaissance using lead isotope ratios ($^{206}/^{207}\text{Pb}$). In: J.-P. Vernet, Ed., *Heavy metals in the environment*, Vol. 2, Elsevier, Amsterdam: 311-325.
- LANGSTON, W.J., 1986. Metals in sediments and benthic organisms in the Mersey Estuary. *Est. Coast. Shelf Sci.*, 23, 239-261.
- LAW, R.J., T.W. FILEMAN, C.F. FILEMAN and D.S. LIMPENNY, 1989. The distribution of hydrocarbons and metals in the North-Eastern Irish Sea prior to development of the Morecambe Bay gas field. *Oil and Chem. Poll.*, 5: 285-320.
- MCCARTNEY, M., P.J. KERSHAW, D.J. ALLINGTON, A.K. YOUNG and D. TURNER, 1992. Industrial sources of naturally occurring radionuclides in the Eastern Irish Sea. *Radiation Protection Dosimetry*, 45: 711-714.
- MORLEY, N.H., C.W. FAY and P.J. STATHAM, 1988. Design and use of a clean shipboard handling system for seawater samples. *Adv. Underwater Technol.*, 16: 283-289.
- NORTON, M.G., S.M. ROWLATT and R.S. NUNNY, 1984. Sewage sludge dumping and contamination of Liverpool Bay sediments. *Est. Coast. Shelf Sci.*, 19: 69-67.
- PARIS COMMISSION, 1990. *The Paris Commission 1990 Survey*. Report of the National Rivers Authority for England and Wales. 4pp. plus tables.
- ROSMAN, K.J.R., W. CHISHOLM, C.F. BOUTRON, J.P. CANDELONE and U. GÖRLACH, 1993. Isotopic evidence for the source of lead in Greenland snows from the late 1960's. *Nature*, 362, 333-335.
- THE IRISH SEA STUDY GROUP, 1990. *The Irish Sea - An environmental review Part 2. - Waste inputs and pollution*. Liverpool University Press, Liverpool, 165pp.

Addresses of the authors:

- 1 Department of Environmental Science, University of Plymouth, Drake Circus, Plymouth, PL4 8AA, U.K.
- 2 Natural Environmental Research Council, Plymouth Marine Laboratory, Prospect Place, West Hoe, Plymouth, PL1 3DH, U.K.

PARTICLE SOURCES AND TRACE ELEMENT REACTIVITY IN THE HUMBER PLUME

G.E. MILLWARD^{1,3}, M.R. WILLIAMS¹ and R.J. CLIFTON²

KEYWORDS: Particles; trace elements; reactivity; North Sea.

ABSTRACT

Samples of suspended particulate matter (SPM) collected from the Humber Estuary had higher concentrations of particulate metals than SPM from Holderness coastal waters (U.K.). Characterised SPM from both sources was used in laboratory experiments involving the uptake of radiotracer ¹⁰⁹Cd, ¹³⁷Cs, ⁵⁴Mn and ⁶⁵Zn. Kinetic experiments, over five days, showed that the rate and extent of uptake was highly dependent on particle type, with ¹⁰⁹Cd, ⁵⁴Mn and ⁶⁵Zn being more reactive with Humber Estuary particles than those from Holderness and ¹³⁷Cs having the opposite trend. Adsorption experiments were also carried out on suspensions in which SPM from the Humber Estuary and Holderness coastal water were mixed in various proportions. These experiments revealed that K_d for ⁶⁵Zn increased linearly with the proportion of Humber SPM, K_d for ¹³⁷Cs decreased linearly with increase in Humber SPM and K_d for ⁵⁴Mn and ¹⁰⁹Cd displayed non-linear behaviour. The results of the study were used to develop an algorithm for predicting the partition coefficients in the Humber Plume based on the extent of particle mixing from the two source regions. The use of ²⁰⁶Pb/²⁰⁷Pb ratios in determining the extent of particle mixing is discussed, along with the application of the algorithm to the modelling of particulate trace metal behaviour in the Humber-Wash coastal zone.

INTRODUCTION

Particle-water interactions of dissolved trace metals have been parameterized using the K_d (ml g⁻¹) concept; defined as the ratio of the particulate phase concentration (μg g⁻¹) to that in the dissolved phase (μg ml⁻¹). Although the exact significance of K_d are yet to be fully understood, it is clear that the magnitude of this interaction function undergoes significant change in the low salinity zone of estuaries (TURNER *et al.*, 1993) and is strongly dependent on particle type (TURNER *et al.*, 1992; 1994). Differential uptake of trace metals by particles has been shown in the North Sea where values of K_d for ¹⁰⁹Cd and ⁶⁵Zn were about an order of magnitude higher in a diatom bloom than for lithogenic particles in the Humber Plume (TURNER *et al.*, 1992). However, the Humber-

Wash region also has two important sources of chemically-different SPM of lithogenic origin. Erosion of the Holderness cliffs provides 1.4 x 10⁹ kg a⁻¹ of unpolluted SPM of which 70% is <63 μm (McCAVE, 1987), whereas the Humber Estuary supplies about 10⁸ kg a⁻¹ (WILMOT and COLLINS, 1981) of anthropogenically modified SPM. Steep particulate metal-salinity gradients arise at the mouth of the Humber due to the mixing of these two contrasting particle populations (TURNER, 1990; TURNER *et al.*, 1991). Furthermore, the contrasting geochemistries of the particles constituting the end-members of a mixing series in the Humber Plume could give rise to differential behaviour in scavenging processes involving dissolved trace elements.

The object of this study was to characterise the end-members of the particle mixing series and

to examine their reactivity with a suite of trace elements. The results from this study are vitally important in the development of algorithms for use in the prediction of the fate of anthropogenic trace metals in the North Sea (HUTNAMER *et al.*, 1993).

METHODS

Particulate matter was collected manually from the Holderness Cliffs and their nearshore waters. The Holderness Estuary and Plume waters (see Fig. 1) were sampled from RRS 'Challenger', during cruise CH99 6-21 December 1992, using established techniques (Burton *et al.*, 1993). Experiments were carried out, on the ship, shortly after sample collection. Suspensions were doped with 30 µl of a cocktail of γ -emitting radiotracers (^{109}Cd , ^{137}Cs , ^{54}Mn , ^{65}Zn) and the runs consisted of (a) kinetic studies involving uptake of the radiotracers onto individual samples of Humber Estuary SPM (salinity 29.3) and Holderness SPM (salinity 34.3) and (b) studies in which the end-members were mixed in various proportions and then incubated with the radiotracers. The suspensions were held in a seawater flow cell and maintained at an ambient seawater temperature of 7°C, the pH was 7.6 and the oxygen tension was maintained at ambient for the duration of the runs. At various times, up to 5 days, the suspensions were filtered and the filters and filtrates stored. The γ -counting of the radiotracers in both fractions (HUTNAMER *et al.*, 1992, 1993) was carried out in the laboratory using a high resolution germanium crystal, coaxial detector (Ortec Ltd) connected to a Canberra Series 80 multichannel analyser. The counts from sections and filters were geometrically corrected and together with the dry weights of SPM on the filters, were used to estimate K_d . Filter blanks and wall adsorption of the radiotracers was found to be negligible. Available trace metal concentrations of SPM samples were determined by extraction with

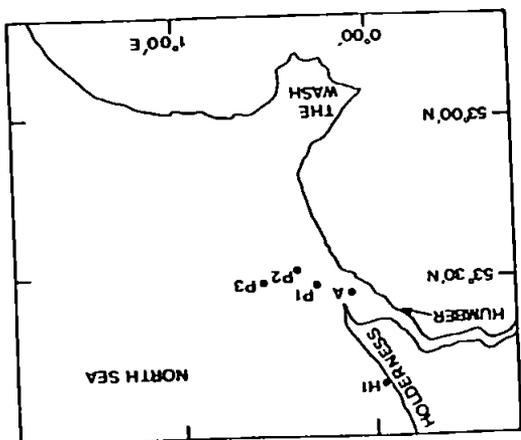


Fig. 1. The Humber-Wash coastal zone and sampling locations. H1 - Holderness nearshore environment; A - Humber Estuary anchor station; P1, P2, P3 - Humber Plume.

1M HCl, for 12 hours, and quantified using flame atomic absorption spectrometry (AAS), for Fe, Mn and Zn and graphite furnace AAS for Cd and Pb. Lead isotope ratios were determined on the digests using inductively coupled plasma-mass spectrometry (ICP-MS).

RESULTS AND DISCUSSION

A comparison of the trace metal content of particles from the Holderness coastal waters, the Humber Estuary and the Humber Plume is given in Table 1. The Holderness particles have relatively low trace metal concentrations compared to the Humber Estuary material, whereas SPM in the Plume has intermediate concentrations. Thus, the compositional differences between these SPMs suggests that the particles in each region have a different capacity for scavenging and retaining dissolved trace metals.

Table 1. Particulate trace metal concentrations ($\mu\text{g g}^{-1}$) and lead isotope ratios of SPM at different salinities (Sal.) from locations in the Humber-Wash coastal zone. The sample codes refer to the positions shown in Fig. 1. ND - Not Detected.

| Element | Holderness Cliffs | Holderness seawater (H1) | Humber Estuary (A) | Humber Plume (P1) | Humber Plume (P2) | Humber Plume (P3) |
|-----------------------------------|-------------------|--------------------------|--------------------|-------------------|-------------------|-------------------|
| Sal | 0.20 | 34.3 | 29.3 | 30.8 | 30.9 | 33.6 |
| Cd | 0.20 | 0.01 | 0.56 | ND | ND | 1.3 |
| Fe | 15150 | 4550 | 20200 | 19000 | 13800 | 12200 |
| Mn | 410 | 350 | 1050 | 960 | 690 | 710 |
| Pb | 4 | 20 | 94 | 172 | 66 | 91 |
| Zn | 43 | 27 | 195 | 142 | 118 | 59 |
| $^{206}\text{Pb}/^{207}\text{Pb}$ | 1.234 \pm 0.015 | 1.192 \pm 0.003 | 1.179 \pm 0.004 | 1.186 \pm 0.012 | 1.179 \pm 0.012 | 1.165 \pm 0.003 |

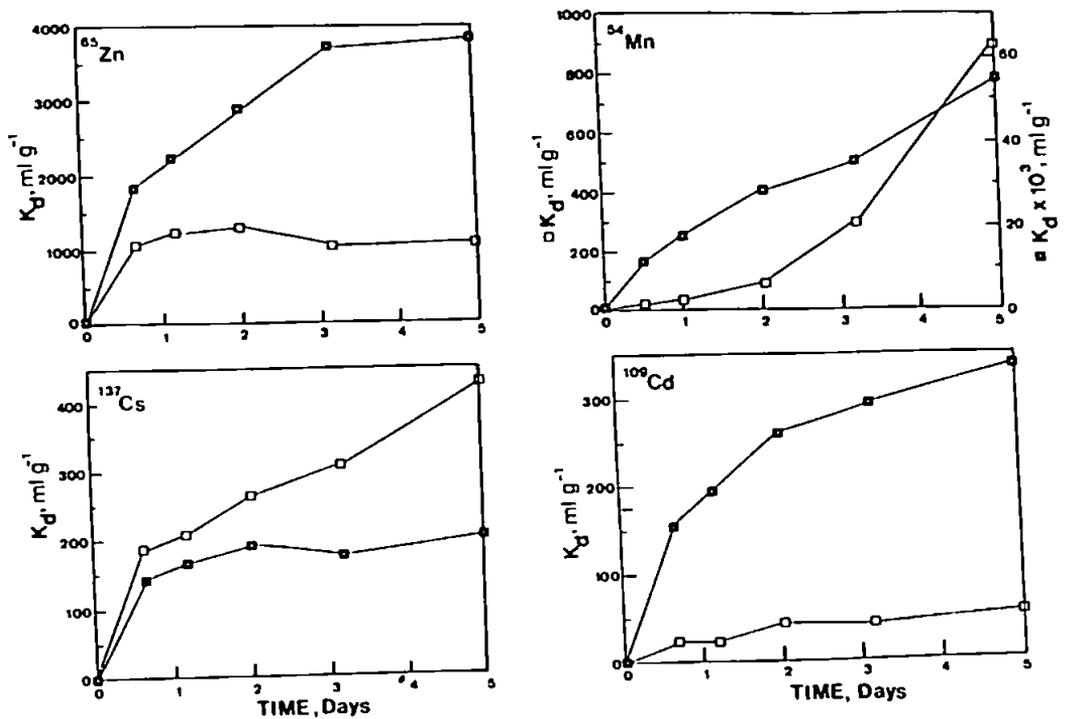


Fig. 2. Partition coefficients (K_d , ml g^{-1}) as a function of time (days) for the uptake of radioisotopes onto Humber Estuary (■) and Holderness (□) SPM for ^{65}Zn , ^{137}Cs , ^{54}Mn and ^{109}Cd .

The rate of uptake of the radio-isotopes by the Humber and Holderness SPM (*i.e.* the potential end-members of the Plume mixing series) is shown in Fig. 2. Dissolved ^{65}Zn is removed relatively slowly but it reaches a quasi-equilibrium state after a few days. The extent of Zn uptake is much greater for the Humber SPM than for the Holderness, possibly due to the higher Fe content of the former (MILLWARD and MOORE, 1982). For ^{137}Cs the extent of uptake is greater for Holderness particles than for Humber SPM. Cesium is thought to be able to penetrate the microstructure of clay particles by displacing potassium located at high energy sites in the matrix (TURNER *et al.*, 1993; 1994). These sites are probably less accessible in the Humber material because the particle surfaces are coated with organic matter and fresh Fe precipitates, which inhibit migration into the matrix.

The uptake of ^{54}Mn is vastly different for the end-members; Humber SPM has K_d values which increase from 0 to about 55,000 ml g^{-1} over 5 days. This dramatic change in K_d is probably related to the autocatalytic effect exerted by pre-existing

Mn (in this case 1050 $\mu\text{g g}^{-1}$, see Table 1) on particle surfaces (MORRIS and BALE, 1979). In contrast, the Mn concentration of Holderness SPM is substantially lower (350 $\mu\text{g g}^{-1}$, see Table 1) and the autocatalytic effect is less effective, resulting in K_d values which are $<100 \text{ ml g}^{-1}$. For ^{109}Cd the reaction profile is similar to that of ^{65}Zn but since the marine speciation of Cd favours the solution phase (TURNER *et al.*, 1981) the K_d is $<350 \text{ ml g}^{-1}$. However, there is a significant difference in the extent of uptake between the Humber and Holderness particles, due to the fact that there is less particulate Fe in the latter material (DAVIES-COLLEY *et al.*, 1984; MILLWARD and MOORE, 1982).

The results of experiments where particles from the Humber Estuary and Holderness are mixed in various proportions are shown in Fig. 3. For ^{65}Zn there is a linear relationship between K_d and the percentage of Humber particles and the particles have an additive effect (HONEYMAN and SANTISCHI, 1988) on the scavenging of Zn from the dissolved phase. The additivity is positive for ^{65}Zn because

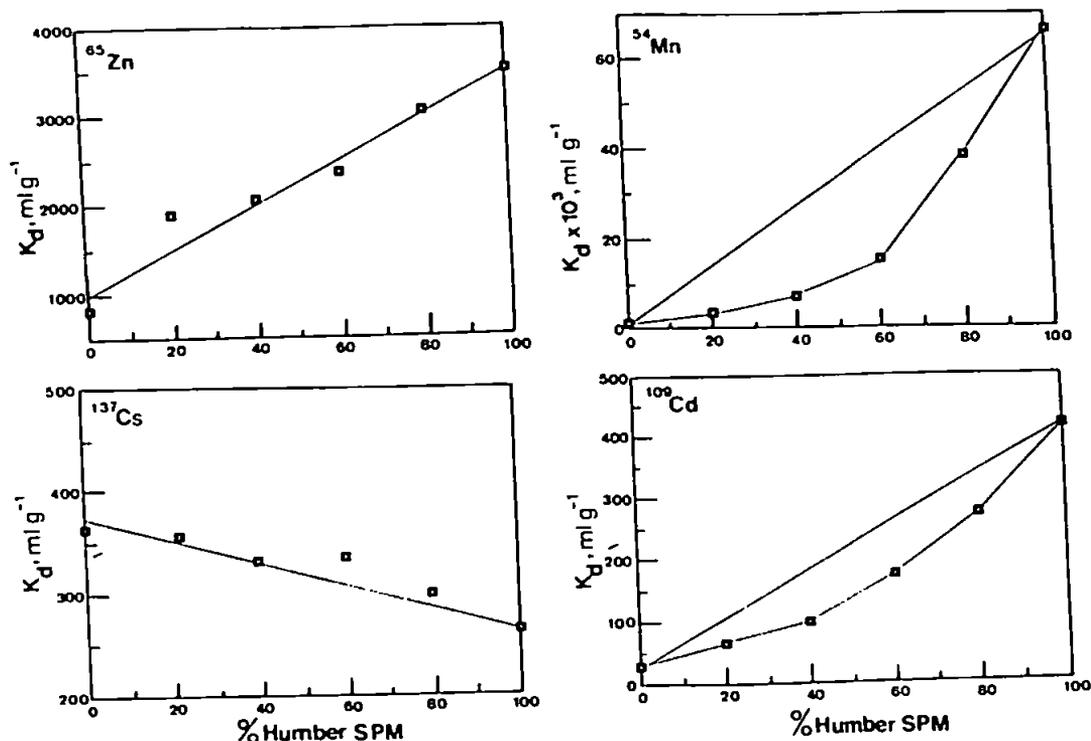


Fig. 3. Partition coefficients ($K_d, \text{ml g}^{-1}$) for ^{65}Zn , ^{137}Cs , ^{54}Mn and ^{109}Cd obtained from suspensions containing various proportions (%) of Humber and Holderness suspended particles (SPM)

the K_d increases with the increase in the proportion of Humber particles. In the case of ^{137}Cs a linear relationship is also obtained but the additivity is negative because ^{137}Cs is more reactive to Holderness particles than to Humber ones. However, for ^{54}Mn the relationship is non-linear presumably because the relatively low particulate Mn content of Holderness SPM suppresses the effective promotion of the autocatalytic removal of dissolved Mn onto particle surfaces. This effect is defined as being non-additive. Non-additive behaviour was also observed for ^{109}Cd which could be caused by depleted particulate Mn and/or Fe (DAVIES-COLLEY *et al.*, 1984; MILLWARD and MOORE, 1982).

These results can be described by an algorithm which enables the estimation of K_d in the Humber Plume from a knowledge of the end-member K_d values, the particle mixing ratio and a factor taking into account the additivity behaviour of the element:

$$K_d^p = K_d^{Ho} + (K_d^{Hu} - K_d^{Ho}) P^a$$

where K_d^p is the partition coefficient for the Humber Plume; K_d^{Ho} is the partition coefficient for the

Holderness Cliff material; K_d^{Hu} is the partition coefficient for the Humber Estuary material; P is the percentage of Humber particles and a is the additivity factor. The values of a are: Cs and Zn 1; Mn 2.5; Cd 1.9.

The remaining problem in the application of this algorithm to the modelling of particulate metal transport in the Humber Plume is the estimation of P. This parameter could be determined if a particle tracing technique could be developed in which the relative proportions of Humber and Holderness material could be estimated. Theoretically, determinations of Pb isotope ratios could yield information on particle mixing, especially in this coastal environment where large quantities of natural particles eroded from the Holderness coastline mix with contaminated particles from the Humber Estuary. Table 1 shows the preliminary results of determinations of lead isotope ratios in the Humber Plume. The Holderness SPM has a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.192 which is indicative of relatively uncontaminated material (WILLIAMS, personal communication). The Humber Plume samples have values less than this

indicating the presence of contaminant Pb, presumably from anthropogenic sources in the Estuary. The ratio increases seaward due to the fact that coarse grained SPM is settling out and the finer SPM carries a greater burden of the anthropogenic Pb fraction. However, the $^{206}/^{207}\text{Pb}$ isotope ratio of the sample taken at the anchor station is not particularly low, suggesting that this sample may not be representative of contaminated estuarine particles. Thus, further investigation isotopic ratios are needed for Humber Estuary material, so that the contaminated estuarine end-member may be identified, thereby allowing quantification of P.

its ability to accommodate Cs in its matrix. Particle mixing experiments showed that both Zn and Cs showed additivity when Humber and Holderness particles were mixed in various proportions. The results from these experiments were interpreted in terms of an algorithm which could be used to predict the K_d in the Humber Plume, providing a knowledge of the extent of the mixing could be obtained. Further sampling campaigns are required to investigate the applicability of the $^{206}/^{207}\text{Pb}$ ratio method to particle mixing in this geochemically unique coastal environment.

CONCLUSIONS

The particulate trace metal concentrations of the Humber SPM are greater than SPM obtained from the Holderness coastal zone. The $^{206}/^{207}\text{Pb}$ ratios for the latter material suggest that it is uncontaminated, whereas the estuarine SPM has a large contaminant load. The consequence of higher concentrations of ferromanganese oxides on the surfaces of the estuarine SPM means that the uptake of Cd, Mn and Zn is much greater than for Holderness SPM. In contrast, the Holderness material is a more significant scavenger of Cs due to

ACKNOWLEDGEMENTS

The authors thank the officers and crew of RRS 'Challenger' for their assistance in carrying out the sampling and ship-board experimental work. We are indebted to Dr A.W. Morris and Mr R.J.M. Howland from the Plymouth Marine Laboratory for their support and help during the fieldwork. The study was supported by NERC (RJC), an NERC Research Studentship (MRW), British Maritime Technology (Ports & Coastal) Ltd (MRW) and the Department of Trade and Industry 'Wealth from the Oceans' Programme (GEM), Contract Number MTD/MD/9/118

REFERENCES

- BURTON, J.D., M. ALTHAUS, G.L. MILLWARD, A.W. MORRIS, P.J. STATHAM, A.D. TAPPIN and A. TURNER, 1993. Processes influencing the fate of trace metals in the North Sea. *Phil Trans. R. Soc. Lond. A*, 343: 557-568.
- DAVIES, COLLEY, R.J., P.O. MCLESON and K.J. WILLIAMS, 1984. Copper and cadmium uptake by estuarine sedimentary phases. *Environ. Sci. Technol.* 18: 491-499.
- HONEYMAN, B.D. and P.H. SANTSCHI, 1988. Metals in aquatic systems. *Environ. Sci. Technol.* 22: 862-871.
- KUHNWANCE, J.M., J.T. ALLEN, A.M. DAVIES, D.J. HYDES, I.D. JAMES, J.E. JONES, G.T. MILLWARD, D. PRANDLE, R. PROCTOR, D.A. PURDIE, P.J. STATHAM, P.B. TITL, S. THOMSON and R.G. WOOD, 1993. Towards water quality models. *Phil Trans. R. Soc. Lond. A*, 343: 569-584.
- MCCAVE, I.R., 1987. Fine sediment sources and sinks around the east Anglian coast. *J. Geol. Soc. Lond.*, 144: 149-152.
- MILLWARD, G.E. and R.M. MOORE, 1982. The adsorption of Cu, Mn and Zn by iron oxyhydroxides in model estuarine systems. *Wat. Res.* 16: 981-985.
- MORRIS, A.W. and A.J. BALL, 1979. Effect of rapid precipitation of dissolved Mn in over water on estuarine Mn distributions. *Nature*, 279: 318-319.
- TURNER, A., 1990. Chemical Dynamics in North Sea Estuaries and Plumes. PhD Thesis, Polytechnic South West, Plymouth, 237 pp.
- TURNER, A., G.E. MILLWARD, A.J. BALL and A.W. MORRIS, 1992. The solid-solution partitioning of trace metals in the southern North Sea. In situ radiochemical experiments. *Cont. Shelf Sci.* 12: 1311-1329.
- TURNER, A., G.E. MILLWARD, A.J. BALL and A.W. MORRIS, 1993. The application of the K_d concept to the study of trace metal removal and desorption during estuarine mixing. *Est. Coast. Shelf Sci.* 36: 1-13.
- TURNER, A., G.E. MILLWARD and A.W. MORRIS, 1994. Particulate trace metal exchange from North Sea estuaries. *Est. Coast. Shelf Sci.* 32: 325-346.
- TURNER, A., G.E. MILLWARD and A.O. TYLER, 1994. The distribution and chemical composition of particles in a macrotidal estuary. *Est. Coast. Shelf Sci.* 38: 1-17.

- TURNER, A., M. WHITFIELD and A.G. DICKSON, 1981. The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure. *Geochim. Cosmochim. Acta*, 45, 855-881.
- WILMOT, R.D. and M.B. COLLINS, 1981. Contemporary fluvial sediment supply to the Wash. Special Publ. of the Int. Assoc. Sedimentol., 5: 99-110.

Addresses of the authors:

- ¹ Department of Environmental Science, University of Plymouth, Drake Circus, Plymouth PL4 8AA, UK.
- ² Plymouth Marine Laboratory, Prospect Place, The Hoe, Plymouth PL4 8AA, UK.