Spatial and Temporal variations in trace metal concentrations in sediments, pore water of the Forth estuary, and their potential impact on water quality

Thesis submitted for the
degree of Doctor of Philosophy

Department of Environmental Science

University of Stirling

by

MOHAMMED MUSAD MOHAMMED ALHARBI

November 1993

LIST OF CONTENTS

CHAPTER 1 INTRODUCTION

CHAPTER 2 LITERATURE REVIEW

CHAPTER 3 SAMPLING **page**

CHAPTER 4 ANALYTICAL METHODS

CHAPTER 5 **RESULTS** **page**

CHAPTER 6 **DISCUSSION** **page**

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

DECLARATION

I hereby declare that this thesis is my own composition, that the results were obtained by myself and that it has not been presented in any previous application for a higher degree.

Mohammed M. M. Alharbi

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor Dr Ian Grieve (Department of Environmental Science) for his supervision of my thesis, encouragement and thoughtful comments.

Many thanks goes to the Department of Environmental Science staff, especially Dr Carol Salt, Dr David Gilvear, Mr Chris Anderson, Mr David Harrison, Mrs Lynn Napier, Mr John McArthur, Mr Bill Jamieson and Miss Tracy Grieve for their help during this study. I would like also to thank the Forth River Purification Board (FRPB) for making the fieldwork possible by using the survey vessel "Forth Ranger", especially Mrs Judy Dobson and the Forth Ranger team. Many thanks goes to Billy Struthers (Aquaculture department) for his help in using Graphite furnace. Special thanks goes to Dr Donald McLusky (Biology department) for his advise and loan of equipment.

Finally I would like to thank King AbdulAziz University (Faculty of Meteorology and Environmental Studies) for sponsoring me during my study. Special thanks goes to my wife here and to my family back home for their encouragement and support throughout my stay in Scotland.

DEDICATION

To my mother, wife and children

To my brothers and sisters.

ABSTRACT

The concentrations of trace metals: cadmium, copper, nickel, lead and mercury, in addition to aluminium, iron and manganese were determined in the sediments and pore water (except aluminium) of the Forth estuary. Organic matter (as loss on ignition), total organic carbon (TOC), total organic nitrogen (TON), particle size and redox potential were also determined in the sediments. In addition, chloride, sulphate, conductivity, alkalinity, pH, dissolved organic carbon, phosphate and nitrate were determined in the sediments pore water. Trace metals in the pore water were determined using a modified preconcentration technique and measurements were carried out by graphite furnace. Mercury was measured using the p.s.a mercury specific fluorescence detector. Organic matter (TOC & TON) in the sediments were measured using CHNS/O analyzer.

Samples were collected at seasonal intervals for a period of 18 months on board the survey vessel "Forth Ranger". Six stations were selected to represent upper, middle and lower estuary. Sediment cores collected at each station were subjected to centrifugation under nitrogen gas atmosphere to separate the pore water after being sectioned at 2.5 cm intervals for a depth of 10 centimetres.

Concentrations of trace metals in the Forth estuary varied from station to station and from one season to another. Mean concentrations for sediments were as follows (mg\kg): lead, 56.9; cadmium, 0.22; copper, 38.9; nickel, 33.7 and mercury, 1.86. For pore water, the mean concentrations (µg\l) were as follows: lead, 3.14; cadmium, 1.86; copper, 31.9; nickel, 24.7 and mercury, 0.075.

Measurements of sulphates, nitrates, phosphate, conductivity and dissolved organic carbon were used to examine the processes controlling their distributions in the pore water. The results indicated that the distributions of nutrients (phosphate and nitrate) in the upper 10 cm seemed to be controlled by macro-infaunal irrigation activities and their values varied according to the overlying water conditions.

The distributions of trace metals in the sediments were found to be controlled by particle size and organic matter both spatially and temporally. Vertical distribution of trace metals in the pore water were found to be controlled by redox potential variations especially for iron and manganese. Concentrations of trace metals (Pb, Hg, Ni, Cd and Cu) in the pore water were found to be higher than that in the overlying water. Enrichment factors were limited to 10-50 fold increase. Lead and mercury were 10 fold higher while 50 fold higher were found for nickel, copper and cadmium.

Benthic flux calculations showed a significant flux of trace metals both in the summer and winter. However, flux of copper, nickel and lead tended to increase in the summer. Spatially, the lower estuary showed a higher flux of trace metals than the upper and middle reaches of the estuary.

CHAPTER 1 INTRODUCTION

CHAPTER 1 INTRODUCTION

1.1 The Forth Estuary System

The Forth estuary and the Firth of Forth represent a significant part of the east coast of Scotland, reaching from Stirling in the centre of the country, eastward past the capital city of Edinburgh to join the North Sea. It represents a deep coastal embayment in the midland Valley of Scotland (Fig. 1.1) and (Fig. 1.2) (McLusky, 1987).

The physical feature of the land surrounding the estuary and Firth of Forth are a blend of gently-sloping, heavily cultivated lowland and hilly ground. The landscape on the southern shore is dominated by the higher ground of the Moorfoot-Lammermuir hills, the Pentland hills and the Riccarton -Bathgate hills. On the northern shore, the Ochil hills dominate the scenery (Browne, 1987).

The landscape has been considerably modified by glaciation. The overdeepened Forth Valley formed an arm of the sea in late glacial times as the ice melted and retreated. Large quantities of gravels, sands, silts and mud were carried down by melt water into the enlarging estuary forming fluviatile and marine sediments up to 100 m in thickness. These were finally overlain by the marine Carse Clays (up to 12 m) laid down in post-glacial times following the final melting of ice and consequent rise in sea level. These clays form the low-lying areas of the Carse of Stirling and the marginal zones bordering the north and south banks of the inner estuary. The Carse Clay resembles

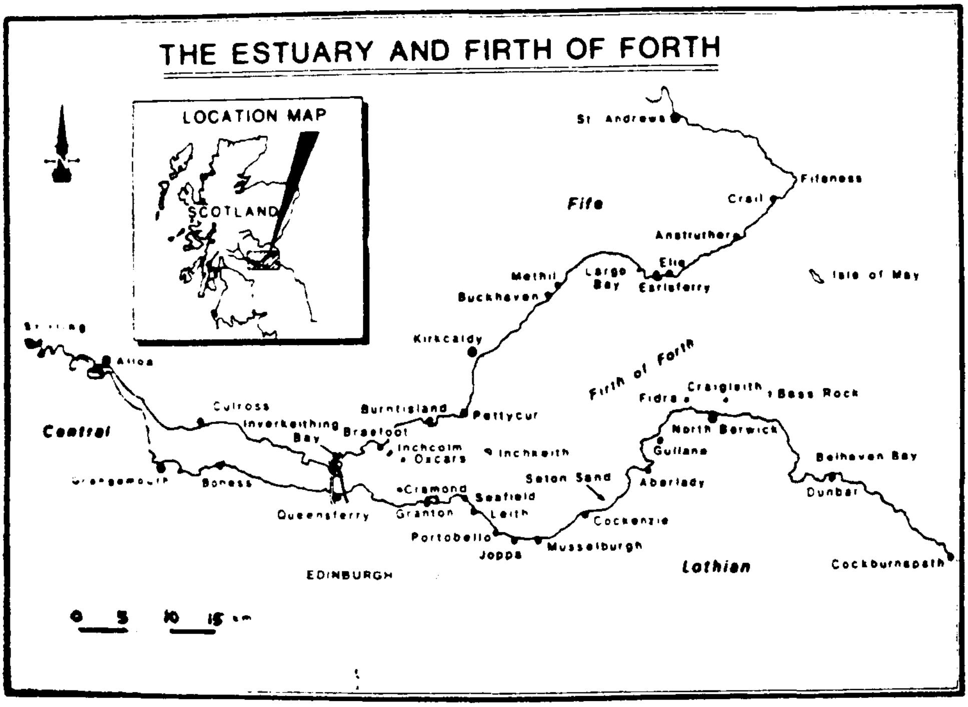


Fig. 1.1

Location map showing the estuary and the Firth of Forth

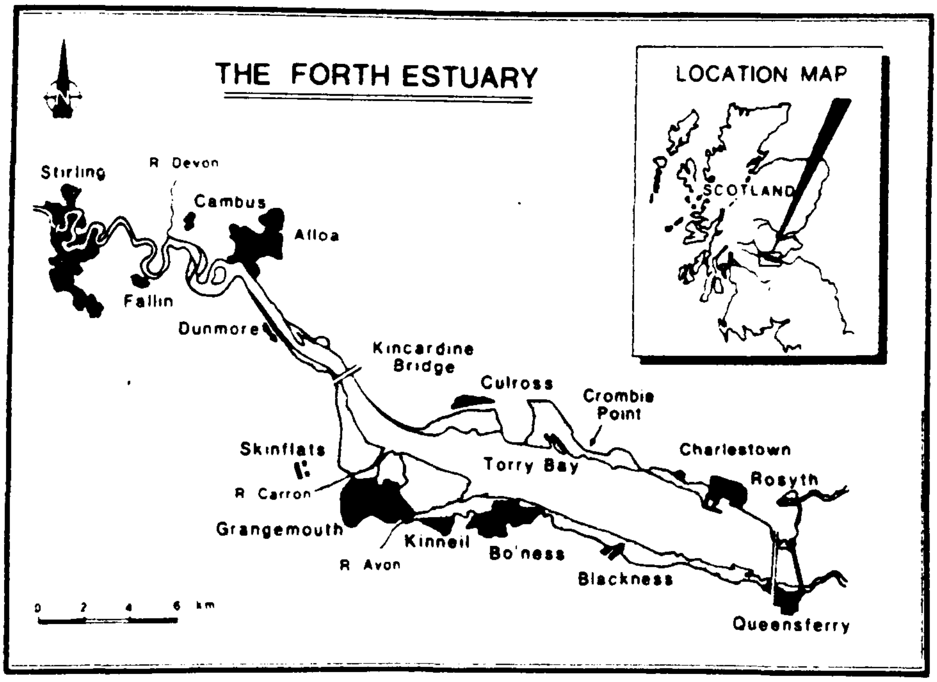


Fig. 1.2

A map showing the Forth estuary

the present-day tidal flats which form extensive deposits on both shorelines especially between Kincardine and Blackness. Extensive areas of saltmarsh and tidal flats have been reclaimed to increase sedimentation and progressively raise the level (Kershaw, 1980).

The Forth divides naturally into the estuarine areas upstream of Queensferry bridges, and the essentially marine coastal areas of the Firth of Forth downstream of the bridges, where fresh water inputs have only a local influence. The tidal waters receive the drainage from a landward catchment area of 4655 Km^2, which includes 1.3 million people, about a quarter of the population of Scotland and a significant proportion of its industry (Leatherland, 1987).

Eleven significant rivers along with several other smaller water courses drain into the tidal waters of the Forth (Table 1.1). Sewage and industrial discharges contribute on average a further 7.5 m^3 s^{-1} of fresh water (Leatherland, 1987) (Table 1.2). Considerable shipping traffic moves in and out of the ports, and Scotland's major petrochemical complex is situated at Grangemouth (British Petroleum companies, Zeneca (formerly ICI) and others). Europe's largest conventionally powered electricity generation plant is located at Longannet. The Forth also receives the domestic effluent from Edinburgh and other major towns, plus distillery and brewery wastes from several sources (Table 1.3).

Table 1.1

River discharges to the Forth estuary and Firth of Forth $m^3 s^{-1}$

Forth estuary		Firth of Forth	
River	Average flow	River	Average flow
River Teith	23.40	River Leven	6.14
River Forth	14.77	River Almond	5.63
River Allan	6.34	Water of Leith	1.39
River Devon	4.36	River Esk	3.99
River Carron	4.70	River Tyne	2.80
River Avon	3.62	Others	4.54
Others	5.50		
Total	62.70	Total	24.50

Source (Leatherland 1987)

Table 1.2

BOD, Ammonia, Organic Nitrogen and TON loadings
for fresh water inputs (1989-1991)

km	Source	BOD mg\l	Ammonia g/s	Org.N g/s	TON g/s
-5.80 *	R Forth &Teith	1.50	0.06	0.65	0.45
-3.20 *	Allan Water	1.55	0.08	1.52	1.37
11.00	Bannockburn	0.99	0.03		1.05
16.00	River Devon	2.09	0.14	4.18	1.03
23.30	R Black Devon	1.68	0.10	1.27	1.42
31.60	River Carron	2.48	0.54	1.74	1.68
33.30	River Avon	2.44	0.83	1.13	2.86

* River inputs at the tidal limit ot the estuary

Source FRPB (TW11/92)

Table 1.3

Mean flows, BOD, Ammonia, Organic Nitrogen and TON loadings
for major industrial and domestic discharges (1989-1991)

km	Source	Flow m3/s	BOD mg\l	Ammonia g/s	Org.N g/s	TON g/s
4.80	Stirling STW	0.38	7.40	6.22	1.26	0.14
16.00	Cambus Cond.	0.03	12.20	0.21	0.08	0.06
16.00	Cambus Cool	0.03	1.50	0.01	0.03	0.03
21.00	Alloa STW	0.16	20.90	1.60	1.69	0.05
21.00	DCL (Y) ltd.	0.06	147.40	2.30	3.76	0.07
26.00	Canal Burn	0.07	25.40	0.05	0.43	0.07
31.30	Zeneca (formerly ICI)	0.16	73.70	2.85	10.89	0.27
31.30	G'mouth W. STW	0.16	8.00	0.77	0.73	0.15
31.30	Falkirk STW	0.43	2.40	2.93	0.83	1.12
33.00	BP Refinery	0.26	44.80	14.85	0.74	0.09
33.10	BP Chemical	0.13	18.50	9.95	2.09	0.92
33.30	BP Kinneil	0.05	15.20	1.32	0.28	0.01
33.70	G'mouth E. STW	0.46	64.10	5.32	5.46	0.12
35.90	Kinneil S.O	0.04	6.70	1.02	0.35	0.01
37.60	Bluther Burn	0.35	0.60	0.04	0.37	0.99
37.60	Bluther S.O	0.03	3.10	0.79	0.38	0.01
38.10	Carriden S.O	0.02	30.90	0.20	0.90	0.01
50.70	Dunfermline STW	0.30	25.20	5.03	1.62	0.11

Source FRPB (TW11/92)

N.B The mean annual looadings (in g/s) have been determined by summing the products of flow (l/s) and concentration (mg/l) for each determinand

Analysis of monthly mean air temperature (Harrison, 1987) for different stations in the Forth estuary and the Firth of Forth, illustrates a significant change in air temperature between the Firth and the upper estuary. The monthly mean amplitude of the diurnal temperature wave increases from east to west. The steepest rate of change occurs during May and June where sea temperature are moderately low and daytime land-surface temperature are relatively high. In the winter months, the probability of sub-zero temperature increases westwards away from the ameliorating effect of the sea, so diurnal amplitudes are again greatest over the upper estuary, (Harrison, 1987).

The water temperature at Grangemouth varies on a seasonal cycle from around 4°C in the months of January and February to around 17°C in July. At any point in the estuary the temperature is determined by the mixing of river water with seawater. In the summer the seawater is cooler than the river water, whereas in the winter the seawater is slightly warmer than the river water (Webb and Metcalfe, 1987).

The majority of rainfall is cyclonic in origin, although convectional storms may occur. These latter may be associated with hail and thunder and can be particularly severe during late summer (Harrison 1981). On average, the wettest months occur from September through to January. These five months may contribute more than 55% of the average annual total. April to June are, on average the driest months. Tides in the Forth estuary are semidiurnal and of average range for the British Isles. At Rosyth the mean spring range is 5.0 m and the mean neap range is 2.5 m.

Sediments of the lower Forth estuary are relatively mobile. Not only is there massive resuspension and redistribution during storm events, but around 800,000 tons of sediment are dredged each year from the approaches to Grangemouth Docks, and pumped back into the water column not many kilometres downstream of the dredging site. The net natural movement of sediments into or out of the lower Forth estuary is a significant unknown. However, it appears more probable that the total inventory of sediment in the estuary is increasing. There is a net input from rivers (up to 50,000 t/annum, and there is also a net input from the sea. (FRPB, TW 04/89).

1.2 State of pollution in the Forth Estuary

1.2.1 Sources of pollution

The Forth estuary receives wastes from a variety of sources including: coal mining, paper making, distilling, electricity generation, domestic dwellings, oil refinery and petrochemicals. In addition to sewage discharges, the Forth estuary receives the flow of eleven rivers, each with a long term average flow in excess of 1 m^3 s^{-1} , (Table 1.1). The bulk of this fresh water enters upstream of the Queensferry Bridges, thus reinforcing the lower salinity of that area. Sewage and industrial discharges contribute on average a further 7.5 m^3 s^{-1} of fresh water (Leatherland, 1987).

1.2.2 Dissolved Oxygen and Nutrients

The upper Forth estuary has a low natural self-purification capacity due to its length, volume, and flushing characteristics. Although the present situation (Griffith, 1987) is very much better than that of the late 1950's (Collet 1961) or 1971 (Collet, 1972) there is still a residual problem. However, low oxygen concentrations are now largely confined to periods when warm dry summer weather coincides with spring tides, whereas previously, oxygen levels were low enough to be lethal to fish (Collet, 1961).

The Forth has been shown to be a particularly turbid estuary with a marked turbidity maximum in its upper reaches (Webb & Metcalfe, 1987). As a consequence of this, it is possible that nitrate production may occur in the sediments to a significant extent, rather than being dominated by water column production as in some other estuaries (Billen, 1975). In the winter months the nitrate distribution has been shown to be essentially conservative in its behaviour. The distribution of nitrate in the estuary during the warmer months, in contrast, demonstrates in situ production of nitrate as a result of oxidation of ammonia (Griffith, 1987).

Inorganic phosphate distributions demonstrate that there is considerable removal of phosphate occurring in the upper reaches of the upper estuary at salinities below 10 ‰. This is in contrast to some other less turbid estuaries such as the Clyde (Mackay & Leatherland, 1976), where phosphate removal does not appear to occur as a regular phenomenon. In the Forth it has been shown to occur when phytoplankton uptake was unimportant, temperatures were low and nitrate was behaving conservatively. Adsorption on to the suspended solids seems likely to be the removal mechanism. Several workers have investigated the likely mechanism of phosphate removal both in other estuaries and in the laboratory (Burns & Salomons, 1969; Chen et al., 1973; Morris et al., 1981). It can be concluded that, in the case of the Forth, the conditions of relatively low pH, high phosphate levels, low salinities and high suspended solids concentrations all favour removal. Further seaward in the middle and lower reaches of the estuary there are also lateral variations in the distribution of water quality parameters. The available data show that a marked lateral discontinuity does exist at certain phases of the tide (FRPB, 1981).

The result of a survey carried out between Kincardine and Queensferry showed that the major inputs of ammonia are located on the south shore and sublittorally around Grangemouth, the gradients that are produced by these inputs are shown to persist many kilometres down estuary. In the summer months, nutrient concentrations can be much depleted by the activity of phytoplankton (Griffiths, 1987).

1.2.3 Trace metals in the water and sediments

The most recent estimates of trace metal inputs to the Forth (Table 1.4) from direct discharges and rivers (FRPB personal comm.) indicate that industrial inputs are dominant for copper, while the rivers are the largest source of cadmium, mercury, nickel, lead and zinc.

The atmospheric inputs of copper and mercury estimated from Davies (1976, 1977) are small, but those of lead and zinc may be significant. The deposition rates of copper, lead and zinc are similar to, or lower than those estimated for the North Sea and Clyde Sea areas (Cambray et al., 1975). Although the upper estuary is worst affected by organic pollution, levels of trace metal contaminants are not significantly elevated; their main sources in the Forth are further downstream. The major industrial discharges in the vicinity of Grangemouth contain many potentially polluting substances, (Table 1.5). The discharge of mercury to the Forth has very substantially reduced over the years and despite the contamination of sediments from past discharges, the contamination of biota with this element is continuing to fall significantly. However, elevated concentrations of mercury are still found in water, sediments and biota. Davies et al.(1986) concluded that around 4 kg of mercury was lost from the estuary each day through the transport of mercury contaminated particulate material. This was similar to the rate of industrial input, and represents perhaps 5-10% of the mercury in suspension in the middle and lower estuary, or 0.01% of that in the deposited sediments.

The comprehensive sediment survey of the Firth carried out by Nicholson & Moore (1978) did not extend west of Queensferry, surface sub-tidal sediments between Queensferry and Kincardine Bridge have been studied collaboratively by DAFS and FRPB. Their survey emphasized the importance of areas around Grangemouth and Bo'ness in the accumulation of fine-grained sediments and associated metallic contaminants especially chromium and cadmium (Davies, 1987).

These areas and the adjacent inter-tidal mudflats at Kinneil and Skinflats, are now included in FRPB monitoring programmes and also those carried out by industrial concerns at Grangemouth, including Zeneca (formerly ICI) and BP. Unpublished DAFS data indicate that the concentrations of a range of metals in surface sediments on Kinneil mudflats are highest in the south-western part, and decrease towards the main channel of the estuary, with a slight increase in the outer edge of the flat (Davies 1987).

Table 1.4

Estimated average inputs of metals to the tidal waters of the Forth Estuary 1992

Source		Cd	Cu	Hg	Ni	Pb	Zn
Rivers	kg/yr	449	12475	43	10110	9798	55661
Industrial	kg/yr	11	15220	8	1039	360	15807
Sewage	kg/yr	100	10210	17	5520	5054	34244
Total	t / yr	0.56	38	0 .068	17	15	106

Source (FRPB)

Table 1.5

Dissolved Trace metal levels in the Forth Estuary Annual mean concentration ug\l

Station	Year	Cd	Cu	Hg	Ni	Pb	Zn
Grangemouth/	1983	0.035	1.68	-	1.08	<0.0	3.85
Longannet	1984	0.042	2.59	-	1.11	<0.0	5.61
	1985	0.036	1.95	0.006	1.06	0.1	4.13
	1986	0.037	2.09	0.006	0.83	0.1	3.11
National	1983	O.04	1.05	-	0.75	<0.0	1.67
Network	1984	0.057	1.5	-	0.81	<0.0	2.63
Station off	1985	0.037	1.11	0.003	0.61	<0.0	2.03
Blackness	1986	0.033	1.13	0.002	0.63	<0.0	1.85

1.3 Aims and objectives of the present investigation

The main objectives of the present investigation can be summarised as follows:

1- To describe the association of trace metals with the various metal phases i.e. estuarine water, pore water, and sediments.

2- To study the spatial and temporal changes in trace metal concentrations in these phases.

3- To predict the potential for release of trace metals when sediments are disturbed e.g. dredging, wave and current mixing.

4- To assess the potential impact of sediment resuspension upon water quality.

CHAPTER 2 LITERATURE REVIEW

CHAPTER 2 LITERATURE REVIEW

2.1 Definition and classification of estuaries

Pritchard (1967) defined the estuary as "a semi-enclosed coastal body of water which has a free connection with the open sea and within which the sea water is measurably diluted with fresh water derived from the land drainage".

Estuaries may be classified as positive, neutral or negative depending on their salinity and the extent of evaporation (McLusky, 1981). Depending on the tidal amplitude and volume of fresh water flow four main types of positive estuaries can be recognised (Dyer, 1973, 1979):

1. Highly stratified example: Mississippi (USA), Esk (UK).
2. Fjords example: Norwegian fjord, west of Scotland lochs.
3. Partially mixed example: James River (USA), Mersey, Thames, Forth (UK), Elbe (FRG).
4. Homogeneous example: Delaware, Raritan (USA), Solway Firth (UK), Mandovi-Zuari (India).

The highly stratified or salt wedge estuary, the fresh water flows seawards on the surface of the inflowing salt water. At the interface between the fresh and salt water, entrainment (mixing) occurs and salt water is mixed into the outflowing fresh water. The fjord type is basically similar to the highly stratified except that the inflow of tidal water is more restricted. Again continuous downstream flow of fresh water at the surface occurs, but the renewal of the tidal water may only occur seasonally and non-renewal of water may lead to anoxic conditions in the deepest part of the fjord.

When the tidal inflow is greater than or similar to fresh water inflow a partially mixed estuary develops. In such an estuary there is a continuous mixing between the sea and the fresh water. Surface water will be less saline than the bottom waters at any given point in the estuary, but unlike the highly stratified estuary undiluted fresh water will only be found near the head of the estuary. Mixing of water from the predominantly inflowing bottom to the mainly outflowing surface will occur throughout the estuary. The pattern of mixing may be less clear at the margins of the estuary, and due to the Coriolis force the sea water will dominate on the left-hand side (looking downstream) in the northern hemisphere, and the outgoing fresh water will dominate the right-hand side. In the southern hemisphere, the dominance pattern is reversed.

When the estuary is very wide the coriolis force will cause a horizontal separation of the flow, with outgoing flow on the right hand-side in the northern hemisphere, and ingoing flow in the left hand side. Thus the circulation in such a homogeneous estuary will be across the estuary from left to right, rather than vertically as in the other types (McLusky 1989).

2.2 Sediments

2.2.1 Composition, transport and sedimentation

Sediments have been classified in a variety of ways according to different criteria such as source, particle size, and composition. Sediments can be divided in two main groups;

(A) Fine sediments with particles smaller than 50 μm, and subdivided in silts and clays; and

(B) Coarse sediments with particle sizes exceeding 50 μm and subdivided into sands and gravels.

These two groups differ in mineralogical, morphological, physico-chemical and mechanical properties. Fine sediments mainly consists of clay minerals, organic matter and fine grained quartz, carbonate and feldspar particles. The mineralogy of coarse sediments is in general less diverse, it consists mainly of quartz with admixture of feldspar. The fine particles are charged, the charge depending on ionic strength and the surface coatings. The surface charge is responsible for the cohesion characteristics of fine-grained sediments (Salomons and Forstner 1984).

The history of an estuarine system is largely determined by its sediment supply. The prime source of sediment is land. Globally, about 12 km^3 or 18 x 10^9 tons of chiefly fine grained sediment are carried from the land to the sea every year, mainly by rivers (Kuenen, 1950; Holeman, 1968). A small quantity is transported through the atmosphere. Another source is coastal erosion.

There are three possible main regions of deposition:

the estuaries, the continental shelf, and the deep sea. The deep sea and continental shelf lodge only a small part of the present sedimentary input, at best some 10 % (see Emery, 1968; Curray, 1969; Swift, 1976; McCave, 1972 and Windom, 1976). This seems to leave estuaries & deltas as the main areas of sedimentation. Of the total sediment input almost one half (8 x 10^9 tons) is supplied by about 30 large rivers and within this group an even smaller number of rivers, which have their sources in the high lands of Tibet and in the Himalayas, provides the biggest share (5.5 x 10 tons). It follows from the above mentioned facts that conditions for sediment deposition in estuaries are much more favourable than on the open shelf. An obvious reason is that estuaries offer an effective shelter against strong waves and currents, so that the fine grained material can settle, whereas shelves are more exposed (Postma, 1980).

2.2.2 Sediments and Trace metals

Sediments in rivers, estuaries, lakes, and the oceans are vital materials as they are the main whereabouts of the heavy elements in the hydrosphere. Sediments can show the current quality of the system as well as the historical development of certain hydrological and chemical parameters.

In addition to their importance as an indicator medium, sediments are, depending on environmental conditions, a sink or a source for trace metals in the surface waters. Metals are not necessarily fixed permanently by the sediment, but may be recycled via biological and chemical means and finally find its way back to the water column.

There are five major sources of heavy metals in aquatic systems (Wittmann and Forstner, 1975):

(i) Geological weathering. This is the source of 'background levels.'

(ii) Industrial processes. Appreciable quantities of metals go to waste during metal refinement processes (e.g. galvanizing and pickling).

(iii) The use of metals and metal compounds. Copper compounds are used as plant protection agents, mercury in chlorine-alkali productions, and tetramethyl lead as an anti-knock agent in gasoline.

(iv) Burning of fossil fuels, production of cement and bricks. Fossil fuel mobilization is particularly high for arsenic, zinc, cadmium, copper, and nickel.

(v) Leaching of metals from garbage and solid wastes dumps.

Heavy metals find their way to sediments of any aquatic system as a result of the low solubility of most of their chemical forms and their tendency to enter into complexation and sorption reactions with solid phases. Hydrous oxides of Fe and Mn are among the most important sorbing agents for other metals.

Calculation from Goldberg (1972) on a global basis, indicate that approx. 140 million tons of wastes are annually dumped by ships into the sea. Furthermore, approx. 15 million tons of carbon and fly ash from fossil fuel combustion and 30 million tons of industrial particulates will reach the sea via atmospheric emissions. It is assumed that wastes from input of rivers are discharged to the same extent or even more. Estuaries tend to act as sinks for heavy elements coming from rivers and the atmosphere.

The determination of metal concentrations in sediments may play an important role in detecting sources of pollution in the aquatic ecosystem such as discharges from industries. In addition to this, pollution sources can even be detected long after they have been discharged. It is also possible to determine the development of pollution intensity from dated sediment cores provided that they contain fine grained deposition, in which the sorbed, precipitated, organically bonded metal concentrations are accumulated (Forstner, 1979).

An important process for trace elements in estuaries is the mixing of the fluvial and marine waters and sediments. Stable particulate suspensions in fresh water become destabilized in saline water, owing to double layer compression, leading to flocculation. For this to occur the particles have to collide, which depends on the flow rate of the water, and concentration of the particulate material (Duinker, J.C. 1980; 1986).

There has been controversy over what happens to the levels of trace elements in fluvial sediments and water on entering a saline environment. It appears, that for many estuaries the concentrations of trace metals in river sediments decrease when mixed with marine water. For example, the decrease in concentrations of As, Pb, Hg, and

Cd in the Rhine, with increase in salinity (Aston, 1978). A similar situation occurs for Cd, Pb, and Hg in the sediments and waters that enter the Elbe estuary, (Muller and Forstner, 1975).

2.2.3 Physical and chemical factors affecting sediment-trace metals chemistry

The physical and chemical measurements usually referred at as geochemical factors, are a requisite in understanding the sediment-trace element chemistry. Although the definitions of physical and chemical factors imply that they are independent of each other, they, however are interrelated.

Physical factors include grain size, surface area, specific gravity and surface charge. The most significant factor controlling sediment ability for concentrating and retaining trace metals is grain size (Gibbs, 1977; Jones and Bowser, 1978; Filipek and Owen, 1979; Jenne, et al., 1980; Thorne and Nickless, 1981; Horowitz and Elrick, 1987).

There is a strong positive correlation between decreasing grain size and increasing trace element concentrations. This correlation results from a combination of both physical (e.g. surface area) and chemical factors (e.g., Fe oxides, Mn oxides, organic matter). Clay sediments (< 2 to 4 µm) have surface areas measured in square meters per gram while sand particles with surface areas commonly measured in tens of square centimetres per gram (Grim, 1968;Jones and Bowser, 1978). Because of this large surface areas of the fine-grained particles, they are the main sites for the collection and transport of inorganic constituents (Krauskopf, 1956; Jenne, 1968; Gibbs, 1973; Jones and Bowser, 1978; Jenne, et al., 1980). However, Jenne (1976) indicates that the clay sized particles may be viewed simply as mechanical substrates upon which trace element can concentrate (without chemical interaction).

A search of the sediment-chemical literature dealing with the chemical factors controlling sediments trace metal associations (Horowitz, 1991) indicates that two approaches have been used. The first approach aims at determining how trace metals are retained on/in sediments the so called mechanistic approach. The second is the phase approach.

According to Gibbs (1977) there are five major mechanisms: (i) adsorption on fine-grained material, (ii) precipitation of trace element compounds, (iii) coprecipitation with hydrous iron and manganese oxides and carbonates, (iv) association either by adsorption or organo-metallic bonding with organic matter, and finally (v) incorporation in crystalline minerals.

These factors are however interrelated and not all are significant at any one site. The most common factors are hydrous manganese oxides, and hydrous iron oxides, organic matter and clay minerals. Forstner (1982a) has listed these geochemical substrates (factors) in descending order as follows: Manganese Oxides> Organic Matter> Iron Oxides> Clay minerals.

The major mechanism for the accumulation of trace elements on a surface is adsorption. This process requires the condensation of atoms, ions, or molecules on the surface of another substance. Materials having large surface areas are good adsorbers. Deposited materials like organic matter, and hydrous iron and manganese oxides, rather than the original surface, may act as a trace element collector by sorbing cations from solutions and releasing equivalent amounts of other cations back into solutions. This process is called ion exchange. Most trace elements behave as cations (have a positive charge) and the surfaces of most materials have a negative charge. The actual mechanism by which cation exchange occurs is a matter of much research and debate, but it appears to be due to the sorptive properties of negatively charged anions such as SiOH. $Al(OH)_2$ and AlOH (clay minerals), FeOH (iron hydroxides), and COOH and OH (organic matter) (Forstner and Wittmann, 1981). Apparently, as surface area increases, so does the amount of these collectors, thus increasing the trace element concentrating capacity of the surface.

The significant characteristics of iron and manganese oxides are that they are fine grained, are amorphous, have large surface area and high cation exchange capacity, and finally both have high negative surface charge. These substances have long been known as excellent scavengers of trace metals from solution. In sediments, iron and manganese oxides also commonly occur as coatings on various minerals and finely dispersed particles (Forstner and wittmann, 1981; Salomons and Forstner, 1984; Horowitz and Elrick, 1987).

The capacity of organic matter to concentrate trace metals in sediments is well recognized (Gibbs, 1973; Jenne, 1976; Nriagu and Coker, 1980; Forstner 1982 a,b ; Horowitz and Elrick, 1987; Hirner, et al., 1990).

Organic matter can concentrate between 1 per cent and 10 per cent dry weight of Co, Cu, Fe, Pb, Mn, Ni, and Zn (Hirner, et al., 1990). This capacity to concentrate trace metals appears to be related to several factors, including: large surface area, high cation exchange capacity, high negative surface charge, and physical trapping. The concentration of organic matter as indicated by such measurements as total organic carbon and total organic nitrogen, tends to show a strong positive correlation with decreasing grain size and increasing surface area (Forstner and Wittmann, 1981; Salomons and Forstner, 1984; Horowitz and Elrick, 1987).

Marine and estuarine environments are known to contain varying quantities of organic compounds of which humic substances, amino and fatty acids and carbohydrates constitute an important part. The close association between many trace elements and the amount of organic carbon in many sediments, especially those from reducing environments (Price and Calvert, 1973a) is often interpreted as being due to the existence of metal organic substances. Baker (1973), found that humic compounds are able to solubilize different metals to different extents. Thus in addition to their ability to complex metals in solution, humic compounds may also play a role in bringing metals into solution.

The second approach seeks to determine where trace elements are retained on/in sediments, the so called phase approach. This approach has been attempted because individual elements (e.g., Fe, Mn, Cd, Zn, Ni, Co, Cd) may be, and usually are associated with several phases. The term phase incorporates categories like interstitial water, clay minerals, sulphides, carbonates, organic matter, iron oxides, etc. (Horowitz, 1991).

2.3 Interstitial water

2.3.1 Significance of interstitial water studies

Interstitial water refers to water trapped in sediment pores during the accumulation of sediment particles. The study of pore water helps in understanding estuarine chemistry and geochemistry.

Recent studies have led to an increased awareness of the important role played by interstitial waters in the sediment water exchange process in any aquatic ecosystem. In particular, the fate of heavy metals deposited in the sediment can be more accurately predicted by analyzing the metal content of the interstitial water as a function of depth for comparison with concentrations in the overlying water.

Chemical reactions (diagenesis) affect both the solid and fluid phases of marine sediments after deposition. Many diagenesis reactions are thought to begin soon after sediment deposits. Chemical changes are easier to detect in the fluid phase of a water saturated sediment.

Seasonal variations in interstitial water composition has been reported for some components in estuarine, salt marsh and tidal flat systems (Lyons & Fitzgerald, 1978; Montgomery et al., 1979; Chapman & Brinkhurst, 1981; Hines et al., 1982).

Spatial variations for a wider range of components has been reported (Martens & Goldhaber, 1978) but only for one sampling occasion. Reports of both spatial and seasonal variations are few, the work of Matissof et al.,(1975) on Chesapeake Bay sediments being limited by sample handling difficulties and that of Aller and Benninger (1981) in Long Island Sound being largely concerned with fluxes across the sediment-water interface.

2.3.2 Components of interstitial water

The major cations Na^+, K^+, Ca^{2+}, and Mg^{2+}, account for more than 99 per cent of the positive charge in seawater salts, and Cl^- and SO_4^{2-} accounts for more than 99 per cent of the negative charge.

2.3.2.1 Major anions (chlorides and sulphates)

Chloride and sulphur are not major components of most recent sediments. These, Cl^- and SO_4^{2-} do not interact strongly with silicate minerals during diagenesis as the major cations do, but rather vary only with salinity, and, in the case of sulphates, with biological activity.

Sulphates can be chemically reduced under certain conditions. This reduction produces sulphide which greatly complicates the geochemistry of a number of other chemical constituents which are involved in the sulphate reduction process. Depletion of pore water SO_4^{2-} concentration and the accompanying increase in carbonate alkalinity was one of the first ever made observations on pore water chemistry (Murray and Irvine, 1895). The sulphate reduction process has been studied by many investigators (Goldhaber et al., 1977; Jorgenson, 1978a; Gunnarsson and Ronnow, 1982; Westrich, 1983; Bernard, 1984). The rate of sulphate reduction varies with geographic locality and with depth. It is generally agreed that the reactions leading to and accompanying sulphate reduction are largely biologically mediated, and the bacteria responsible for the sulphate reduction require anoxic conditions because they are unable to compete for food with oxygen utilizing organisms in the presence of oxygen. Anoxic conditions result when oxygen is used faster than it can be renewed from the atmosphere. This is rather seldom in marine waters but in the sediment column, oxygen renewal by advection is restricted and the likelihood of anoxic conditions is common.

The process of sulphate reduction can be simplified by the following reaction:

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$$

As demonstrated by the equation a primary result of sulphate reduction is the conversion of sulphate to sulphide and in many samples H_2S can be detected by its odour. However, in a particular situation the extent of sulphate reduction cannot be detected due to sulphide removal mechanism related to its reaction with iron to produce iron sulphide. Iron sulphide formation, and conversion to pyrite, is an extremely complex process which is not completely understood (Sweeney, 1972). The reactivity of sulphide towards iron minerals may be an important control on pore water sulphide (Goldhaber and Kaplan, 1974; Hines et al., 1982; Canfield and Berner, 1987). Evidence for this comes from many anoxic sediments where near the sediment water interface, the concentrations of dissolved sulphide may be quite low despite active sulphide production by sulphate reduction (Chanton et al., 1987).

In contrast to the complex chemistry of sulphur, chloride is a conservative element and tends to remain stable in the pore water. Measurement of chloride is important in pore water studies. In the absence of perturbing influences such as nearby fresher or more saline water, chloride concentrations should be very close to those in the overlying water (Presley and Trefrey, 1980) .

2.3.2.2 Alkalinity, pH and *Eh*

Alkalinity, pH, and *Eh* are interrelated properties of an aquatic ecosystem. Their values are important to living organisms. Pore water can have an alkalinity higher than that of sea water. A number of reactions can affect alkalinity of pore water. Liberation of ammonia by hydrolysis of basic nitrogen compounds increases alkalinity. Respiration and photosynthesis and the decay products of organisms cause changes in the carbon dioxide and the ammonia content of sediment pore waters, and both of the latter determine to a large extent the pH of the interstitial waters. Almost no pH values outside the range 7.0-8.0 can be found in the hundreds of measurements reported in the literature (Presely and Trefry, 1980). Variations in the populations of organisms and the abundance of organic matter will thus considerably influence the acidity of the interstitial environment within sediments.

A large number of *Eh* measurements have been made in estuarine and other near-shore environments. ZoBell (1946), was perhaps the first user of *Eh* in marine sediments. It is generally agreed that reduction of the various oxidized species in a sediment-water mixture will proceed in a stepwise manner. Thus, dissolved oxygen will be depleted first as *Eh* is lowered, followed by nitrate, manganese oxides, iron oxides, and finally sulphate. Attempts to define critical *Eh* values at which one redox system gives way to another have been only partially successful. Nevertheless, work by Takai and Kamura (1966), Turner and Patrick (1968), Ponnamperund (1972) permits the following generalisation: oxygen disappears at *Eh* values slightly below about + 250 mV, nitrate and manganese oxides can only be reduced at values slightly below +100 mV and sulphate is only below -150 mV. Some overlap occurs, for example sulphate reduction certainly starts before all iron oxide is reduced, but neither iron oxide nor sulphate is reduced in the presence of oxygen or nitrate.

2.3.2.3 Nutrients and organic carbon

Nutrients and organic carbon concentrations in pore water are closely related to other parameters discussed above especially alkalinity, *Eh* and sulphate.

Nitrogen, phosphorus and inorganic carbon are the main products of the degradation of organic matter. In oxygenated sediments, the degradation of organic matter can be described by the relation:

$$5(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 690\ O_2 \rightarrow 530\ CO_2 + 80\ HNO_3 + 5\ H_3PO4 + 610\ H_2O$$

This reaction proceeds until all oxygen is consumed, after oxygen has been depleted, oxidation by NO_3^- commences according to the following reaction:

$$5(CH_2O)_{106}\ (NH_3)_{16}(H_3PO_4) + 472\ HNO_3 \rightarrow 530\ CO_2 + 276\ N_2 + 886\ H_2O + 5\ H_3PO_4$$

Following NO_3^- exhaustion, oxidation continues by SO_4^{2-} reduction as follows:

$$(CH_2O)_{106}\ (NH_3)_{16}(H_3PO_4) + 53\ SO_4^{2-} \rightarrow 106\ HCO_3^- + 16\ NH_3 + H_3PO_4 + 53\ H_2S$$

In sediments where SO_4^{2-} reduction is significant, this process is responsible for most of the oxidation of organic matter, because the SO_4^{2-} available can oxidize 56,000 µmole of CH_2O roughly 225 times as much as oxygen and nitrate combined.

There are several ways in which real systems may deviate from the above mentioned reactions. First, NO_3^- may be removed in ways other than by oxidizing organic matter for example, it is possible that nitrate reducing bacteria will only oxidize either ammonia produced in the sulphate reduction zone or organic nitrogen according to the following reduction (Bender, et al 1977):

$$3\ HNO_3 + 5\ NH_3 \rightarrow 4\ N_2 + 9\ H_2O$$

Although interstitial waters of oxic sediments often differ little in PO_4^{3-} concentration from the overlying seawater, anoxic sediment interstitial waters may contain very high concentrations of phosphate. These differences in the PO_4^{3-} contents of interstitial water of sediments from different environments are only partly explained by differences in the compositions and abundance of organic matter. The lack of phosphorus in the pore waters of some oxygenated sediments (Fanning and Pilson, 1971) may be caused by the adsorption of phosphorus by clay minerals (Weaver and Wampler, 1972; Berner, 1980) and the precipitation of phosphates. For instance, the formation of iron phosphates, or the adsorption of phosphorus onto hydrous ferrous oxides, may also be an important control on the geochemistry of phosphorus, especially in the upper levels of oxic sediments.

It is well established that benthic regeneration in estuarine and shallow coastal environments is a potentially important source of nutrients to the overlying waters (Hartwig, 1976; Zeitschel, 1980). Benthic regeneration may supply an important fraction of nutrient requirements of primary producers in overlying water (Nixon et al., 1976; Aller, 1980; Hopkinson, 1987).

A substantial part of the nutrients taken up by the phytoplankton is recycled in the sediments (Billen, 1978; Blazer, 1984; Klump & Martens, 1987; Van Raaphorst et al., 1988, 1990). It is therefore crucial to study the nutrient early diagenesis to identify the factors influencing regeneration of nutrients to the overlying water column.

It is apparent that organic matter is decomposed as it is buried in the sediment column, producing dissolved CO_2 and H_2CO_3. Where bacterial sulphate reduction is evident it will also be added as $HCO_3^-{}_{(aq)}$. Dissolved organic matter (DOM) is also produced, according to the few measurements of this parameters that have been made. In seawater DOM values are relatively constant at 2-3 mg/l, but Nissenbaum et al., (1971) found 50-150 mg/l in pore-waters from Saanich Inlet.

2.3.2.4 Trace metals

Trace metal concentrations in estuarine interstitial water are often several orders of magnitude higher than in the overlying water (Brooks et al., 1968; Presely et al., 1972; Duchart et al., 1973; Elderfield and Hepworth, 1975; Elderfield et al., 1981; Heggie and Burrell, 1982; Emmerson et al., 1984). This enrichment is most striking for Mn and Fe which are very susceptible to dissolution under the reducing conditions often found in estuarine sediments. Steep concentration gradients may thus be established and significant remobilization of reduced species and fluxes of metals from pore water to overlying water column may be observed.

2.4 Chemistry of interstitial water

Pore water chemistry responds not only to physical factors such as advection of new water and molecular diffusion, but to chemical interactions between the water and the surrounding solid phases of the sediments. In areas of low deposition rates, the organic carbon content is usually low, and most of this material is oxidized in the upper few centimetres by organisms utilizing dissolved oxygen as their main oxidation agent. This is sometimes reflected in the interstitial waters by an increase in the dissolved nitrates (Hartmann et al 1973b).

If dissolved oxygen is completely depleted, nitrate reduction or denitrification may occur. Upon total depletion of dissolved oxygen and nitrate, the process of sulphate reduction becomes predominant. Finally, upon depletion of dissolved sulphate, the reduction of carbon dioxide to methane, as well as fermentation processes, becomes important (Nissenbaum et al 1972).

The behaviour of iron and manganese in pore-waters is fairly well known (Berner, 1980; Presley and Trefry, 1980). When oxic waters overlie anoxic sediments, maximum metal remobilization occurs at the sediment-water interface or in the top few millimetres of sediments. Any net diffusive flux from the sediment is a function of the depth of the oxidized layer. In mildly reducing conditions, a well defined oxic layer is developed in the sediment where remobilized metals may be trapped and greatly concentrated over natural levels. These two cases are typical for estuarine environments (Li et al., 1969; Calvert and Price, 1972; Robbins and Callender (1975); Holdren et al., (1975).

Identifying the specific chemical reactions which control interstitial metal concentrations and subsequent metal mobility remains a somewhat elusive goal. The presence or absence of free oxygen is certainly a primary factor in the behaviour of Mn and Fe and perhaps other metals. Where interstitial oxygen and nitrate are depleted, concentrations of dissolved Mn and Fe clearly increase and vice versa.

Metal sulphide solubility is one important constraint on the activity of several metals in sulphate-reducing sediments. Copper, Pb, Cd, and Zn sulphides, have a very low solubility and might be expected to remain relatively immobile in reducing estuarine sediments. Despite this prediction, Presley et al., (1972) and Elderfield and Hepworth (1975) contend that measured interstitial Co, Cu, Fe, Ni, Pb, and Zn concentrations exceed calculated solubility levels by several order of magnitude. These investigators believe that metal complexations with natural organic ligands can maintain metals at observed levels. Bender and Klinkhammer (1978), however, found very low concentrations of interstitial Cd (< 0.1 ppb), Cu (<1 ppb) and Ni (< 2 ppb) in sulphate-reducing sediments from Narragansett Bay, Rhode Island. Comparison data (Bender and Klinkhammer, 1978) from non-sulphate reducing sediments supports the importance of sulphides as a major controlling factor of the chemistry of these metals in the interstitial water. Furthermore, Bender and Klinkhammer's (1978) data for oxygen and nitrate reducing sediments from the Eastern Tropical Atlantic show high interstitial Cu (6-8 µg/l) which they believe reflects copper input from dredged organic matter. Experimental data of Lu and Chen (1977) on the migration of trace metals between the interface of seawater and polluted surface sediments suggest that under reducing conditions the concentrations of trace metals in the interstitial waters are controlled by sulphide complexes for Cd, Hg, and Pb, by organic complexes for Fe and Ni, chloride complexes for Mn, and by hydroxide complexes for Cr. The high values measured for dissolved copper in comparison with calculated values may be explained by slow precipitation or nucleation, or may be due to the presence of humic-copper complexes (Hallberg 1973; Elderfield and Hepworth, 1975; Emerson, 1976; Lyons et al., 1980).

In contaminated estuarine sediments of Bellingham Bay, Washington, Bothner et al. (1980) observed interstitial mercury concentrations up to 3.8 µg/l, from 16 to 126 times higher than the concentrations in overlying sea water. This is similar to the enrichment of mercury in contaminated anoxic sediments of Mobile Bay, Alabama. It has been suggested that, in general, higher Hg fluxes were associated with low oxygen or reducing conditions in the overlying seawater (Bothner et al., 1980) and the chemical form of dissolved mercury in such sediments has been calculated to be (98%) HgS_2 (Lu and Chen, 1977). Holmes et al. (1974) reported that the cadmium introduced into Corpus Christi Bay Harbour from industrial effluent in the Summer when the harbour waters are stagnant reaches the surface sediment with the sulphide ions and precipitates as CdS; in the Winter months, however, the increased flow of oxygen-rich water into the Bay results in the desorption of some of the precipitated metal. Significant enrichment of trace metals in pore waters of sediment samples has been explained by complexation effects with organic substances (Brooks et al., 1968; Presley et al., 1972; Duchart et al., 1973). In a comparative investigation Nissenbaum and Swaine (1976) found that, with the exception of Fe, Ni, and Co, which occur mostly as sulphides under anaerobic conditions, the elements concentrated in the interstitial solutions are those which are also enriched in sedimentary humates. The transport of dissolved metals in the pore-waters is, therefore, strongly influenced by the vertical gradient of dissolved humic substances (Krom and Sholkovitz, 1978).

Data of Elderfield (1981) from anoxic sediments of Narragansett Bay indicate that approx. 80% of the total Fe and Cu, approx. 40% of the total Ni, 10% of the total Mn were organically bound in the interstitial water of surface sediments. The concentrations of trace elements copper and iron in pore water of sediments from a salt marsh along the Delaware estuary have been found to be controlled mainly by sulphide formation. Data of Hart and Davies (1977) indicate that the major portion of cadmium in the interstitial water from sediment sample of an urban creek at Melbourne, Australia, was associated with colloidal labile species and more strongly bound complexes; zinc and lead to the major proportion was associated with the colloidal phase, 20% in labile forms and 10% in more tightly bound (organic) forms.

2.5 Toxicological aspects of heavy metals

From the stand point of environmental pollution, metals may be classified according to three criteria (i) non critical, (ii) Toxic but very insoluble, and (iii) very toxic and relatively accessible (Wood, 1974).

Heavy metals in sediments react differently under different physical, biological and chemical conditions.

Mercury is considered to be the most important element since aquatic organisms and man may concentrate mercury within living tissues and the subsequent accumulation with time may become lethal. In aquatic ecosystem, inorganic mercury is converted to methyl mercury or dimethyl mercury by anaerobic bacteria. The methyl mercury is thought to be soluble in water and therefore its incorporation in living tissues is inevitable, the result is its accumulation in the food chain and ultimately in man.

The people of Japan who died from "Minimata disease" consumed fish and shellfish from a bay receiving waste from a nearby plastic factory containing elevated amounts of methyl mercury compound (Kurland, et al.,1960). Toxicity levels of 8 ppm caused mercury poisoning in humans in Iraq who consumed wheat treated with methyl mercury (Bakir, et al., 1973).

Lead is another element of concern to be found in sediment. Numerous studies have been made for lead mining and smelting, with emphasis on environmental pathways and distribution in aquatic ecosystem. Horses are especially sensitive to lead toxicity, and lead levels in humans are considered to be toxic at 40 μg/100 g of blood for children under 12 years of age and 80 μg/g of blood in adults (Hammond, P.B. 1978).

Cadmium is probably the most toxic element and is regarded as a primary pollutant. It is widely used in various industrial products and processes including electroplating, pigments, plastic stabilizer, batteries and metallic alloys.

Copper is another trace element often found in aquatic sediments. The continued ingestion of copper may lead to accumulation in animal tissues, especially in the liver (Underwood, E.J. 1971). Copper is the most common heavy metal to which aquatic organisms are exposed, based on its common use as an algicide. Where irrigation is practised, 1 ppm copper in water may be a factor in the development of toxic reactions in plants and animals (Davis, G.K.1974).

Arsenic (As) is one of the earliest known poisons to humans. Arsenic compounds had been used as war chemicals and biocides. Arsenic is now used in paint pigments, medical preparations, biocides, textile dyes and in glass industry.

Chromium levels in sediments are usually associated with man-induced pollution. Mertz et al (1974) believe that human health effects are due to a deficiency rather than an excess, of chromium but recommended a level of 0.05 ppm in water used for domestic use.

Nickel, iron and other trace elements related to health and disease have been studied by the National Academy of Sciences and the results are summarized in volumes I,II and III entitled Geochemistry and the Environment.

CHAPTER 3 SAMPLING

CHAPTER 3 SAMPLING

3.1 The study area

The area selected for this investigation is the Forth estuary at the east coast of Scotland (Fig. 3.1). The study area extends downstream from Alloa to Forth rail bridge, a distance of about 31 km. Between Alloa and Kincardine, a distance of about seven kilometres, the estuary widens and lateral water movements become more important giving rise to sand banks. The estuary narrows at the point of crossing of the Kincardine bridge, giving rise to high turbulence and resuspension. From Kincardine to Forth bridge, the estuary is straight (Fig. 1.2).

3.2 Sampling strategy

3.2.1 The preliminary survey

Previous work in the study area has been summarized in chapter one. A preliminary survey was carried out to study the physical nature of the Forth estuary in addition to selection the sampling stations for future survey. During this survey sediment samples were collected from the middle of the estuary and brought to the laboratory to evaluate the analytical methods to be applied in the current investigation.

The only major problem identified was with the measurements of H_2S. Attempts to measure hydrogen sulphide in the pore-water using ISE H2S meter were not successful due to the low values of H_2S (below detection limit). This could be the result of the loss of H_2S during the sampling.

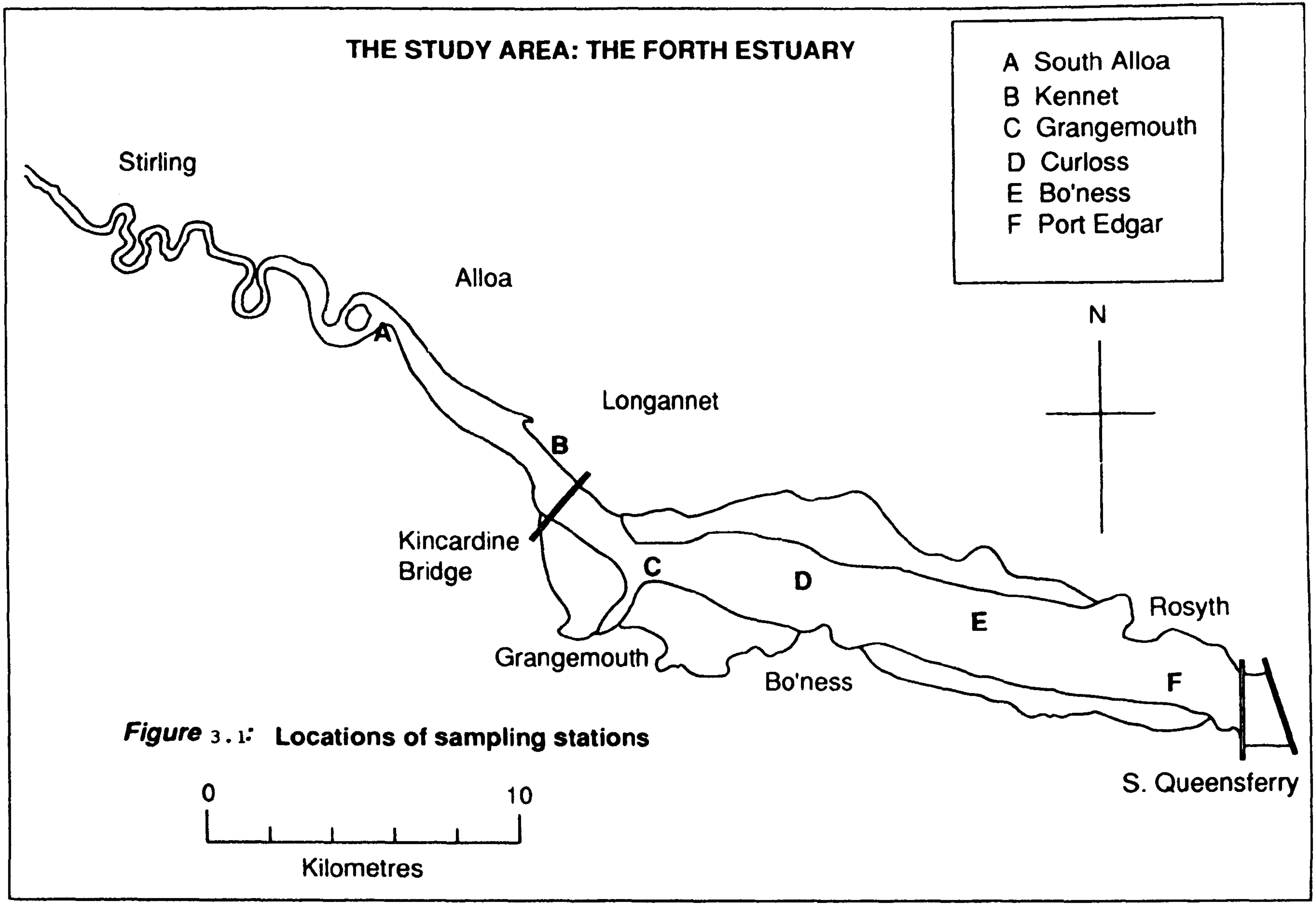


Figure 3.1: **Locations of sampling stations**

The fact that sulphide concentration in the study area cannot be detected, can be attributed to the sulphide removal mechanism which is the reaction with active iron to produce iron sulphide. Iron sulphide formation and its conversion to Pyrite, is an extremely complex process which is not completely understood (Sweeney, 1972; Goldhaber and Kaplan, 1974; Hines et al., 1982; Canfield and Berner, 1987). Also it has been found out that dissolved sulphide is not detectable in the upper few centimetres of the sediment column, in some environments anoxic conditions are established only after some depth (Hines et al., 1982; Canfield and Berner, 1987; Chanton et al., 1987).

3.2.2 The Sampling programme

Sampling programme aimed to identify seasonal and spatial variations in the Forth estuary. Six sampling sites down estuary were sampled at three months intervals. Originally intended to sample over a two year period to cover two complete annual cycles, but due to some technical and administrative difficulties, it was only possible to sample on six occasions: Summer 1991, Autumn 1991, Winter 1992, Spring 1992, Summer 1992, and Autumn 1992.

3.2.3 The Sampling stations

The locations of sampling stations were chosen to reflect the objectives of the study, the available resources, the state of pollution of the investigated area, and finally the accessibility of each location.

Sampling location should also consider local variability and depth variations. The former can be mastered by taking replicate samples in order to determine the confidence limits to the results. In general, and depending on the objectives of the investigation, between one sample and three replicates are taken at each station. The ICES Benthos Working Group guideline suggesting two replicates per station are adequate (FRPB, TW2/88). In the annual studies of monitoring the benthos, the FRPB takes three replicates. In this study, it was also necessary to examine vertical variations down each core. This practice is rarely followed in routine sampling.

In the present investigation six sampling stations were selected to represent the main sectors of the Forth Estuary. These stations represents the two end members i.e River water and Sea water and the gradation between. Station A (S.Alloa) represent the river end-member, where conductivity reach its minimum value (10.9 mS cm^{-1}) while station F (Port edgar) represents the sea end member where conductivity values reach its maximum (49.9 mS cm^{-1}) (Fig. 3.1). The six stations selected were as follows:

1- Station A (South Alloa).

2- Station B (kennetpans).

3- Station C (Grangemouth).

4- Station D (Culross).

5- Station E (Bo'ness).

6- Station F (Port Edgar).

3.3 Sampling methods

The most widely used methods for sampling bottom sediments are of two types: grabs and corers. Sampling techniques depend on the physical nature of the water body. Areas of shallow water may be sampled directly by hand at low tide.

Grabs

The Grabs are of various shapes and sizes usually used to collect pinpointed "surface" sediments. In most of the cases the sample is mixed and the depth profile is not preserved. The most common types are:(i) the Pettersson which comprises of a pair of quarter cylinder buckets hinged so that they may be held apart as the grab is lowered to the bed, released on contact, and lifted from the hinge line. Sediment may escape if the jaws are jammed open by gravel or shells during lifting. (ii) the van Veen; its operation is somewhat similar to the Pettersson, but the jaws are held together firmly during withdrawal. This type normally has inspection hatches in the flat side of the sampler bucket. (iii) the Shipek grab which is widely used in shallow marine investigations. It consists of semi-cylindrical bucket which is lowered to the bed open downwards. As it touches the bottom a powerful spring is activated, causing the bucket to rotate in the bed. The spring holds the sampler tightly closed during retraction (Buller and McManus, 1979).

Corers

Corers are simply of two types. The simplest gravity corer consists of a metal tube which has weights and stabilising fins at the upper end. The corer penetrates the bed after free fall through the water. The core is withdrawn in its liner and may be stored for later analysis. The penetration achieved is partly related to the length of the corer, the depth of the water, the number of weights attached and the nature of the bed sediments. Gravity corers can easily sample three or four times deeper than the box corer and have been found to be efficient in recovering the sediment surface (Flanagen, 1970). Piston corers, such as the type developed by Kullenberg in the 1940s are widely used in deep sea surveying. Impact with the sea-bed releases a piston which produces a vacuum within the core liner. This helps to reduce internal friction and compression of the core, resulting in improved penetration. A typical piston corer can sample 10 to 20 meters of the sediment column depending on circumstances and sediment type. Sampling deeper than 20 metres can only be achieved by a drilling rig similar to those used in drilling oil or water wells (Buller and McManus, 1979; Presely and Trefery 1980).

The second type of corer is the box-corer. This is mainly used for studies in which the internal structure of the sediment is under investigation. An open steel box is driven vertically into the sediment until the top rests on the surface, and then a blade cuts through the sediment and covers the end of the box. The box is lifted and sediment is examined in undisturbed form. The relatively large size of the box corer provides enough material for many analytical determinations. The disadvantage of the box corer is its limited depth to which it samples (Buller and McManus, 1979), (Cauwet, G. 1987).

3.3.1 Sampling methods of the present study

3.3.1.1 Sampling intertidal stations

Due to the inability of the Forth Ranger to proceed beyond Kincardine bridge, The intertidal stations i.e stations A (S.Alloa) and B (Kennet) were sampled by hand at low tide one day before or after the sampling of the tidal stations.

Redox potential was measured insitu and then three cores were taken by pressing the core into the sediment by hand and then the core was taken out of the sediment, capped quickly and frozen immediately using dry ice. At the same day, the cores collected were sectioned at 2.5 cm intervals and put into plastic bags previously labelled and numbered and then the samples were put in a deep freezer until used.

3.3.1.2 Sampling tidal stations

Sampling for the tidal stations C (G'mouth), D (Culr-ɔss), E (Bo'ness), and F (P.Edgar) were carried out using the survey vessel "Forth Ranger" which belongs to the Forth River Purification Board. Positions were fixed in the preliminary survey. The Decca navigator grid co-ordinates were used to relocate the station positions on subsequent surveys. To obtain an undisturbed sediment sample, coring was the only practical way to sample.

Four cores were obtained at each station using the

Craib corer. This apparatus is piston operated and triggered by a frame resting on the sea bed, A PVC core liner of internal diameter 5.7 cm is pushed into the sediment. The depth of final core varies depending on the nature of the sediment; in some areas a core of depth > 12 cm is produced. The corer takes undisturbed bottom samples and the core is retained by a ball-device. The liner is capped on return to the surface (FRPB, 1988).

After the core-liner is removed from the sampling frame, the first core was used for redox potential measurement on board of the survey vessel laboratory (Section 4.6.2). The remaining three sediment cores were extruded by a plunger and quickly sectioned at 2.5 cm intervals. The samples were put in labelled plastic bags and frozen immediately with dry ice for transport back to the Environmental Science Department laboratories.

Sediment samples collected were checked upon arrival to ensure numbering and labelling were correct and then the samples were stored in a deep freezer until analysis.

3.4 Sample preparation for analysis

The first step in sample preparation for analysis was the separation of interstitial water. Within two or three days after coring, sediment samples were processed for interstitial water extraction.

3.4.1 Extraction of interstitial water

Extraction methods

Interstitial waters are usually recovered from sediments by leaching, centrifugation, or squeezing.
The advantages and disadvantages of each of the three techniques were reviewed by Presely and Trefery (1980) and Carignan, et al. (1985). However, the most commonly used method is centrifugation (Emerson, 1976; Bothner, 1980; Elderfield et al., 1981; Boudreau and Westrich, 1984; Socha and Carpenter 1987; Calvert and Karlin 1991). This method was used here.

Interstitial water was separated from sediments using centrifugation at 7000 rpm for 30 minutes at 4°c. Sections for each depth from each of the three replicate cores were centrifuged separately and then the pore water obtained after filtration were combined to secure an adequate volume of pore-water for all determinations.

To avoid oxidation, sediments were extruded from their containers and filled into centrifuge bottles in a dry box under a nitrogen gas atmosphere. The centrifuge bottles were sealed, taken out of the dry box for centrifugation and then, after centrifugation was completed the centrifuge bottles were taken back to the dry box for filtration. The interstitial water was vacuum filtered under nitrogen gas through a pre-rinsed 0.45 µm membrane filter and the portion to be used for trace metal analysis was acidified to pH 1-2 using Aristar nitric acid and stored in a plastic bottles and put in a refrigerator for subsequent analysis.

3.4.2 Sample preservation and storage

A well known problem in the study of interstitial water chemistry is sample preservation especially when dealing with reducing sediment cores. Dissolved ammonia has been shown to decrease upon storage (Gieskes 1974). For the storage of samples intended for trace metals analysis, storage at low pH is recommended because under those conditions the reduced valency states are stabilized. Storage of high alkalinity samples is not recommended as in such cases calcium carbonate may precipitate upon storage (Berner et al., 1970, Gieskes 1973).

The best practice is to carry out the analysis of nutrients as soon as possible, preferably during the day of extraction of interstitial water as has been exercised. In the present investigation, phosphate, nitrate, pH and alkalinity were analyzed immediately after the extraction of pore water. Other parameters were analyzed on the following day.

The centrifuged sediment samples were dried in an oven at 80 - 90°C. They were then reduced to a fine powder using a pestle and a mortar. The ground sediments were stored in plastic bottles for subsequent analysis.

There has been some controversy over freezing interstitial water after extraction. A depletion of dissolved phosphate and silica was detected in interstitial waters that were quick frozen compared with in situ samples analyzed soon after collection (Murray et al 1978). The authors attributed this to the formation of amorphous phases during freezing. Similar results were reported by Martens et al (1978) who found that precipitation of struvite ($MgNH_4PO_4$-$.6H_2O$) could be induced by freezing interstitial water samples. Krom and Sholkovitz (1978) stated that up 40% of the total interstitial dissolved iron can be precipitated with humic substances as a result of freezing or acidification.

3.5 Routine procedure diagram

The following routine procedure were followed throughout this investigation.

Sediment cores

Sectioning

Centrifugation

Filtration

Interstitial water		Sediment	
Others	Metals	Others	Metals
Conductivity	Lead	T.O.N	Lead
Alkalinity	Cadmium	T.O.C	Cadmium
Chloride	Copper	L.O.I	Copper
Sulphate	Nickel	E*h*	Nickel
Nitrate	Mercury	P.S.A	Mercury
Phosphate	Iron		Iron
DOC	Manganese		Manganese
pH			Aluminium

CHAPTER 4 ANALYTICAL METHODS

CHAPTER 4 ANALYTICAL METHODS

4.1 Trace metals determinations in sediments

Trace metals determinations in the sediments and pore water are of course a two stage process; namely extraction (pore water) and digestion (sediments) followed by determination of the element. Analysis will be discussed first.

Sediment samples were analyzed for Al, Fe, Mn, Cd, Pb, Hg, Ni, and Cu. A Flame Atomic Absorption Spectro-photometer was used to measure all these metals except cadmium which has been measured using flameless A.A.S. and mercury which was determined using the P.S.A mercury specific atomic fluorescence detector. A nitrous oxide flame was used for the determination of aluminium in the digested sediments. Machine conditions were set according to the manufacturer guidelines.

4.2 Methods of trace element analysis

There is a wide range of techniques for the analysis of trace elements in solution. The selection of a specific technique is governed by many factors: accessibility of the equipment; selectivity; sensitivity; accuracy and precision and finally the resources available.

The selectivity of an analytical method is based on its ability to determine one constituent without any interference from other substances. The accuracy of a method is determined by systematic errors which bias the analysis. The accuracy is best assessed by the analysis of samples of known compositions which have been previously analyzed by other well established methods. Precision of an analytical technique is a function of random errors arising from poor operator technique and/or faulty equipment. These errors can be adequately expressed by one or more standard deviations from the mean.

4.2.1 Atomic absorption spectrophotometry

Atomic absorption spectrophotometry (AAS) has become the most commonly used method for the trace element analysis of environmental materials. The technique involves the absorption of light of a specific wavelength by atomic species of the element as it is excited in a flame or other thermal device. The amount of light absorbed is proportional to the concentration of the element present in its ground state. The light source used is a hollow cathode lamp, with the cathode constructed of the same element as that under analysis or an electrodeless discharge lamp (EDL) which contains a small quantity of the element to be determined. Table 4.1 summarizes the typical sensitivities of the conventional flame and the more sensitive graphite furnace method. It shows that for many elements the flameless technique offers higher sensitivities than the flame atomization method (Fernandez & Manning, 1971 ; Segar and Gonzales, 1972).

Interference is a problem in almost all of the techniques and has to be dealt with carefully. The interference results from a variety of physical, chemical and matrix effects, e.g. molecular absorption; line interferences; suppression of ionization by alkali metals; interelement compound formation; scattering by particulates etc.

Table 4.1

Typical detection limits of the conventional flame and graphite furnace methods of atomic absorption spectrophotometry

	Detection limits ($\mu g\ ml^{-1}$)	
Elements	Flame	Graphite furnace
Ag	0.02	-
Al	0.1	5×10^{-6}
As	0.1	5×10^{-4}
Cd	0.01	1×10^{-6}
Co	0.05	5×10^{-5}
Cr	0.05	5×10^{-5}
Cu	0.05	5×10^{-6}
Fe	0.05	5×10^{-5}
Mn	0.02	5×10^{-6}
Ni	0.05	1×10^{-4}
Pb	0.1	5×10^{-5}
Sn	1.0	-
Ti	1.0	-
V	1.0	1×10^{-4}
Zn	0.01	2×10^{-6}

After Aston, S.R (1985)

Other methods such as colorimetry, pulse polarography and anodic stripping voltametry, molecular fluorescence and others have been reviewed by many investigators (See Aston, S.R. 1985). Some techniques for example neutron activation analysis or X-ray fluorescence do not require prior digestion of the sediments.

Here three subsamples of sediment from each section were digested prior to A.A.S and the average were taken throughout the course of this investigation.

4.2.1.1 The individual elements

Aluminium

A completely satisfactory determination of aluminium was first possible after the introduction of the nitrous oxide/acetylene flame. Since aluminium is ionized by about 10 % in a nitrous oxide/acetylene flame, about 0.1 % potassium chloride was added. Aluminium was measured at wavelength of 309.3 nm.

Iron and Manganese

Iron and manganese can be determined in an air/acetylene flame without major interferences. For the determination of iron there are a large number of resonance lines of different sensitivities. The most frequently used line at 248.3 nm, gives a detection limit of about 0.005 mg\l at a spectral bandpass of 0.2 nm.

For manganese the best sensitivity can be achieved at the 279.5 nm resonance line and detection limit of about 0.001 mg\l. Manganese is an exception in that several lines can be used simultaneously without the usual disadvantages.

Copper

Copper is one of the elements most frequently and easily determined by atomic absorption. It exhibits no interferences in an air/acetylene flame. It was measured at 324.7 nm wavelength. Two standards were used to calibrate the instrument.

Lead

Lead can be determined in the most widely varying flames without noticeable interferences occurring. Usually an air acetylene flame is used. Although the 217.0 nm line is noticeably more sensitive than the 283.3 nm line, it does not give a better detection limit owing to a poorer signal to noise ratio. Furthermore more background attenuation effects occur at the 217.0 nm line, so that the 283.3 nm line is used with greater success.

Nickel

Nickel is one of the metals frequently determined by atomic absorption spectrometry. The best characteristic concentration is obtained in an air/acetylene flame at the 232.0 nm resonance line; the detection limit is 0.004 mg\l. To be able to use the 232.0 nm line meaningfully, a spectral bandpass of 0.2 nm is necessary since the two strong emission lines at 231.716 nm and 232.138 nm otherwise cause a considerable curvature in the analytical curve and a strong reduction in the sensitivity (Welz, B. 1985).

4.2.1.2 Standards preparation

Standards should be made up to reflect the expected concentration in the sample. Composite standards, of all of the metals to be measured within a particular concentration range are especially useful. During this investigation two standards were made for each element and a composite standard were made for the elements which had the same range.

The standards were prepared at a regular intervals using stock solutions and were kept in a refrigerator. Calibration curves were linear for all elements measured.

4.3 Digestion methods

The aim of all of the various methods available for the digestion of sediments is to convert all the metal present in the sediments into a form available for quantification by the final method of analysis.

4.3.1 Total digestion

Sediments must be brought into aqueous solution for most modern methods of trace element analysis. Total digestion of estuarine sediments requires the use of hydrofluoric acid to dissolve the silicates and silica which are inevitably present in estuarine sediments to a greater or lesser extent. In the present study a total digestion method was applied for the measurement of aluminium, iron and manganese.

4.3.1.1 Weight optimization

An experiment was set to determine the optimum weight of sediment to be used in the total digestion. Reference material MESS-1 (marine sediments) was used. Three weights were chosen; 0.1, 0.3 and 0.5 g. Five replicates were employed in the experiment. Table 4.2 shows the mean values with one standard deviation together with the certified reference material values.

It can be concluded from the data in the table below that the optimum weight for total digestion is the 0.1 g. This is mainly due to the complete destruction of silicates minerals present in the sediment. At this weight the highest values were obtained compared to the reference material values for all the three metals (particularly for Mn and Al).

Table 4.2

Table showing the results of the weight optimization experiment

	Fe g/kg	Mn mg\kg	Al g\kg
0.1 g	32.2 ± 0.29	520 ± 17	56.34 ± 1.2
0.3 g	29.0 ± 0.48	432 ± 15	36.7 ± 1.7
0.5 g	28.3 ± 0.52	374 ± 14	34.72 ± 2.3
Reference material	30.5 ± 0.18	513 ± 25	58.2 ± 2

4.3.1.2 Summary of the method

The following procedure were used: A 100 mg of dried sediment were placed in a TEFLON beaker, and evaporated to dryness with a mixture of 5 mls HF and 2 mls HNO_3 on a sand bath. Evaporation was repeated with 2 mls HNO_3. The samples were finally dissolved with 5 mls dilute HNO_3 (15%) by heating for 30 minutes and transferred to a 50 ml volumetric flask (Forstner 1981). Other methods were reported in the literature and they involved the use of strong acids e.g hydrofluoric or perchloric acids (Bernas, 1968; Langmyhr and Paus, 1968; Adams et al., 1980).

4.3.2 Selective extraction

Selective extraction methods were used for the digestion of the trace metals in sediments such as Pb, Cu, Ni, Cd, and Hg. Several methods are available including the use of aqua regia (HNO_3-HCL, 1:3) or concentrated nitric acid. Decomposition is sufficient for trace metal analysis. It has been suggested that for this type of study it is not necessary to obtain full digestion of all sediment components including detrital minerals since the pollution effects are usually associated with the surface of the sediment particles including their inorganic and organic coatings.

Simple HCL-HNO_3 (1:1) digestion has therefore been proposed for the determinations of trace metals by atomic absorption spectroscopy. The digestion method was modified from (Anderson 1974; Adams et al. 1980).

4.3.2.1 Summary of the method

10 ml of concentrated HNO_3 (Aristar) and 10 ml of concentrated HCL (AR) were added to 0.5 g of dried sediment. The samples were placed in a 200 ml pyrex beakers on a hot plate at 90°C for a digestion period of 5 hours. A minimum volume of deionized water was added to rinse the sides of the beakers and to avoid dryness. Careful monitoring of the beakers dictated the need for sample rotation every 30 minutes to ensure even heating. After cooling the samples were diluted with deionized water and filtered through n.42 Whatman filter paper into 50 ml volumetric flask.

Reagent blanks were prepared by running the procedure without the sediment and the blank results were used to auto-zero the instrument. At least one reagent blank is included for every ten samples analyzed. Three or more samples of the reference material were incorporated with every batch of sediments.

Calculations:

Concentration mg\kg =

(instrument reading x 50) / weight of sediment

4.4 Validation of the analytical methods

Reference material MESS-1 (marine sediment) from the National Research Council, Canada was regularly cycled through the whole analytical methods in order to validate the results. The use of certified reference materials (CRM) for environmental chemistry is recommended. MacDonald and O'Brien (1985) discussed the value of certified reference materials for environmental chemistry and Keith et al. (1983) recommended their incorporation in any environmental sampling program.

The results of the certified reference material were summarized in table 4.3. The certified values and the present-study values were in good agreement. However, cadmium in the present study was found to be noticeably lower (78%).

Table 4.3

Summary of the results of the analyses of sediment reference material

Element	Standard	This work	Recovery (%)
Aluminium g\kg	58 ± 2	64 ± 5.6	110
Iron g\kg	30.5 ± 0.18	27 ± 0.16	88.6
Manganese g\kg	0.513 ± 0.025	0.55 ± 0.06	107
Cadmium mg\kg	0.59 ± 0.1	0.46 ± 0.02	78
Copper mg\kg	25.1 ± 3.8	23.2 ± 2.0	92
Lead mg\kg	34.61 ± 6.1	32.35 ± 3.13	93.5
Nickel mg\kg	29.5 ± 2.7	27.32 ± 1.76	92.6

4.5 Other parameters

4.5.1 Organic matter (loi, toc, ton and c:n)

In any description of the sediment regime it is necessary to estimate the quality and the quantity of the organic fraction. This will give: (i) An indication of oxygen demand within the sediment and therefore aids in interpreting redox-potential profiles; (ii) aids in interpreting contaminants levels which may be associated with the organic fraction; (iii) provides an indication of the sediments suitability in supporting deposit/detritus feeding infauna.

The standard method adopted for the analysis of organic matter follows the recommendations of Byers, et al. (1978). Parker, (1983) also gives a comparison of methods for marine sediments. The dried sediment samples were sub-sampled to give a sample (A) for combusting in a muffle furnace at 475°C for 4 hours to give the organic matter (as loss on ignition). A second sub-sample (B) was left untreated and then the % carbon and nitrogen of both (A) and (B) samples were determined using a Perkin-Elmer model PE 2400 series 2 CHNS/O analyzer in the Aquaculture department laboratories.

In the CHN operating mode the PE 2400 analyzer uses a combustion method to convert the sample elements to simple gasses. The sample is first oxidized in a pure environment using a classical reagent. Products produced in the combustion zone include (CO_2, H_2O, and N_2). Elements such as halogens and sulphur, are removed by scrubbing reagents in the combustion zone. The resulting gasses are homogenized and controlled to exact conditions of pressure, temperature, and volume. The homogenized gasses are allowed to depressurize through a column where they are separated in a stepwise steady-state manner and detected as a function of their thermal conductivities. Two or three replicates were analyzed depending on the reproducibility using acetanilide as a standard. The analysis gives the carbon and nitrogen in the inorganic (A) and total (B) subsamples. The values for (A) are corrected to the pretreatment weight and then the total organic carbon value (TOC) is derived by difference (B-A). Finally, the carbon to nitrogen ratio, as an indication of labile/ refractory nature of the organic matter present, is calculated as %TOC/%TON.

4.5.2 Redox potential *Eh*

This parameter has been found useful as a semi-quantitative indicator of the intensity of reducing conditions. Furthermore, *Eh* measurements of sediments have been increasingly used to categorise the physico-chemical condition of marine sediments (Fenchel and Reidl, 1970) and to assess the impact of organic inputs to the sediments (Pearsons and Stanley, 1979).

The redox determinations were carried out immediately after sampling in the ship-board laboratory for stations C, D, E, and F (tidal stations). For stations A and B, (Intertidal stations) *Eh* measurements were carried out *in situ* using a platinum electrode system. The electrode and a double junction calomel reference electrode were made by

Russel pH and were used with a PHM 53 Radiometer specific ion meter. The system was tested using Zobells solution which provided a check on the reproducibility of the liquid junction of the calomel electrode and also acted as a cleaning process for the platinum electrode . The core liner containing sediment to a depth of approximately 12 cm with overlying water is clamped in position and the temperature and redox potential of the overlying water are measured. A 2-minute equilibration period is used for all readings. The protective glass rod and the platinum electrode are moved into the core and readings are taken at a 1 cm intervals from 0.5 to 10 cm depth. The sum of measured potential and 244 mV for the reference electrode gives the true redox potential after a temperature correction is made. The latter is given by :

$$Eh = E + 244 - 0.76(t - 25).$$

Where t = overlying water temperature (C^{o}) ,

Eh= true redox potential,

E = measured potential .

In addition to this information, a sediment description was taken including depth of black layer, type of coarse material, etc. FRPB, TW2/1988.

4.5.3 Particle size analysis

The dried and desegregated sediment were subjected to a wet sieving to give the percentage < 63 µm. Two grams of the sediment were wet sieved in a < 63 µm sieve and the percentage of less than 63 µm were calculated.

4.5.4 Preparation of sediment for the < 63 μm analysis

A small portion of the dried and ground sediments were dry sieved in a < 63 μm plastic mesh and digested to give the less than 63 μm sediment concentrations. This experiment was only performed for summer 1992 samples. This would aid in understanding the relationship between particle size and trace metals concentration, and to standardize the procedure with that in use elsewhere.

4.5.5 Normalization procedure

Correction for grain size was to be carried out to investigate the effect of grain size on the trace metals distributions in the study area. The correction method was taken from Horowitz (1991). The first step was to calculate the dilution factor and the normalized chemical concentration was then calculated by multiplying the bulk sample chemical concentration by the dilution factor as follows:

Dilution factor = 100/(100 - percent of size fraction greater than the range of interest)

Normalized chemical data = (dilution factor)(chemical concentration in mg\kg).

4.6 Trace metals determination in pore water

4.6.1 Iron and Manganese

Iron and manganese were measured in a diluted sample by direct aspiration into flame atomic absorption spectroscopy. To validate the method an experiment was set up to determine the recovery of Fe and Mn in spiked solutions of different salinities. Four ranges of salinities were selected to cover the whole range of salinity in the Forth estuary. Effects of acidification of the solutions were also tested by adding 2%, 0.4% and 0.1% of Aristar nitric acid to a 100 ml of deionized water and then the acidified solutions at various salinity ranges were spiked by 5 mg\l of iron and 2 mg\l manganese.

The results are shown in tables (4.4 and 4.5). The results showed the possibility of measuring iron and manganese at different salinity ranges by acidifying the solutions. Acidification with 0.1 ml of nitric acid per 100 ml of sample yielded relatively better recoveries.

Table 4.4

Recoveries of iron at different salinity ranges and at different acidification ranges

Iron = 5 mg\l

	2 %		0.4 %		0.1 %	
Salinity (%)	Fe Found	% recovery	Fe found	% recovery	Fe found	% recovery
30	4.85	97	4.93	98.6	4.89	97.8
20	4.79	95.8	4.84	96.8	4.83	96.6
10	4.7	94	4.78	95.6	4.84	96.8
0.0	4.8	98	4.96	99.2	4.98	99.6

Table 4.5

Recoveries of manganese at different salinity ranges and at different acidification ranges

Manganese = 2 mg\l

	2 %		0.4 %		0.1 %	
Salinity (%)	Mn Found	% recovery	Mn found	% recovery	Mn found	% recovery
30	1.89	94.5	1.92	96.0	1.93	96.5
20	1.95	97.5	1.97	98.5	2.01	100.5
10	2.07	103.5	2.06	103	2.13	106.5
0.0	2.17	108.5	2.19	109.5	2.11	110

A second experiment was set up to complement the first one in an attempt to eliminate the effect of spectral interference i.e sodium chloride by adding ammonium nitrate. The addition of ammonium nitrate to the sample is thought to achieve a matrix modification effects. This reagent can serve either to increase the volatility of the matrix or to improve the thermal stability of the analyte element i.e to reduce its volatility. Matrix modification serves to make the volatilities of the analyte element and the matrix sufficiently different to permit easier separation through the thermal pretreatment. According to the equation below:

$$NaCl + NH_4No3 \rightleftharpoons NaNO3 + NH4Cl$$

sodium nitrate and ammonium chloride are formed, and these volatilize at temperature below 400°C.
Ammonium nitrate 30 % was prepared and added to spiked solutions of iron and manganese at different salinity ranges.

The results of ammonium nitrate addition are summarized in table (4.6). It can be seen from the table that although the recovery improved when using 10 % of ammonium nitrate (30% w/v) compared to 40 %, it still did not give as full recovery as nitric acid. Iron and manganese were thus determined on samples which had been acidified by adding nitric acid (0.1 ml per 100 ml of sample).

Table 4.6

Recoveries of iron and manganese at different salinities and ammonium nitrate ranges

	Ammonium nitrate 30% (w/v)							
	Iron 5 mg\l				Manganese 2 mg\l			
	40 %		10 %		40 %		10 %	
Salinity	Fe	%	Fe	%	Mn	%	Mn	%
30	3.6	71.8	4.5	89.8	1.3	65	1.8	87.6
20	3.5	70.6	4.4	87.8	1.4	67.5	1.8	89
10	3.5	69.8	4.4	88.2	1.5	73.5	1.9	96.5
0.0	3.6	72.8	4.5	90.6	1.6	80	2.1	102.5

4.6.2 Trace metals (Pb, Cd, Ni and Cu)

Preconcentration technique

The sensitivities of conventional flame and other flameless techniques are not adequate for the direct determination of many trace elements in marine and estuarine waters including interstitial water of marine and estuarine sediments. Furthermore, there are serious inter-element interferences involving both major and trace elements which require that a pre-concentration procedure be adopted for A.A.S. analysis. The problem of interferences from the matrix of the sample is particularly relevant for estuarine waters which consist of a wide range of mixtures of marine and fresh waters. The most widely used pre-concentration techniques now in use for both flame and flameless AAS are chelation solvent extraction and chelating ion-exchange. The most commonly used chelation solvent extraction method is probably the APDC-MIBK (ammonium pyrrolidine dithiocarbamate -methyl isobutyl ketone) procedure (Brooks et al., 1967). In addition to APDC, other derivatives of dithiocarbamic acid have been used prior to extraction, principally sodium diethyl dithiocarbamate (NaDDC) and diethylammonium diethyl dithicarbamate (DDDC). The chelate may be extracted into MIBK, chloroform or Freon TF (1,1,2 trichloro-1,2,2-triflur-oethane). Details for using APDC and DDDC with Freon TF are given by Danielsson et al. (1978) and with chloroform by Bruland et al. (1979).

During this investigation trace metals in the interstitial water were determined using APDC and DDDC with Freon after Danielsson et al, (1982). Ionic and labile dissolved trace metals are converted into their dithiocarbamate complexes, extracted into Freon-TF and back extracted into dilute nitric acid solution. Portions of the back-extracts were injected into a graphite furnace. The method gives complete separation from the matrix irrespective of salinity. Therefore, the method is useful throughout the full salinity range of an estuary . The effect of high iron concentrations on the extraction were eliminated by using a mixed acetate buffer complexing agent solution (Danielsson et al, (1982).

4.6.2.1 Summary of the method

Reagents

Acids and ammonia were of Aristar quality. Complexing agents and FREON (1,1,2-trichloro-2,2,1-trifluoroethane) were of analytical grade. Deionized water was obtained from a Milli-Q purification system. The buffer solution (2 M acetate) was made by mixing 11.8 ml concentrated acetic acid and 23 ml ammonia solution and made up to 100 ml with deionised water. The extractant (complexant) solutions was made by dissolving 0.5 g of ammonium pyrrolidine-dithiocarbamate (APDC) and 0.5 g of diethylammonium diethyl-dithiocarbamate (DDDC) in 100 ml of water. This solution was purified by shaking for 2 minutes with 30 ml of Freon.

Procedure

To a 250 ml separatory funnel were added 10 ml FREON, 5 ml sample and 0.05 ml of mixed reagent solution. The funnel was shaken intensely for 2 minutes and the phases were allowed to separate. the FREON phase was drawn off, and the aqueous phase was shaken with a further 5 ml of FREON for 30 seconds. After phase separation, the two organic phases were combined. For back extraction, 100 µl of concentrated nitric acid were added to the combined extracts. The container was capped and shaken for a few seconds and allowed to stand for about 5 minutes. After addition of 4.9 ml of deionized water, the container was shaken and allowed to stand for > 30 minutes. Finally the aqueous phase was separated using a clean and acidified plastic pipette and stored in a polythene containers in a refrigerator for subsequent measurements. These extracts can be stored for several months. Before analysis, the containers should be shaken vigorously for 30 seconds.

4.6.3 Mercury determination

Mercury was determined using the P.S.A. mercury specific atomic fluorescence detector. The P.S.A. system offers performance at sub ppb levels . The P.S.A. system detector measures mercury as the cold vapour by fluorescence. Mercury vapour is transported in to the detector through a chimney interface and is further sheathed in an additional stream of argon gas. This constrained the mercury in the argon stream and provides a rapid flush-out time between samples. This technique is used by the Forth River Purification Board and the analysis of mercury were carried at their laboratories.

4.7 Other parameters

4.7.1 pH determination

The pH is one of the most frequently measured parameters. pH gives an indication of the acidity and alkalinity which makes it valuable for water characterization. It is defined as the reciprocal of the hydrogen ion concentration: $pH = -\log H^+$.

In chemically pure water, water molecules split up to form H_3O^+ (hydronium ion) and OH^- (hydroxyl ion) according to the following formula:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

The concentration of hydrogen ions in chemically pure, neutral water is 1×10^{-7} g/l, corresponding to the dissociation constant of the water $K_w = 10^{-14}$ at 25 °C deducible from the principle of mass action;

$$[H^+] + [OH^-] = K_w \qquad (K_w = 10^{-14})$$

$$[H^+] = K_w/[OH] = 10^{-14}/10^{-7} = 10^{-7} \text{ g/l; } OH^- = 10^{-7} \text{ g/l}$$

The conversion of the fraction $(H^+) = 10^{-7}$ into the negative logarithm pH 7 is in the interest of simplification,

pH of 7 = neutral

pH >7 to 14 = alkaline range

pH 0 to < 7 = acid range

pH was measured using the Corning 150 pH/Ion meter. This pH meter is an automatic meter providing a relative accuracy of 0.0001 pH. Calibration was carried out using pH 4 and 7 buffer solutions.

4.7.2 Conductivity

The electrical conductivity of water is based on the presence of ions. It expresses the resistance of a 1 cm cube of water to the passage of a current, usually at 25°C (specific resistance). Electrical conductivity is expressed as the reciprocal of electrical resistance in ohm (Ω) . It is given in Siemens ($S = 1/\Omega$) per cm (Siemens per cm) ($S.cm^{-1}$).

Conductivity measurements were carried out on a diluted volume of pore water using the ELE 4070 conductivity meter. The meter provides an automatic temperature compensation over 0°C. The accuracy of the meter is 1.5 % plus or minus 2 digits.

4.8.3 Chloride and Sulphate

Chloride and sulphate were determined using Ion Exchange Chromatography (DIONEX). Ion chromatography is a liquid chromatographic technique using ion exchange mechanisms and suppressed detection for the separation and determination of anions and cations. Several methods have been developed to determine sulphate in small volumes of marine waters which are typically obtained from sampling pore water. They include volumetric, nephelometric and chromatographic methods which require variable investments in terms of analytical equipment and yield varying degrees of precision. Of particular interest is the recent development of an ion chromatography procedure which requires few manipulations and provides precise measurement of sulphate in diluted sea water solutions (Subosu et al. 1989).

Principles

A liquid sample is introduced into a pumped carrier stream (eluent) which is transported through an ion-exchange column (separator column). Ions compete for the active exchange sites and this results in the separation of the ions into discrete bands. The retention time can be used to identify the fraction which flows through the detector. Ions are separated on the basis of size and charge, monovalent ions being eluted first, and within the same valency the smaller ionic radius ions come through quicker. Eluent pH affects the retention times as both the nature of the eluent and the form of the sample ion may be altered.

4.7.4 Alkalinity

Alkalinity is usually imparted by the bicarbonate, carbonate and hydroxide compounds of a natural or treated water supply. It is determined by titration with a standard solution of a strong acid. Phenolphthalein indicator enables the measurement of the alkalinity fraction contributed by hydroxide and half of the carbonate. Indicators responding in the pH range 4-5 are used to measure the alkalinity contributed by hydroxide, carbonate and bicarbonate.

4.7.5 Phosphate determination

Phosphorus occurs in natural waters in the form of various types of phosphate. These forms are commonly classified into orthophosphate, condensed phosphate (pyro-meta and poly phosphate) and organically bound phosphates. These forms of phosphates may occur in the soluble form, in particles of detritus, or in the bodies of aquatic organisms. Phosphorus is an element which is essential to the growth of organisms. phosphate analysis embodies two general procedural steps :

- Conversion of phosphorus form of interest to soluble ortho phosphate.
- Colorimetric determination of soluble orthophosphate.

Stannous chloride method

The principle of this method involves the formation of molybdophosphoric acid, which is reduced to the intensely coloured complex, molybdenum blue, by stannous chloride.

4.7.6 Total oxidized nitrogen (NO_3 + NO_2) determination

Measurements of nitrate in pore waters of marine sediments provide information on the oxidation of organic matter above the sulphate reduction zone and give qualitative estimates of oxygen concentrations in the pore water. Nitrate data also identify the beginning of sulphate reduction, which can begin only below the depth at which nitrate is exhausted. Finally nitrate data can contribute to a better understanding of fixed nitrogen regeneration from various sediment types, and of rate of denitrification during nitrate reduction(Bender et al 1977).

Nitrate was measured using the Palintest nitrate method by which nitrate is first reduced to nitrite, the resulting nitrite is then determined by a diazonium reaction to form a reddish dye. The reduction stage is carried out using Zinc-based Nitratest powder, and Nitratest tablet. The nitrite resulting from the reduction stage is determined by reaction with sulphanilic acid in the presence of N-(1-naphthyl)-ethylene diamine to form a reddish dye. The intensity of the colour produced is proportional to the nitrate concentration and is measured using a Palintest photometer. The Nitratest method will also respond to any nitrite present in the sample.

4.7.7 Dissolved organic carbon (DOC) determination

Dissolved organic carbon were measured using TOC analyzer in the Environmental Science Department.

Principle of operation

A continuous flow of water in the form of sample is pumped to the oxidation furnace by a peristaltic pump.
The analytical technique measures the difference in signal response of the sample, or standard, above the level of a blank. Potassium hydrogen phthalate (KHP) solutions were used as standard. The sample is pumped via a flow of surge device through a heated capillary inlet tube into a high temperature oxidation furnace where all the carbon is converted to carbon dioxide which is carried by nitrogen through a dryer mixed with hydrogen and reacted over a nickel catalyst. The carbon dioxide is reduced quantitative-

ly to methane which is dried and then measured using a conventional flame ionization detector (FID). The signal produced is proportional to the concentration of carbon in the sample.

4.8 Cleaning procedure

Beakers and watch glasses are soaked in a 5% v/v 'Decon 90' detergent solution for 24 hrs. The detergent is subsequently rinsed off and the glassware is placed in a bath of 20% v/v nitric acid in DDW. After soaking for at least 24 h, the acid is removed by copious rinsing with deionised water and the glassware is dried at 50 °C. It is stored wrapped in 'cling film' until used. This cleaning method was modified from Harper et al., (1989).

4.9 Analytical precision

Table 4.7 shows the analytical precision for all parameters measured as one standard deviation.

Table 4.7

Comparison of parameters analytical precision (standard deviation pooled over all seasons)

Pore water parameters	Analytical precision	Sediment parameters	Analytical precision
pH	0.11	Particle size <63 μm	2.0
Alkalinity meq\l	0.29	Organic matter (LOI) %	1.0
Chloride meq\l	5.9	TOC %	1.0
Sulphate meq\l	1.65	TON %	1.0
Conductivity mS cm^{-1}	0.5	Al g\kg	1.9
Phosphate μmol l^{-1}	0.9	Fe g\kg	1.2
Nitrate μmol l^{-1}	1.0	Mn g\kg	0.05
DOC mg\l	1.3	Cd mg\kg	0.02
Fe mg\l	0.2	Cu mg\kg	1.15
Mn mg\l	0.4	Ni mg\kg	1.4
Cd μg\l	0.1	Pb mg\kg	1.38
Cu μg\l	1.5	Hg mg\kg	0.12
Ni μg\l	1.5		
Pb μg\l	0.42		
Hg ng\l	5.1		

CHAPTER 5 RESULTS

CHAPTER 5 RESULTS

The results of the present investigation will be presented in three main parts as follows: (i) sediment results, (ii) pore water results and (iii) variations of sediment and pore water with depth.

The first part comprises the spatial and temporal sediment results of the following: site description, particle size, redox potential, organic matter (as loss on ignition), total organic carbon, total organic nitrogen, carbon to nitrogen ratio, major elements (aluminium, iron and manganese) and trace metals (lead, cadmium, copper, nickel and mercury).

The second part is the spatial and temporal pore water concentrations of hydrogen ion (pH), alkalinity, chloride, sulphate, conductivity, phosphate, nitrate, dissolved organic carbon, major elements (iron and manganese), and trace metals (lead, cadmium, copper, nickel, and mercury).

Finally, variations of sediment and pore water results with depth were investigated. Here, two stations were selected, namely, station B (Kennet) and station E (Bo'ness) were studied in detail.

At the end of the analysis, data were collated, analyzed and presented as pooled data of four readings per site and triplicate per reading, expressed as mean values of spatial and temporal variations.

The concentrations at first depth (surface) was compared with their respective mean values. This roughly showed the variations with depth. Detailed variations with depth are presented in a later section (section 5.2).

When discussing the temporal variations, the first four seasons were the main targets because they formed a complete annual temperature cycle. The other two seasons were kept for the sake of comparison.

Results are all recorded in Appendices A1-A33 at the end of the thesis.

5.1 Spatial and temporal variations

5.1.1 Results of sediments parameters

5.1.1.1 Sediment and sites description

Table 5.1 presents a description of the sediment cores at different stations and seasons. The predominant sediment feature of the Forth estuary were organic-rich clays with sand and sandy silt layers in some areas.

Station A (S.Alloa) was characterised by a soft brown mud mixed with deposited plant debris. This station was on the southern bank of the river and sampled together with station B (Kennet) by hand at low tide.

Station B (Kennet) was typified by a top 4 centimetres of brown mud, followed by a black mud layer. In this particular station, the mud was found to be compact. Station B was located on the northern side of the Forth river bank. At stations A and B particularly A, the depth of the Brown layer which could be an indication of oxic conditions was greater than those of other stations. This could be a function of the rate of accumulation of sediments.

Station C (G'mouth) and station D (Culross) shared similar properties in summer and autumn 1991, characterised by a fine black mud changing to sandy mud for the remaining seasons. Station C (G'mouth), was close to several sources of pollutants, including; Zeneca (formerly ICI) discharges, Longannet power station, Grangemouth Water Sewage Treatment Work and River Carron discharges.

At station D (Culross), the nearest sources of pollution could be the discharges from BP chemicals and refinery in addition to the discharges from river Avon.

At station E (Bo'ness), the sediment type was muddy throughout the seasons except in spring and autumn 1992 when it became sandy mud. The nearest source of contamination at this station was the effluent from British Petroleum Kinneil Gas Separation Plant.

Station F (P.Edgar) was generally typified by a fine grain sediment with a strong smell of hydrogen sulphide, indicating anoxic condition. This station was abandoned after the first sampling cruise which took place in summer 1991, due to the difficulty in obtaining a core and replaced with nearby site at the same location. The nearest sources of pollution at this station were the Dunfermline Sewage Works and South Queensferry Sewage Works in addition to Rosyth Base which could be responsible for a high lead concentration (FRPB, pers. comm.).

Table (5.1)

Sediment description at different stations and seasons

Stations	Summer 91	Autumn 91	Winter 92	Spring 92	Summer 92	Autumn 92
S.Alloa A	Top 5 cm grey layer, dark layer below. (tree leaves)	Fine brown mud	Top 5 cm grey mud, black mud mixed with tree leaves below.	Soft, grey mud mixed with tree leaves	Top 5 cm brown mud, mixed layers below	Light brown mud
kennet B	Top 4 cm brown layer, black layer below	Top 4 cm fine mud, black mud layer below	Top 4 cm gray mud, black mud below.	Top 6 cm brown grey mud ,black mud below	Top 3 cm brown mud, black mud below	Top 4 cm light brown mud mixed layers below
G'mouth C	1.5 cm brown mud, black mud below	Fine black mud	Top 6 cm sandy mud, black mud below	Sandy mud	N.A	Very shelly
Culross D	Top 5 cm mud/gravel, brown mud below	Top 2 cm shelly layer, brown mud below	Top 2 cm sand, 4 cm brown muddy sand, black layer below.	Top5cm sandy, black below.	N.A	Sandy top layer, mud below
Boness E	1 cm brown layer, 2 cm black layer then brown mud below	Top 1 cm brown layer, black layer below	Grey mud.	5 cm sandy mud, grey below.	Muddy sand	5 cm light brown mud, black below
P.Edgar F	0.5 cm layer of fine mud, 5 cm shelly mud then black mud below	Top 1 cm brown mud, black mud layer below	Brown mud.	Top 6cm brown muddy sand, black below, H2S smell.	Brown surface layer, black below	Blackmud, Sulphorous smell, (Strongly anoxic.

5.1.1.2 Particle size distribution

Table 5.2 shows the mean percentage of particle size < 63 µm in the sediment at each season for the six sampling sites. Spatially, Fig. 5.1.A1 shows the mean distribution of particle size in the Forth estuary. It indicates that the Forth estuary had a heterogeneous composition, showing fine particle sediment at stations A (S.Alloa) and E (Bo'ness) with around 76 % < 63 µm , a predominantly silt sediment with 91 % < 63 µm at station B (Kennet) and relatively sandy sediments at stations C (G'mouth), D (Culross) and F (P.Edgar) with around 60 % < 63 µm. It also shows slight variations between the surficial and the bulk particle size with depth for all the stations.

Figure 5.1.A2 shows the seasonal variation within each station. It illustrates the seasonal variability of particle size in the tidal stations (C, D, E and F) due probably to the difficulty of relocating sample sites exactly. This variability was not evident at stations A and B (intertidal stations) where there was little seasonal variation. These two stations were sampled by hand and were relocated easily.

Temporally, Fig. 5.1.B1 shows that the lowest values were in spring 1992. The overall mean value of grain size was found to be of the medium silt with a value of 70% < 63 µm and the overall range was between 15.5 and 98 %.

Insignificant or slight variation with depth was observed ($p > 0.05$). This was verified by the variation of particle size between the surficial and the bulk sediments (Fig. 5.1.A1).

Table 5.2

Mean percentage of particle size < 63 um in the sediment

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	83.63	97.13	76.38	56.38	79.88	26.25	69.94	61.58
Autumn 91	74.13	88.00	78.13	51.38	86.00	83.63	76.88	72.58
Winter 92	76.25	93.13	92.13	69.00	71.25	77.50	79.88	81.25
Spring 92	72.75	91.88	27.13	42.38	55.25	47.25	56.10	61.75
Summer 92	75.88	87.75	61.13	66.00	80.50	61.38	72.52	78.50
Autumn 92	72.50	89.63	20.25	65.00	89.38	51.50	64.71	59.83
Mean Spatial (Bulk)	75.85	91.25	59.19	58.35	77.04	57.92	70.00	
Mean Spatial (Surficial)	74.83	94.00	55.33	54.75	79.08	57.50	69.25	

Data derived from Appendix A1

Fig. 5.1.A1

Mean values of particle size in sediments at the six sampling sites

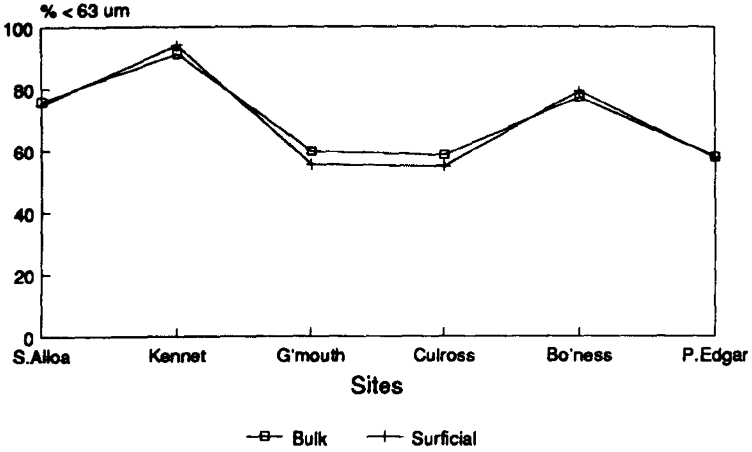


Fig. 5.1.A2

Seasonal variations of particle size in sediments at the six sampling sites

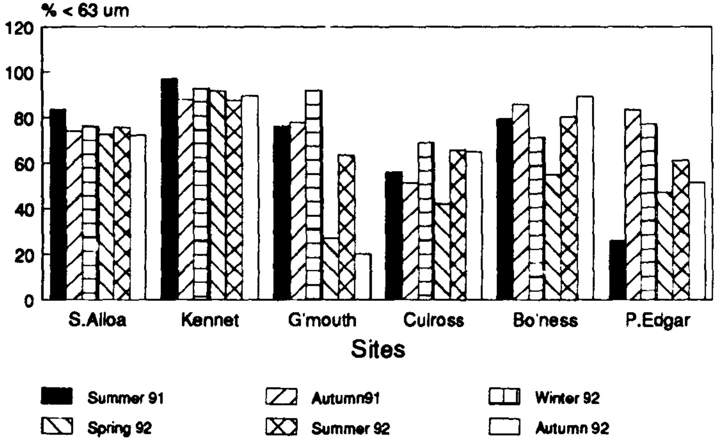


Fig. 5.1.B1

Mean values of particle size in sediments on the six sampling seasons

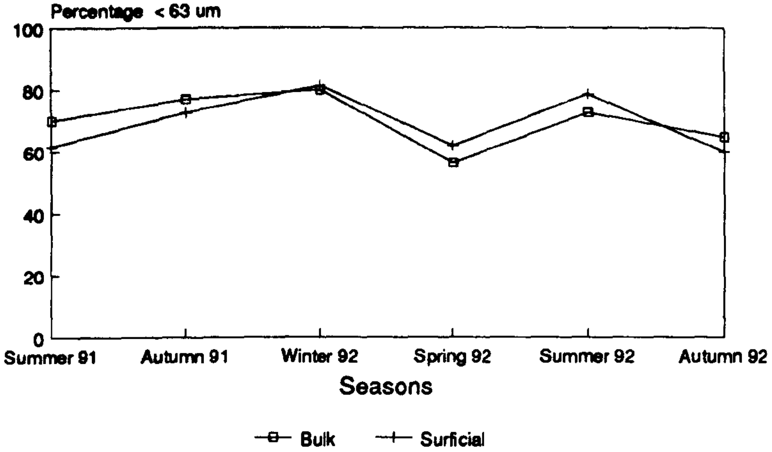
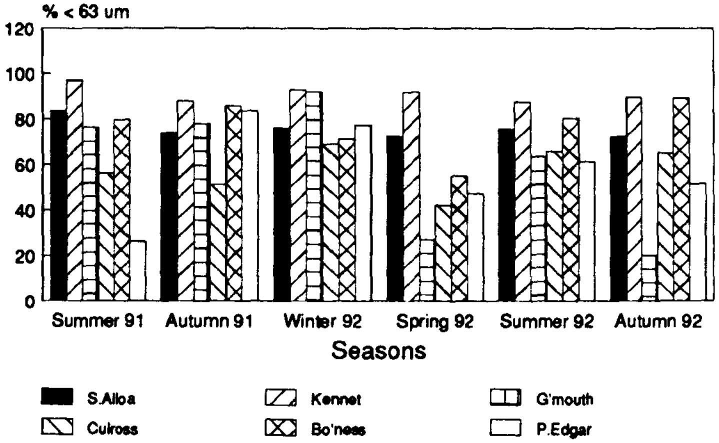


Fig. 5.1.B2

Spatial variations of paricle size in sediments on the six sampling seasons



5.1.1.3 Redox potential (*Eh*)

The depths (cm) of RPD (redox potential discontinuity) at which the sediment *Eh* = zero mV, where sediment changes from oxic to anoxic conditions are presented in Table 5.3.

The redox profile for the first four seasons at each of the six stations is illustrated in Fig. 5.2. The redox values showed a rapid decrease with depth at some stations to values below zero millivolt indicating anoxic conditions. However, station D in autumn 1991 remained well oxidized (Appendix A 30).

The redox profiles at stations A (S.Alloa) and B (Kennet) showed similar seasonal trend in the summer and autumn 1991. Anoxic conditions occurred as indicated by RPD values in table 5.3 at lower depths while in the spring season, anoxic condition was observed in the first 1.5 cm. In stations (C, D, E and F), higher redox potentials were observed ranged between -260 and 360 mV. the overall trend was fairly normal in that anoxic condition in the summer and autumn commenced at the first or second depth while in the winter and spring seasons, anoxic conditions started at greater depths except at station D in the winter.

The mean redox potential at each station (see Table 5.32) suggests that sediments at stations A, B, E and F were reducing with negative mean values (-19.75, -16, -19.92 and -13.63 mV respectively). The sediments of stations C and D were oxidizing having positive mean values (11.92 and 18.7 mV).

Table 5.3

Sediment depth where redox potential = 0 cm
Redox potential discontinuity (RPD)

Stations/	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
Seasons	A	B	C	D	E	F
Summer 91	5.50	4.50	2.00	4.20	2.50	2.00
Autumn 91	8.50	8.00	1.70	*	1.10	3.40
Winter 92	4.00	5.00	7.00	2.20	8.00	5.00
Spring 92	0.50	1.40	3.50	4.50	7.50	7.50
Summer 92	3.40	3.20	0.70	2.70	3.00	4.60
Autumn 92	3.50	1.50	2.00	5.00	1.00	0.00

* = sediment core is oxic

Data derived from Appendix A 30

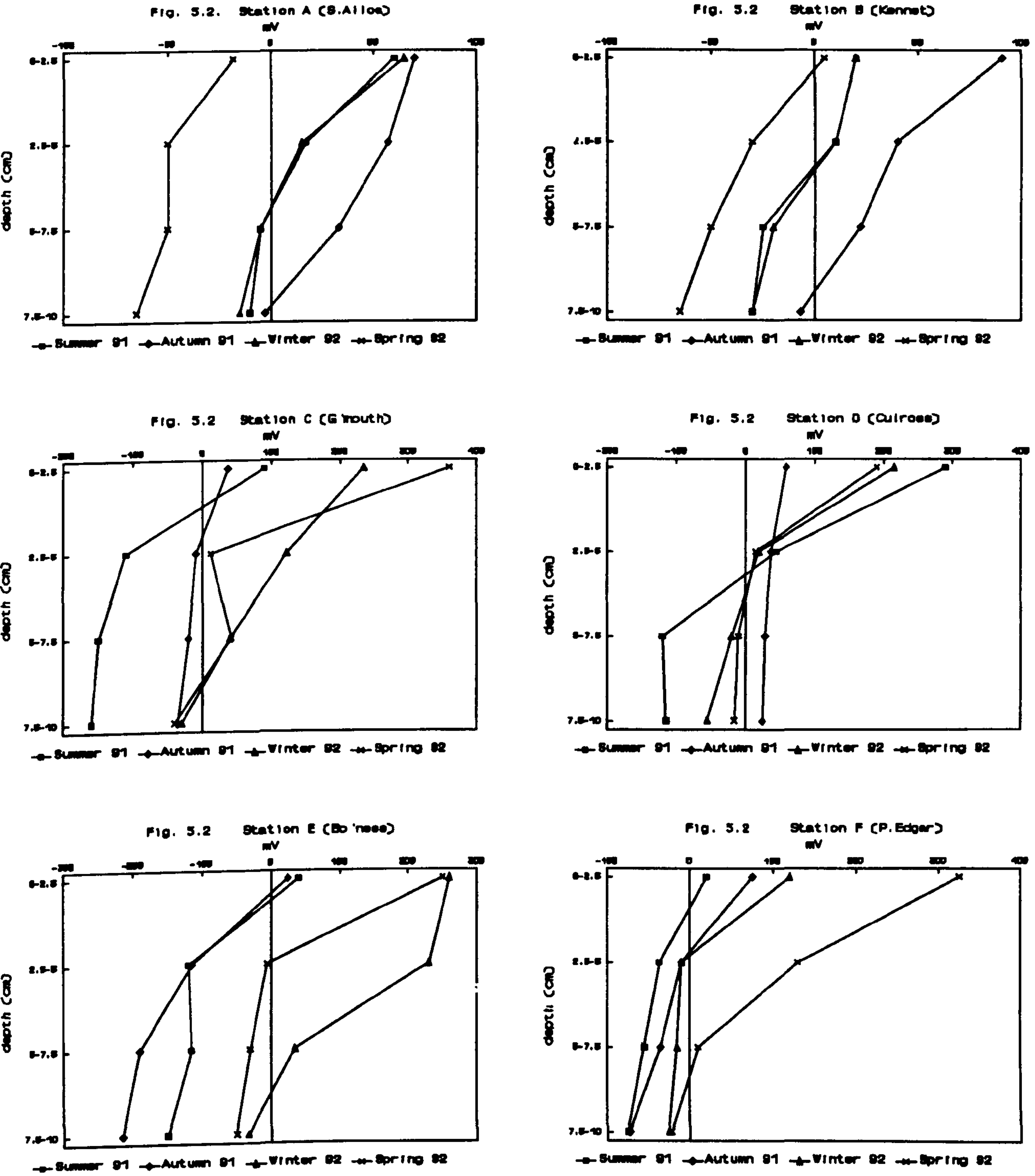


Fig. 5.2 Temporal variations of redox potential at the six sampling sites.

5.1.1.4 Organic matter (LOI, TOC, TON, and C:N)

Tables 5.4 and 5.5 show the mean values of organic matter (as loss on ignition) and total organic carbon (TOC). Figures 5.3.A1 and 5.4.A1 illustrate the mean values of LOI and TOC spatial distribution. Both showed similar trends with station A (S.Alloa) in the upper estuary and station E (Bo'ness) down the estuary showing the highest values (11.33% and 10.92%).

Organic matter (as LOI) contents ranged from 3% to 15% with a mean of 9.25% for the whole data set. The corresponding range for TOC was 0.68% to 9.27% with a mean of 3.68%.

A high correlation ($r = 0.9$ $p < 0.05$) between LOI and TOC was found. A strong correlation was observed between the organic matter (LOI, TOC) and particle size ($P < 0.05$).

Temporal variations (Figures 5.3.B1 and 5.4.B1) showed the lowest values in the spring season for both LOI and TOC (7.67 % and 3.24).

Organic matter LOI and TOC generally decreased with depth in the sediment cores. The extent of this decrease varied from station to station. This difference between surface and bulk sediment was clearest in station B (kennet) as shown in Figures 5.3.A1 and 5.4.B1. A strong correlation was observed between the organic matter (LOI, TOC) and particle size.

Total organic nitrogen (TON) data are shown in Table 5.6. Spatially, nitrogen contents were highest at stations A (S.Alloa), E (Bo'ness) and F (P.Edgar) (0.32%, 0.31% and 0.28%) as illustrated in Fig. 5.5.A. The spatial distribution of TON in the sediment was found to be strongly correlated with that of organic matter (r = 0.9).

The overall mean was 0.28% and the range was between 0.07 and 0.74%. A remarkable decrease with depth was observed in all stations. However, stations D and F remained constant (Fig. 5.5.A1).

Temporally, spring concentrations were the lowest (Fig. 5.5.B1). This was also observed in the LOI and TOC values of the sediments in this season. Significant decrease with depth was observed in the winter.

The carbon to nitrogen ratio is presented in Table 5.7. Gradual sea-ward decrease of C:N in the surface sediment was observed in the tidal stations (C-F) (Fig. 5.6.A). The overall mean ratio was 16.20 and the range was between 4.2 and 62.6 (Table 5.32).

Temporally, the highest C:N ratio (23.39%) was observed in the summer 1991 and the lowest (11.21%) in the autumn 1991 (Fig 5.6.B).

Table 5.4

Mean percentage of organic matter Loss On Ignition in the sediment

Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Seasons	A	B	C	D	E	F		
Summer 91	13.50	14.75	10.00	7.50	11.25	6.50	10.58	10.50
Autumn 91	12.25	10.00	7.25	5.00	12.75	10.75	9.67	10.17
Winter 92	10.50	11.75	12.25	8.50	10.50	9.75	10.54	10.83
Spring 92	12.50	7.75	4.00	5.25	8.75	7.75	7.67	8.50
Summer 92	11.50	8.00	8.75	8.75	10.75	8.50	9.38	10.67
Autumn 92	7.75	7.00	4.75	8.75	11.50	6.25	7.67	8.00
Mean Spatial (Bulk)	11.33	9.88	7.83	7.29	10.92	8.25	9.25	
Mean Spatial (Surficial)	11.33	12.67	8.00	7.67	11.00	8.00	9.78	

Data derived from Appendix A2

Fig. 5.3.A1

Mean values of organic matter (LOI) in sediments at the six sites

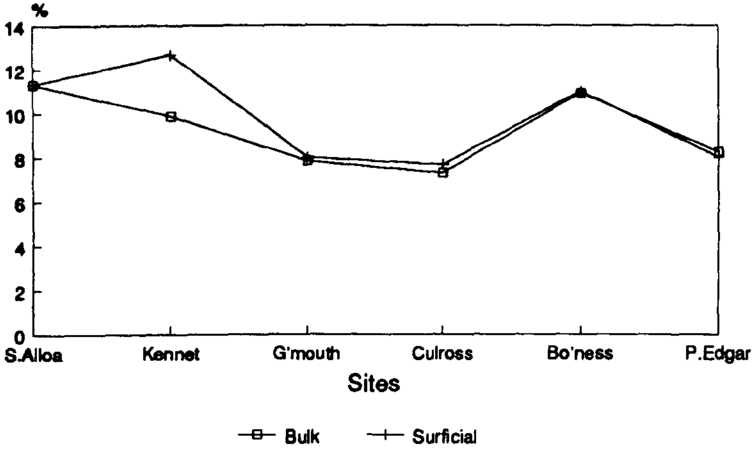


Fig. 5.3.A2

Seasonal variations of organic matter (LOI) in sediments at the six sites

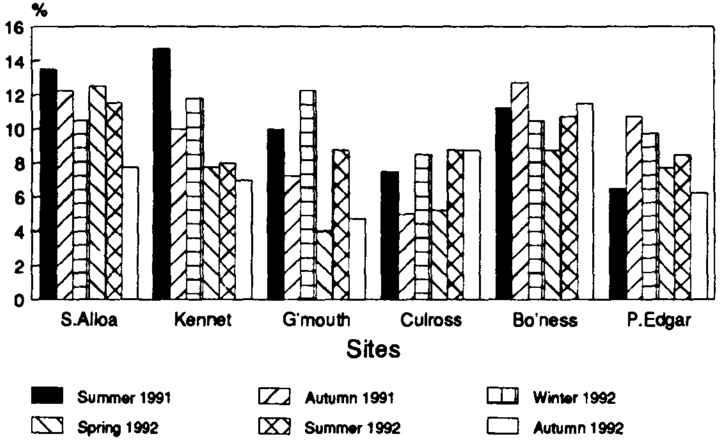


Fig. 5.3.B1

Mean values of organic matter (LOI) in sediments on the six seasons

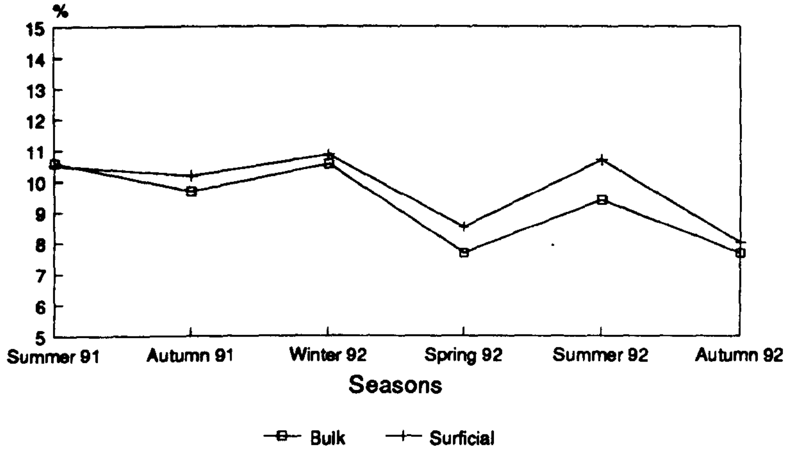


Fig. 5.3.B2

Spatial variations of organic matter (LOI) in sediments on the six seasons

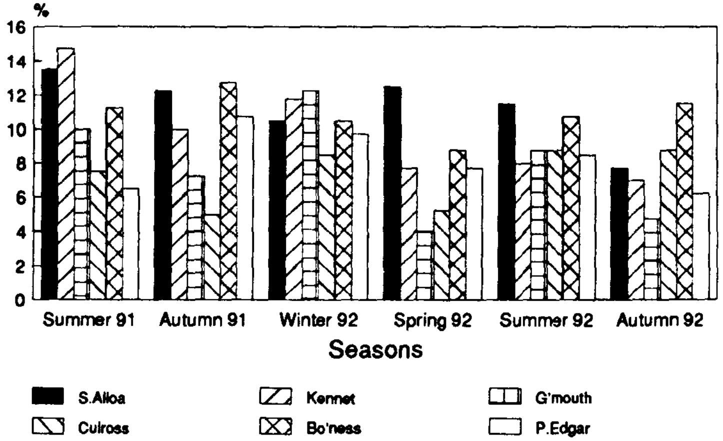


Table 5.5

Mean percentage of total organic carbon in the sediment

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	6.38	4.92	4.16	2.93	4.31	2.90	4.27	5.06
Autumn 91	4.90	4.30	2.10	1.98	5.39	4.13	3.80	4.07
Winter 92	4.69	4.00	4.36	3.40	3.72	3.47	3.94	4.23
Spring 92	5.63	2.74	2.51	2.28	3.20	3.06	3.24	3.79
Summer 92	4.31	2.68	3.74	3.22	4.02	2.68	3.44	4.02
Autumn 92	3.70	2.48	3.36	3.84	4.31	2.83	3.42	3.53
Mean Spatial (Bulk)	4.93	3.52	3.37	2.94	4.16	3.18	3.68	
Mean Spatial (Surficial)	5.56	4.62	3.78	3.44	4.14	3.17	4.12	

Data derived from Appendix A3

Fig. 5.4.A1

Mean values of TOC in sediments at the six sampling sites

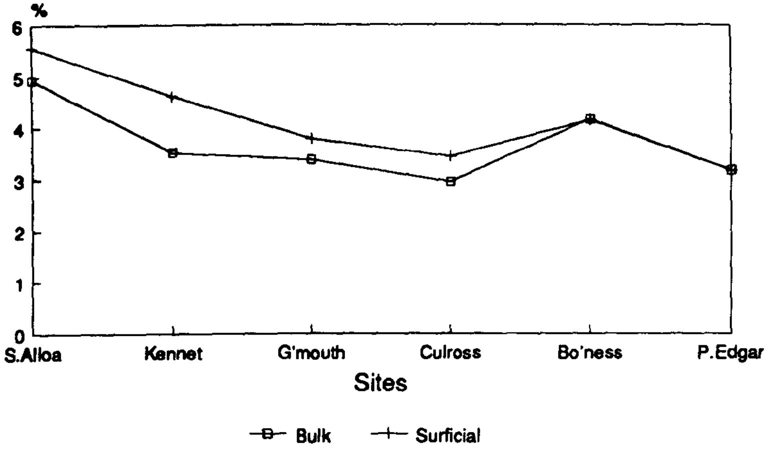


Fig. 5.4.A2

Seasonal variations of TOC in sediments at the six sampling sites

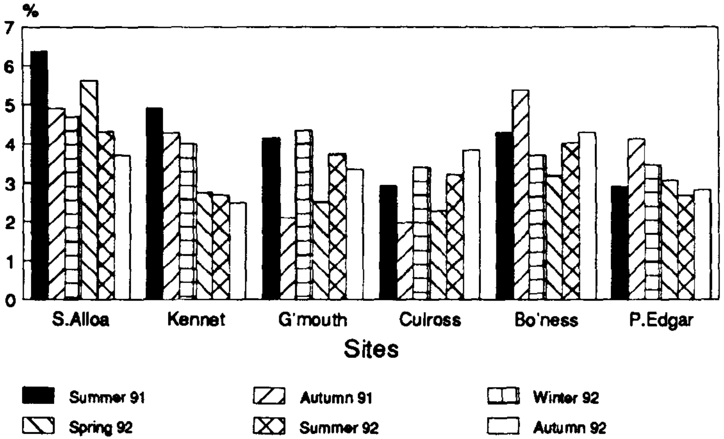


Fig. 5.4.B1

Mean values of TOC in sediments on the six sampling seasons

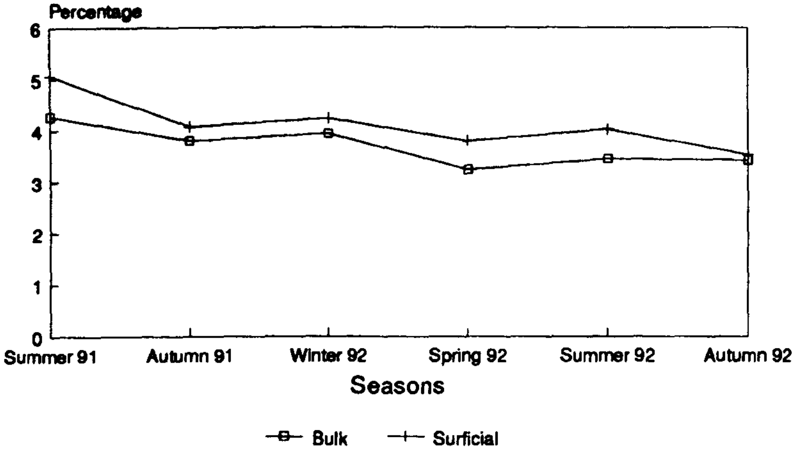


Fig. 5.4.B2

Spatial variations of TOC in sediments on the six sampling seasons

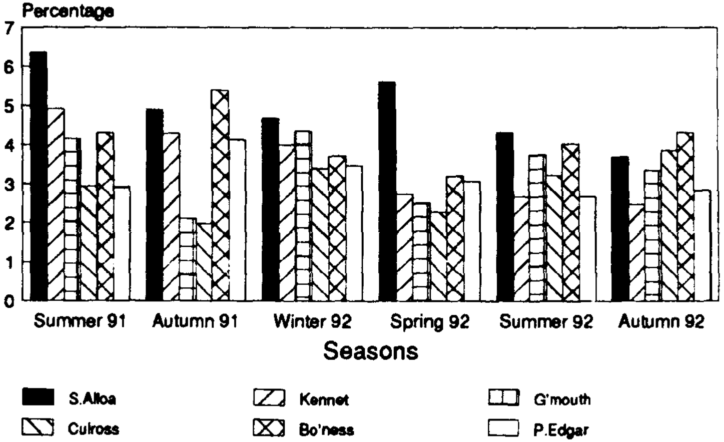


Table 5.6

Mean percentage of total organic nitrogen in the sediment

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	0.21	0.14	0.13	0.19	0.38	0.38	0.24	0.26
Autumn 91	0.49	0.40	0.32	0.28	0.43	0.38	0.38	0.38
Winter 92	0.42	0.45	0.43	0.26	0.36	0.34	0.37	0.48
Spring 92	0.25	0.15	0.15	0.09	0.14	0.13	0.15	0.17
Summer 92	0.25	0.23	0.20	0.17	0.22	0.16	0.20	0.25
Autumn 92	0.29	0.28	0.30	0.30	0.36	0.29	0.30	0.30
Mean Spatial (Bulk)	0.32	0.27	0.25	0.21	0.31	0.28	0.28	
Mean Spatial (Surficial)	0.35	0.35	0.30	0.22	0.34	0.28	0.31	

Data derived from Appendix A4

Fig. 5.5.A1

Mean values of TON in sediments at the six sampling sites

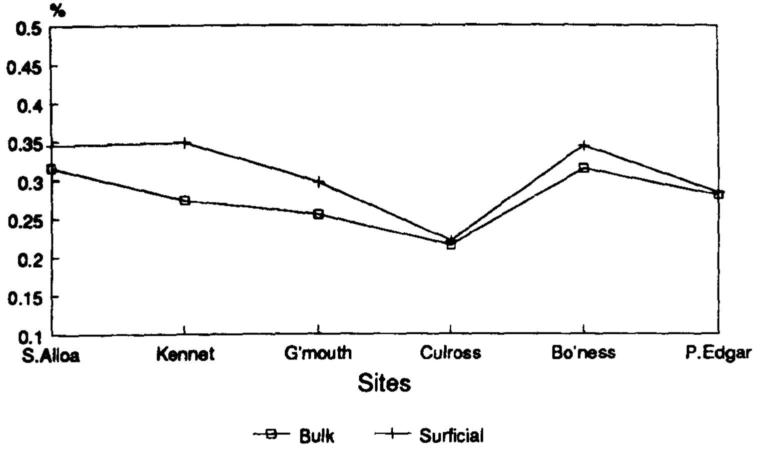


Fig. 5.5.A2

Seasonal variations of TON in sediments at the six sampling sites

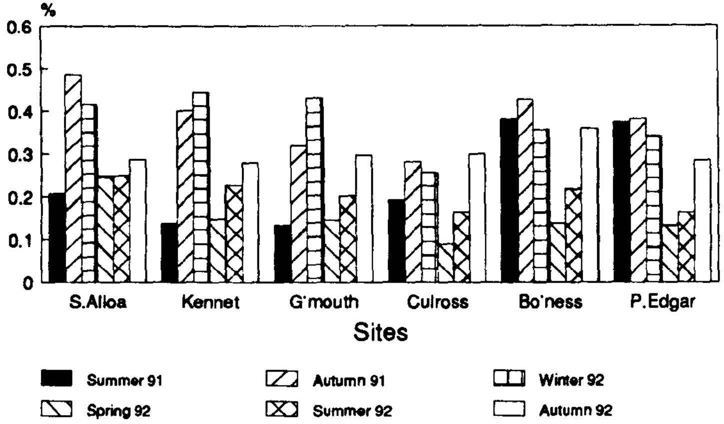


Fig. 5.5.B1

Mean values of TON in sediments
on the six sampling seasons

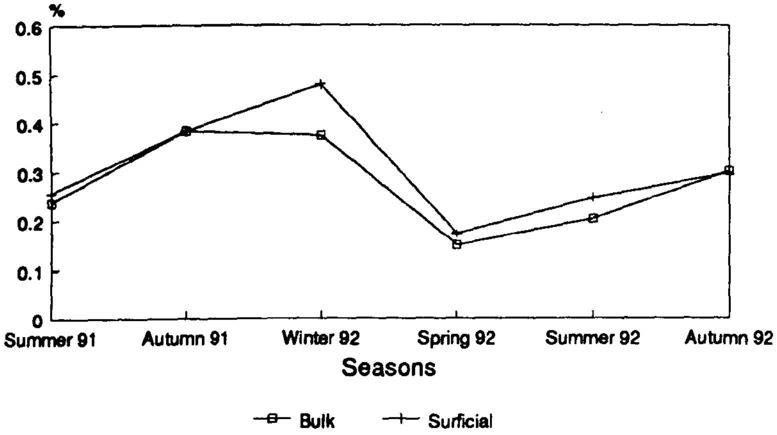


Fig. 5.5.B2

Spatial variations of TON in
sediments on the six sampling seasons

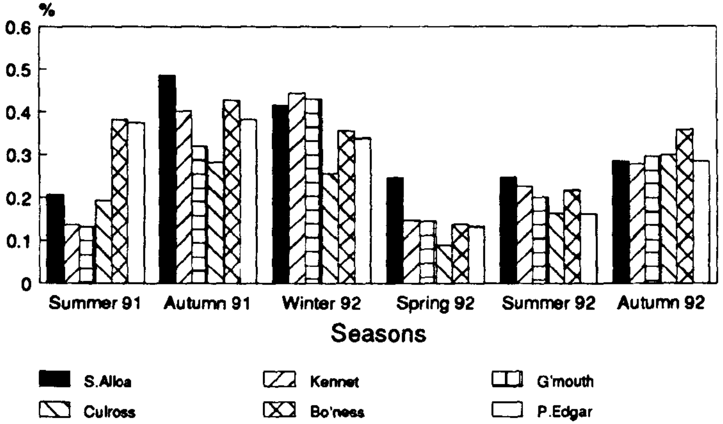


Table 5.7

Mean ratio of carbon : nitrogen in the sediment

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	31.14	40.11	32.36	17.33	11.58	7.80	23.39	21.89
Autumn 91	10.98	10.12	6.67	7.22	12.89	10.82	9.78	10.70
Winter 92	12.27	8.77	11.98	17.14	12.11	11.62	12.32	9.35
Spring 92	23.23	19.06	23.50	24.56	25.81	23.30	23.24	23.81
Summer 92	17.16	11.92	18.71	19.71	18.84	17.26	17.27	16.98
Autumn 92	12.92	8.59	11.24	12.97	11.95	9.59	11.21	11.62
Mean Spatial (Bulk)	17.95	16.43	17.41	16.49	15.53	13.40	16.20	
Mean Spatial (Surficial)	18.56	14.89	17.61	18.93	12.65	11.73	15.73	

Data derived from Appendix A5

Fig. 5.6.A1

Mean values of Carbon:Nitrogen in sediments at the six sampling sites

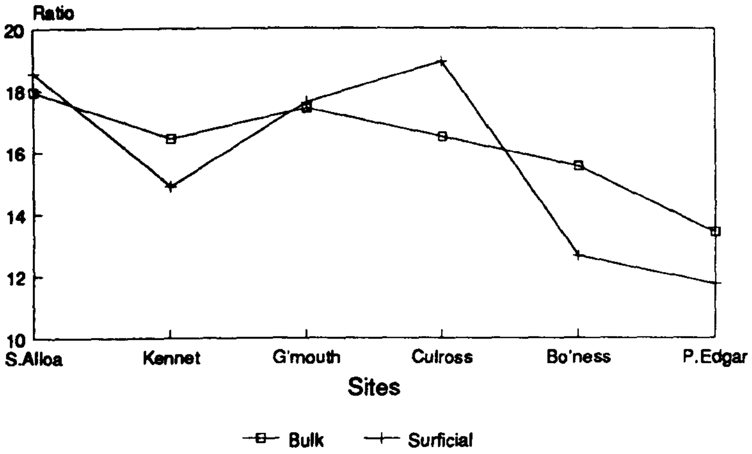


Fig. 5.6.A2

Seasonal variations of Carbon:Nitrogen in sediments at the six sites

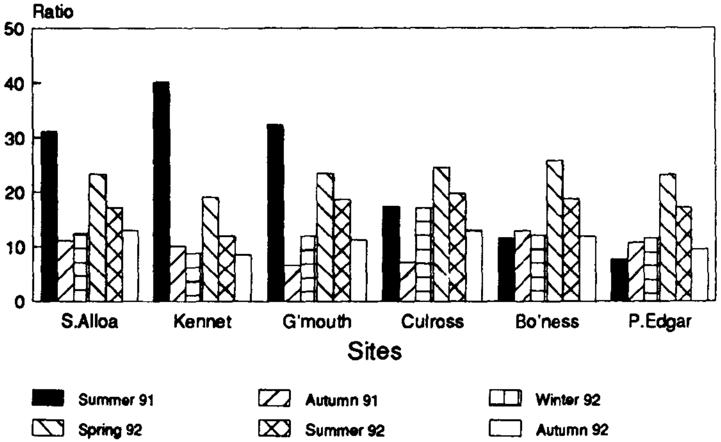


Fig. 5.6.B1

Mean values of Carbon:Nitrogen in sediments on the six sampling seasons

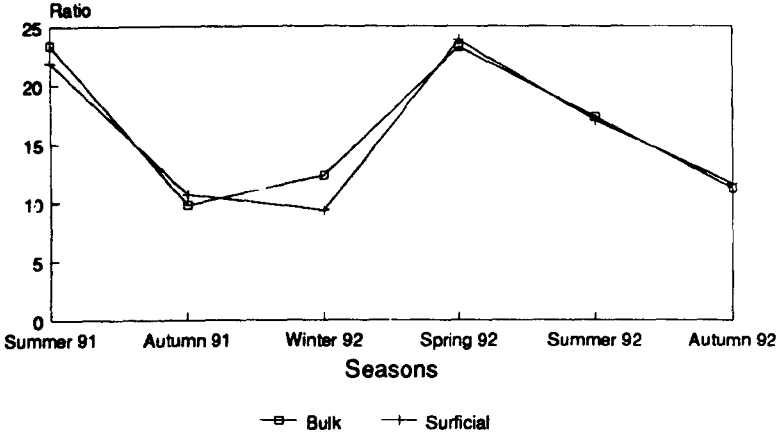
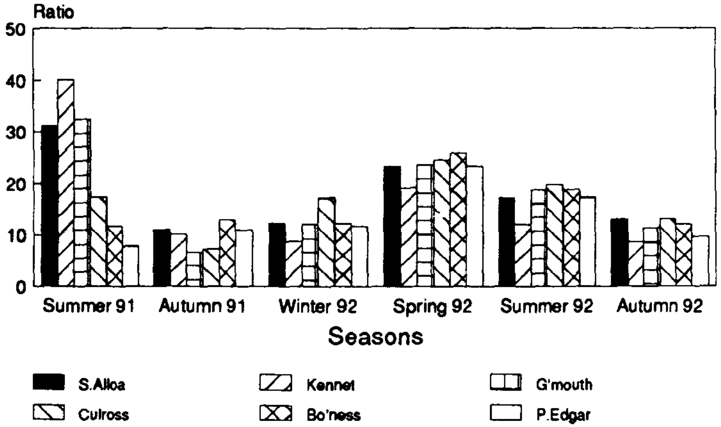


Fig. 5.6.B2

Spatial variations of Carbon:Nitrogen in sediments on the six sampling seasons



5.1.1.5 Major elements (aluminium, iron and manganese)

Table 5.8 shows the mean concentrations of aluminium as also illustrated in Fig. 5.7. Spatially, station B (Kennet) recorded the highest concentration (7.98%), while station D (Culross) and station F (P.Edgar) had the lowest concentration (6.18% and 6.41%) (Fig. 5.7.A1). The overall mean was 7.1% and the range was between 4.3 and 8.9%. Temporally, the spring season had the lowest concentration with a value of 6.56% (Fig. 5.7.B1).

Iron and manganese data are shown in Tables 5.9 and 5.10. Spatially, the lowest concentration of iron was recorded at station D (Culross) and F (P.Edgar) (24.34 and 26.2 g/kg) (Fig. 5.8.A1). Manganese recorded its highest level at stations C (G'mouth) (0.75 g/kg) and E (Bo,ness) (0.78 g/kg)) (Fig. 5.9.A1). The lowest value of 0.48 g/kg was observed at station D (Culross).

The overall mean was 29.5 g\kg for iron, 0.63 g\kg for manganese and the overall range was between 16.0 and 44.0 g\kg, and between 0.23 and 1.2 g\kg for iron and manganese respectively.

Iron and manganese were found to be highly correlated both spatially ($r = 0.67$) and temporally ($r = 0.9$).

Temporally, iron and manganese recorded a remarkable decrease in the spring season with values of 25.88 g/kg for iron and 0.47 g/kg for manganese (Figs. 5.8.B and 5.9.B). Iron showed a strong correlation with organic matter and particle size < 63 μm ($r = 0.7$).

A random insignificant increase or decrease with depth was observed in all the stations for all major elements. This was verified by anova value of $p > 0.05$.

The mean ratio of iron to aluminium in sediments is presented in Table 5.36. The overall mean ratio of iron to aluminum in the Forth estuary was found to be 0.42. A reasonably consistent distribution of Fe/Al was observed in all stations. However, station A (S.Alloa) and station C (G'mouth) recorded the highest values of 0.44 for both.

No obvious spatial or temporal trend was observed, suggesting that the iron was held in structural position within the alumino-silicates.

Table 5.8

Mean concentrations of Aluminium in the sediments %

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	7.63	8.48	7.20	6.08	7.90	4.73	7.00	6.55
Autumn 91	7.55	7.88	7.35	5.90	7.58	7.75	7.33	6.97
Winter 92	7.23	8.25	8.28	6.90	7.35	6.58	7.43	7.33
Spring 92	6.85	7.33	5.60	5.85	7.18	6.58	6.56	6.50
Mean Spatial (Bulk)	7.31	7.98	7.11	6.18	7.50	6.41	7.08	
Mean Spatial (Surficial)	7.00	8.35	6.45	5.85	6.85	6.53	6.84	

Data derived from Appendix A6

Fig. 5.7.A1

Mean concentrations of Aluminium in sediments at the six sites

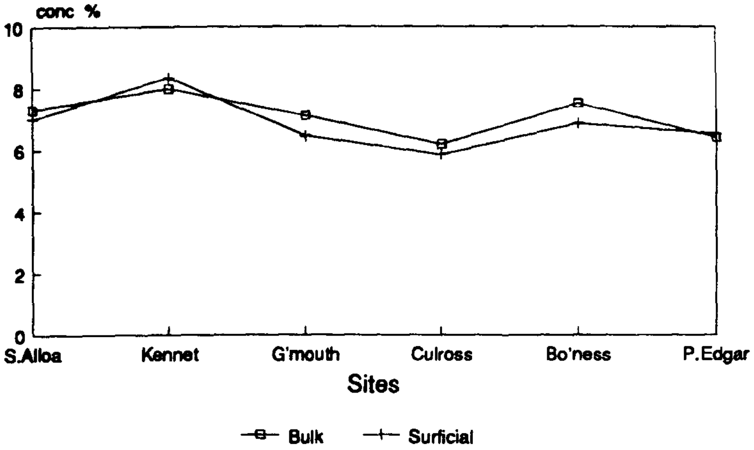


Fig. 5.7.A2

Seasonal variations of Aluminium in sediments at the six sites

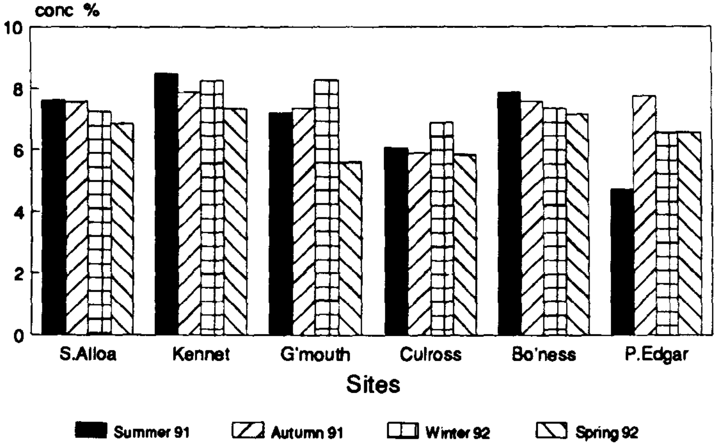


Fig. 5.7.B1

Mean concentrations of Aluminium in sediments on the six seasons

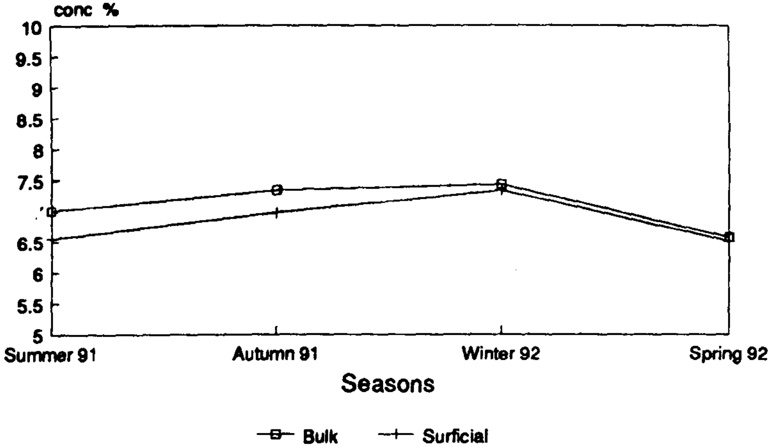


Fig. 5.7.B2

Spatial variations of Aluminium in sediments on the six seasons

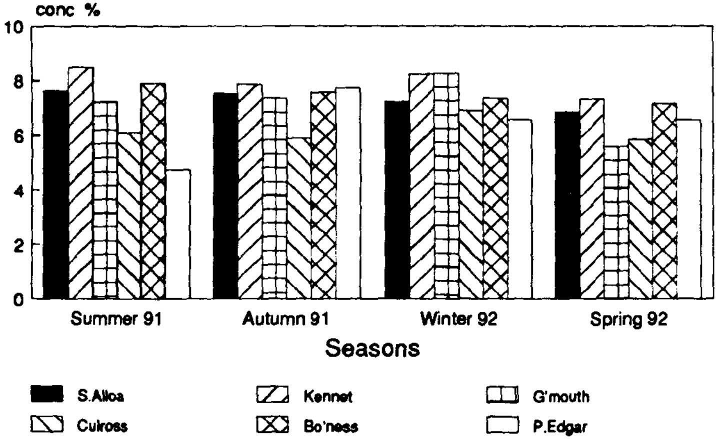


Table 5.9

Mean concentrations of Iron in the sediments g\kg

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	38.00	36.75	31.75	25.75	32.50	18.25	30.50	28.67
Autumn 91	29.75	31.75	32.25	25.00	30.75	31.75	30.21	29.83
Winter 92	30.50	35.00	36.25	28.00	33.50	32.50	32.63	32.17
Spring 92	30.25	30.25	24.25	18.50	28.75	23.25	25.88	27.17
Summer 92	30.00	31.92	30.30	25.18	30.54	25.14	28.85	30.37
Autumn 92	25.72	28.99	32.19	23.61	36.79	26.34	28.94	28.48
Mean Spatial (Bulk)	30.70	32.44	31.17	24.34	32.14	26.20	29.50	
Mean Spatial (Surficial)	29.90	35.23	30.97	23.49	31.53	25.57	29.45	

Data derived from Appendix A7

Fig. 5.8.A1

Mean concentrations of Iron in sediments at the six sites

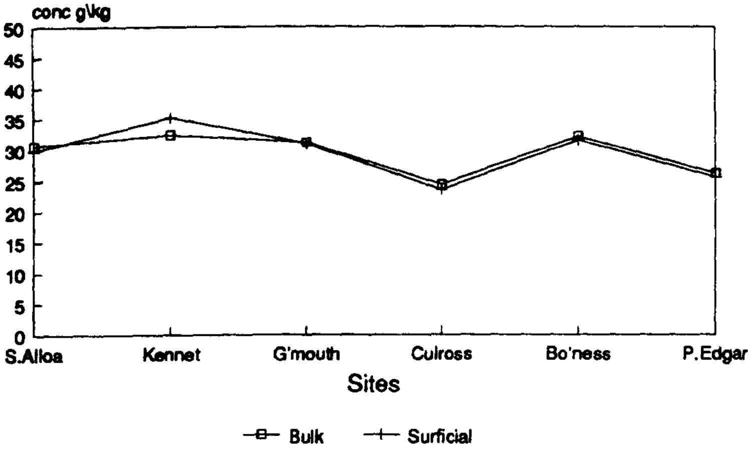


Fig. 5.8.A2

Seasonal variations in mean Iron in sediments at the six sites

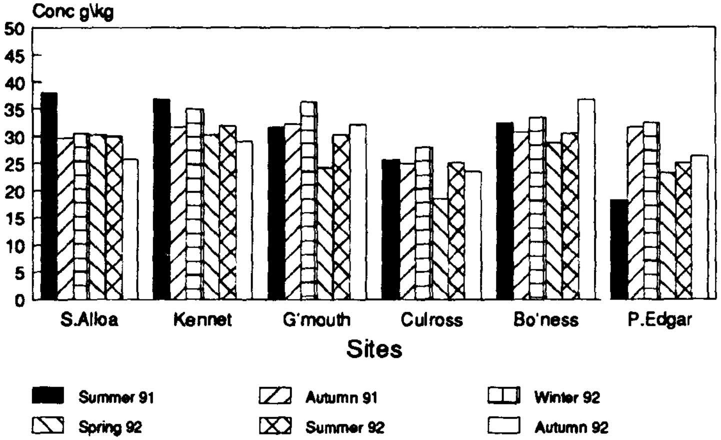


Fig. 5.8.B1

Mean concentrations of Iron in sediments
on the six sampling seasons

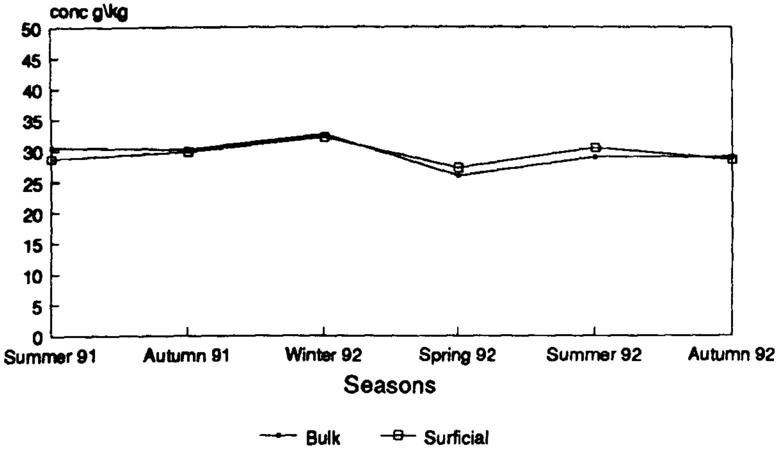


Fig. 5.8.B2

Spatial variations of Iron in sediments
on the six sampling seasons

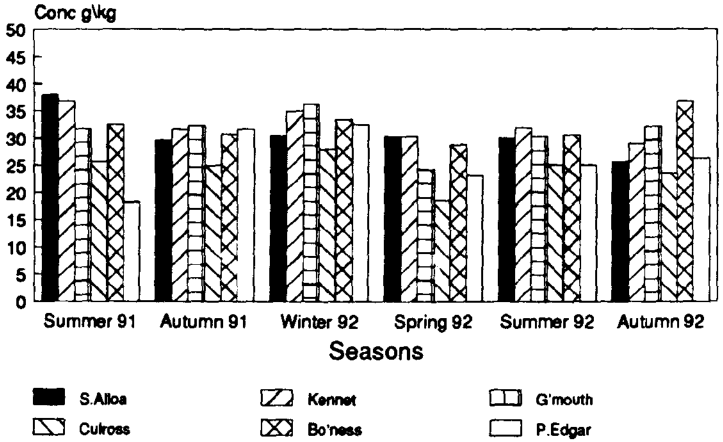


Table 5.10

Mean concentrations of Manganese in the sediments g\kg

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	0.76	0.43	0.93	0.52	0.95	0.57	0.69	0.64
Autumn 91	0.65	0.74	0.64	0.45	0.82	0.70	0.67	0.68
Winter 92	0.63	0.73	0.75	0.51	0.80	0.61	0.67	0.59
Spring 92	0.49	0.40	0.57	0.34	0.60	0.44	0.47	0.46
Summer 92	0.73	0.73	0.73	0.73	0.76	0.76	0.74	0.65
Autumn 92	0.36	0.40	0.91	0.34	0.73	0.44	0.53	0.52
Mean Spatial (Bulk)	0.60	0.57	0.75	0.48	0.78	0.59	0.63	
Mean Spatial (Surficial)	0.51	0.61	0.65	0.47	0.73	0.57	0.59	

Data derived from Appendix A8

Fig. 5.9.A1

Mean concentrations of Manganese in sediments at the six sites

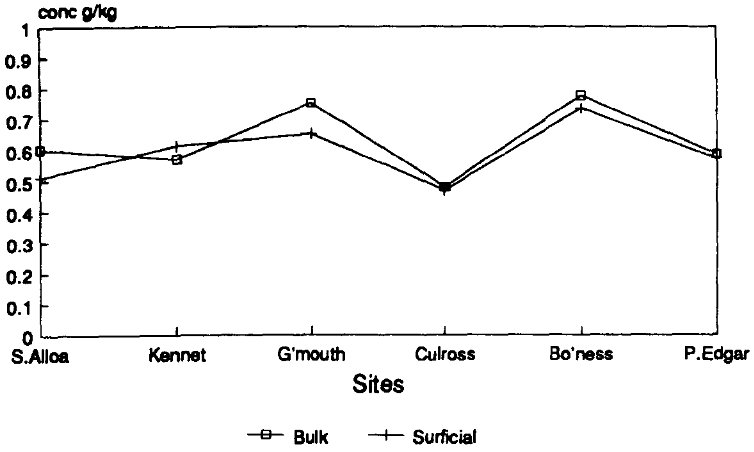


Fig. 5.9.A2

Seasonal variations in Manganese in sediments at the six sites

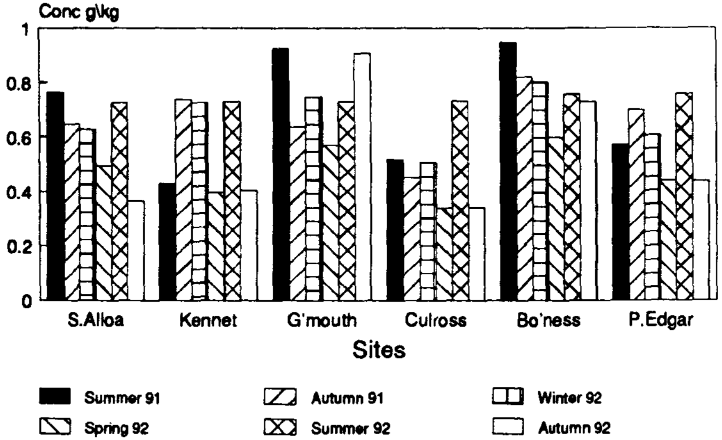


Fig. 5.9.B1

Mean concentrations of Manganese in sediments on the six seasons

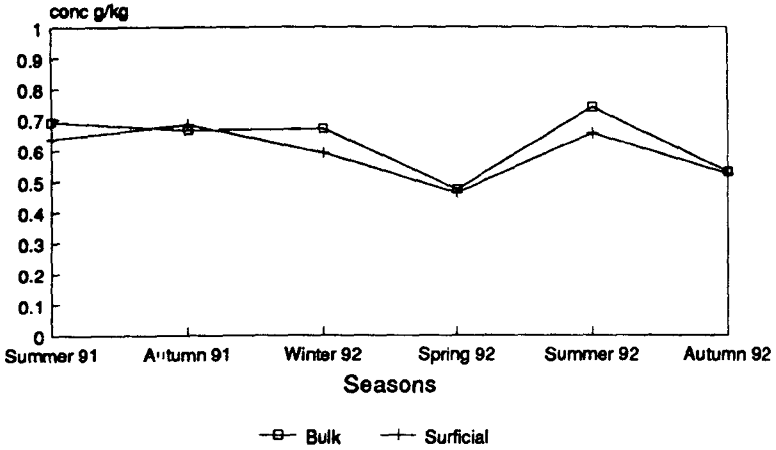


Fig. 5.9.B1

Spatial variations of Manganese in sediments on the six seasons

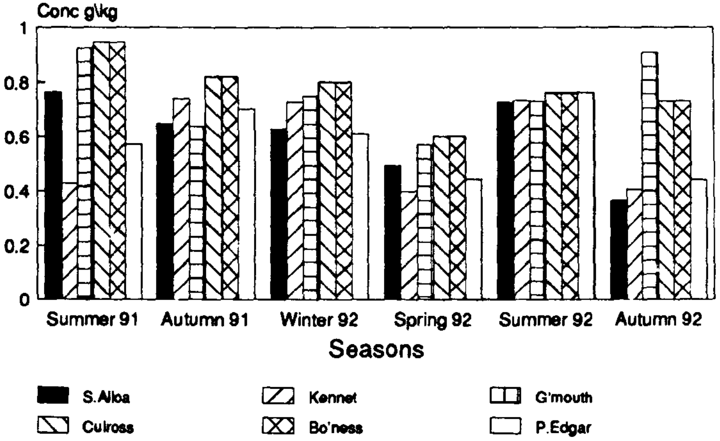


Table 5.36

Mean ratio of Iron : Aluminium in the sediments

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal
Summer 91	0.50	0.43	0.44	0.42	0.41	0.39	0.43
Autumn 91	0.39	0.40	0.44	0.42	0.41	0.41	0.41
Winter 92	0.42	0.42	0.44	0.41	0.46	0.50	0.44
Spring 92	0.44	0.42	0.44	0.32	0.40	0.36	0.40
Mean Spatial	0.44	0.42	0.44	0.39	0.42	0.41	0.42

Data derived from Appendix A33

5.1.1.6 Trace metals (Pb, Cu, Hg, Cd, and Ni)

Lead concentrations in the sediments are shown in Table 5.11. Fig. 5.10.A1,A2 shows the mean spatial distribution. The low concentrations were found in the middle of the estuary at stations C (G'mouth) and D (Culross) (49.9 and 44.3 mg/kg). High concentrations (> 65 mg/kg) were recorded at stations A (S.Alloa), B (Kennet) in the upper estuary and at stations E (Bo'ness) and F (P.Edgar) in the lower estuary. However, the elevated concentration recorded at stations B was in the surficial sediment. This trend is similar to that of the particle size and many other metals in the study area. The overall mean concentration of lead was found to be 56.9 mg/kg and the overall range was between 8.0 and 179 mg/kg.

Spatially, copper and lead showed a high correlation ($r = 0.94$), in addition lead correlated well with mercury ($r = 0.74$). Obvious trend with depth was noticed at station B (Kennet) where lead concentration decreased with depth, in contrast with station F (P.Edgar) where it increased with depth (Fig. 5.10.A1). Anova results showed no significant seasonal variation ($p > 0.05$), as depicted in Fig. 5.10.B1.

The behaviour of cadmium in the sediment is shown in Table 5.12. Cadmium showed both spatial and temporal distributions. Spatially, cadmium concentrations were high at station A (S.Alloa) giving a mean concentration of 0.35 mg/kg. In the other stations, mean cadmium concentrations varied between 0.17 and 0.21 mg/kg (Fig. 5.11.A). Spatially, cadmium correlated well with nickel.

The overall mean concentration was 0.22 mg/kg and the overall range was between 0.07 and 0.7 mg/kg. Again, no obvious variation with depth was noticed except at station B (Kennet) where concentration decreased with depth. Temporally, cadmium showed a gradual decline towards the cold seasons (i.e winter and spring) and recorded the highest concentration in the summer season (Fig. 5.11.B).

Table 5.13 presents the behaviour of copper concentrations in the study area. Spatially, Fig. 5.12.A shows high concentrations of copper in station A (S.Alloa), station E (Bo'ness) and station F (P.Edgar). station B (Kennet) recorded its highest concentration of 54.3 mg/kg in the surficial sediment while station F (P.Edgar) recorded its highest value deep in the sediment.

The overall mean of copper concentrations was found to be 38.9 mg/kg and the overall range was between 3.3 and 267.0 mg/kg (Appendix A11). Spatially, copper correlated positively with all trace metals.

Temporally, the highest mean temporal bulk concentration of copper was recorded in the summer season 1991 with a value of 52.69 mg/kg (Fig. 5.12.b). This variation could be attributed to the exceptionally high concentration measured in summer 91 at station F (P.Edgar) of 267.0 mg/kg (Appendix A 11). Temporally, copper concentrations correlated strongly and positively with all other metals ($p < 0.05$).

Table 5.14 shows the average spatial and temporal variations of nickel concentrations in the sediments. Spatially, Fig. 5.13.A showed that there was no significant variation in nickel concentrations ($p > 0.05$). However, High concentrations were found in stations A (S.Alloa) and B (Kennet) (the intertidal stations). Spatially, nickel was found to be highly correlated with iron and aluminium in the sediments ($r = 0.86$ and 0.9 respectively). The overall mean was 33.7 mg/kg and the range was between 15.5 and 52.3 mg/kg. The same seasonal trend was observed in the spring with the low nickel concentrations (Fig. 5.13.B). Seasonally, nickel showed high correlations with all other metals.

Table 5.15 shows the variation of mercury concentrations. Fig. 5.14.A shows the spatial variation of mercury with a peak concentration at station E (Bo'ness) with a value of 2.58 mg/kg while station D (Culross) recorded the lowest concentration with a value of 1.31 mg/kg. The overall mean of mercury concentration was found to be 1.9 mg/kg and the overall range was between 0.2 and 4.9 mg/kg. Temporally, Fig. 5.14.B depicts mercury concentrations, decreasing markedly in the spring season.

Table 5.11

Mean concentrations of Lead in the Sediment mg\kg

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	71.00	70.00	47.50	36.50	63.00	87.00	62.50	54.17
Autumn 91	61.73	47.68	38.70	24.45	76.75	72.68	53.66	59.82
Winter 92	59.65	56.68	57.98	40.70	55.88	61.95	55.47	57.43
Spring 92	73.55	53.05	45.60	41.43	64.58	77.53	59.29	64.53
Summer 92	64.15	24.05	63.40	52.28	64.73	45.70	52.38	57.72
Autumn 92	64.78	38.80	46.30	70.60	69.43	58.73	58.10	56.42
Mean Spatial (Bulk)	65.81	48.38	49.91	44.33	65.73	67.26	56.90	
Mean Spatial (Surficial)	62.85	68.63	52.32	46.38	63.90	56.00	58.35	

Data derived from Appendix A9

Fig. 5.10.A1

Mean concentrations of Lead in sediments at the six sampling sites

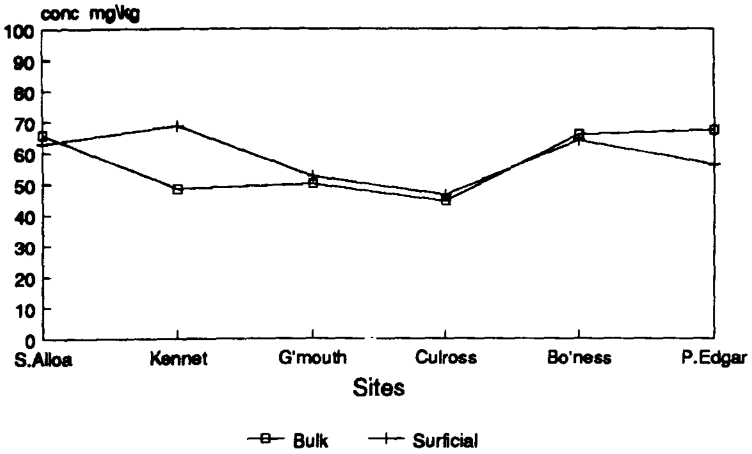


Fig. 5.10.A2

Seasonal variations of Lead in sediments at the six sampling sites

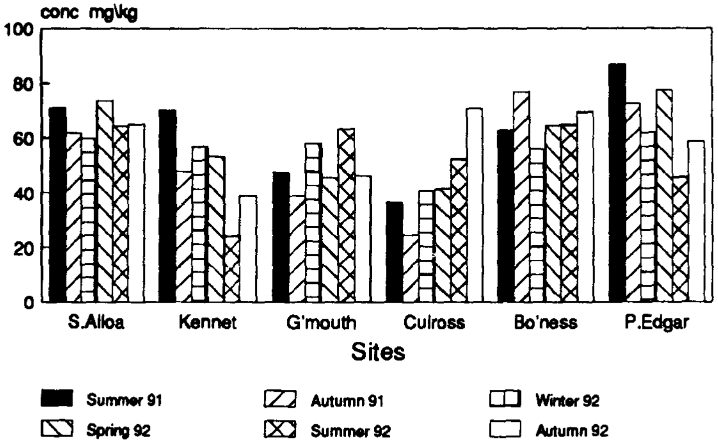


Fig. 5.10.B1

Mean concentrations of Lead in sediments on the six sampling seasons

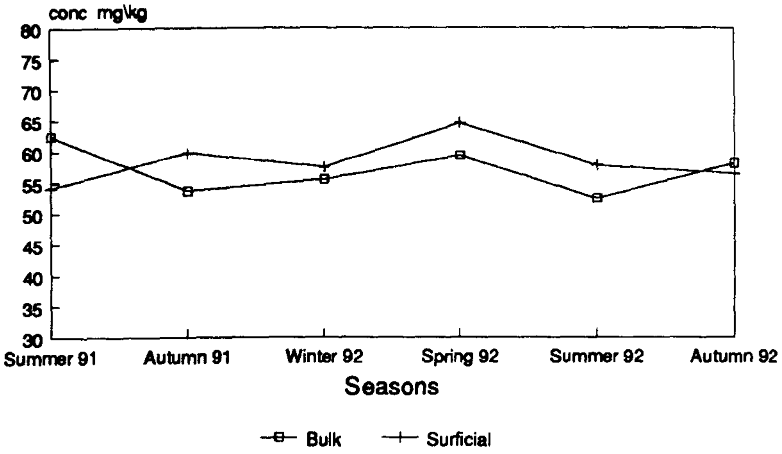


Fig. 5.10.B2

Spatial variations of Lead in sediments on the six sampling seasons

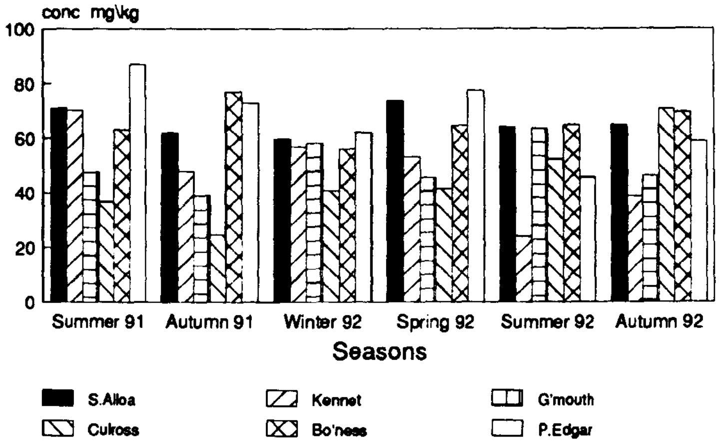


Table 5.12

Mean concentrations of Cadmium in the sediment mg\kg

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	0.30	0.22	0.21	0.23	0.32	0.29	0.26	0.27
Autumn 91	0.37	0.29	0.19	0.18	0.28	0.23	0.25	0.26
Winter 92	0.50	0.28	0.12	0.15	0.14	0.10	0.21	0.23
Spring 92	0.35	0.21	0.11	0.11	0.12	0.14	0.17	0.19
Summer 92	0.32	0.12	0.27	0.31	0.24	0.15	0.23	0.23
Autumn 92	0.29	0.15	0.12	0.17	0.19	0.11	0.17	0.19
Mean Spatial (Bulk)	0.35	0.21	0.17	0.19	0.21	0.17	0.22	
Mean Spatial (Surficial)	0.38	0.28	0.15	0.19	0.20	0.17	0.23	

Data derived from Appendix A10

Fig. 5.11.A1

Mean concentrations of Cadmium in sediments at the six sampling sites

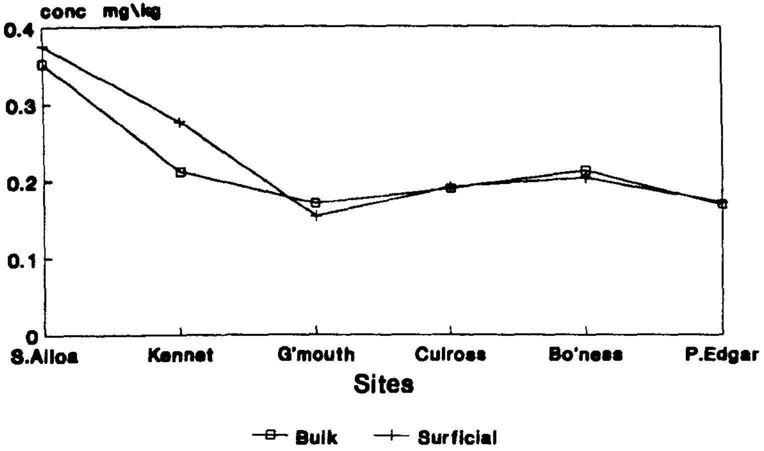


Fig. 5.11.A2

Seasonal variations of Cadmium in sediments at the six sampling sites

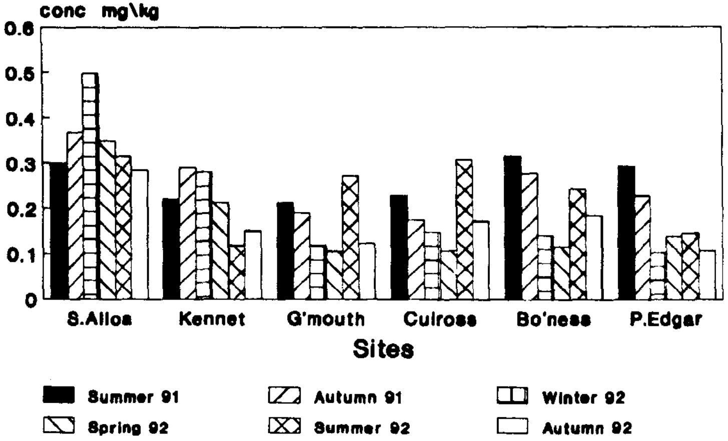


Fig. 5.11.B1

Mean concentrations of Cadmium in sediments on the six sampling seasons

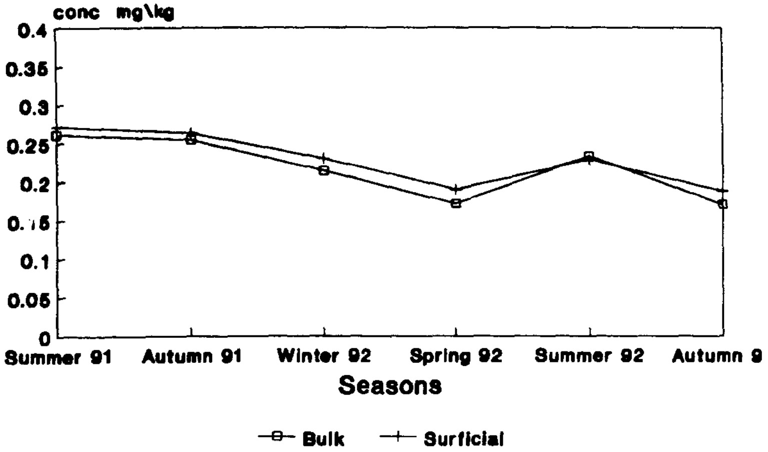


Fig. 5.11.B2

Spatial variations of Cadmium in sediments on the six sampling seasons

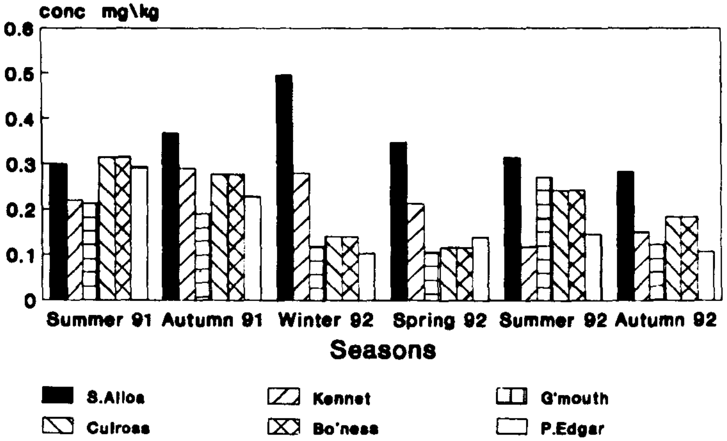


Table 5.13

Mean concentrations of Copper in the sediment mg\kg

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	63.88	61.08	34.63	20.38	51.80	84.35	52.69	40.42
Autumn 91	43.50	36.08	30.55	12.70	62.45	38.13	37.23	44.35
Winter 92	44.18	46.98	38.80	30.15	41.80	34.63	39.42	40.92
Spring 92	47.93	27.43	19.58	17.63	35.28	58.53	34.39	34.82
Summer 92	46.95	25.40	38.58	38.95	54.63	30.40	39.15	44.12
Autumn 92	45.70	20.38	12.20	27.00	49.65	27.15	30.35	35.42
Mean Spatial (Bulk)	48.69	36.22	29.06	24.47	49.27	45.53	38.87	
Mean Spatial (Surficial)	48.53	54.30	33.60	26.52	47.68	29.40	40.01	

Data derived from Appendix A11

Fig. 5.12.A1

Mean concentrations of Copper in sediment at the six sampling sites

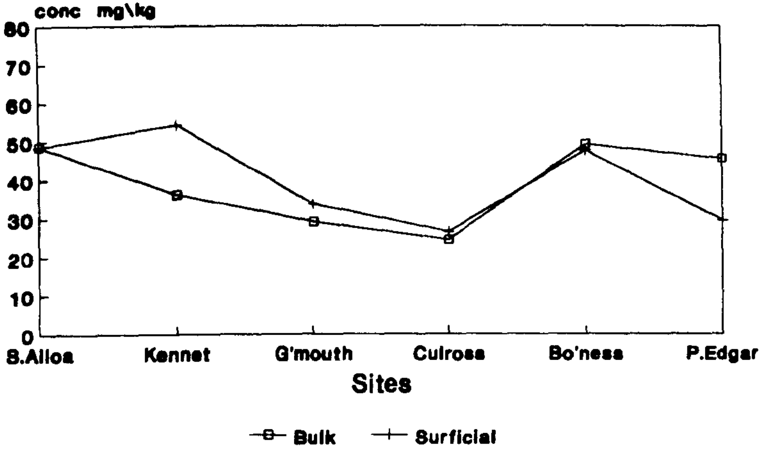


Fig. 5.12.A2

Seasonal variations of Copper in sediments at the six sampling sites

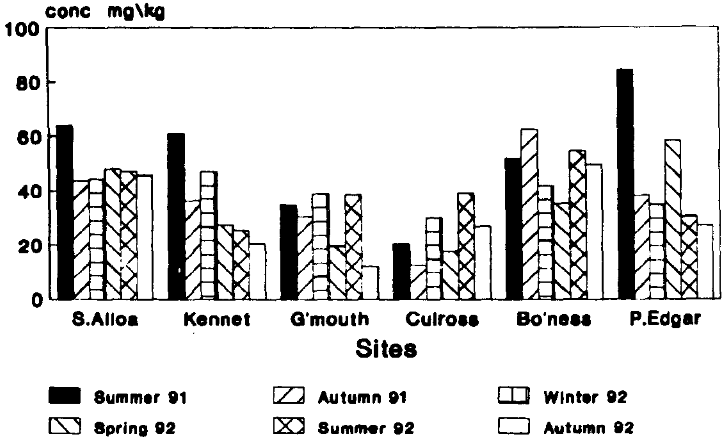


Fig. 5.12.B1

Mean concentrations of Copper in sediments on the six sampling seasons

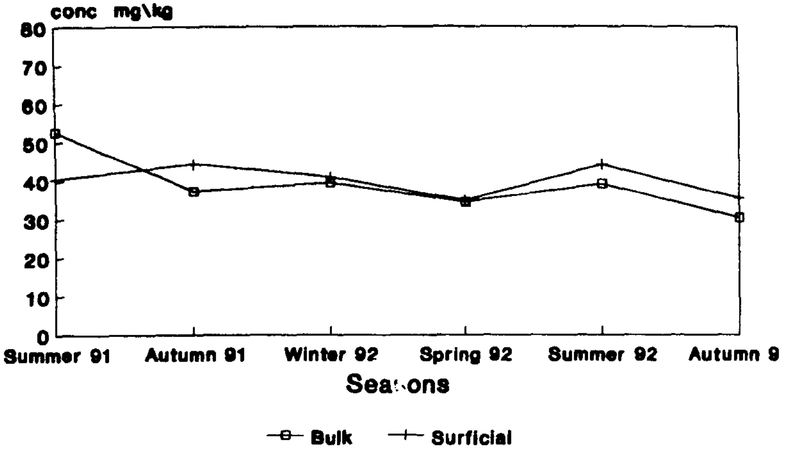


Fig. 5.12.B2

Spatial variations of Copper in sediments on the six sampling seasons

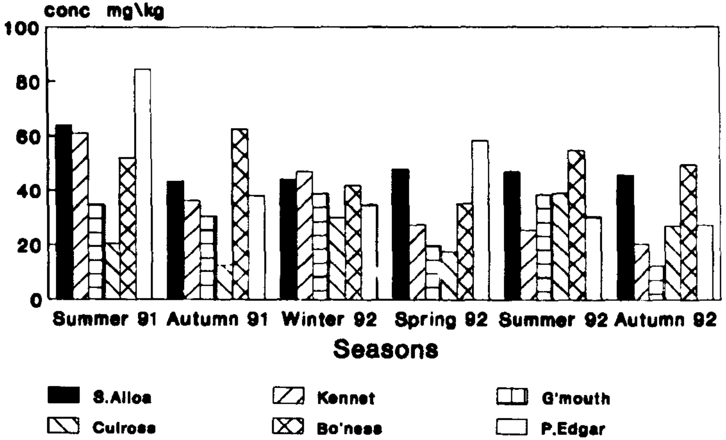


Table 5.14

Mean concentrations of Nickel in the sediment mg\kg

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	43.25	41.75	32.93	24.53	36.88	16.33	32.61	29.18
Autumn 91	33.88	37.35	34.00	22.38	36.53	36.75	33.48	33.58
Winter 92	32.28	35.58	38.95	28.98	31.48	33.88	33.52	32.53
Spring 92	37.38	38.45	21.38	20.85	28.53	25.93	28.75	30.68
Summer 92	47.43	36.78	37.95	22.70	34.33	35.08	35.71	36.65
Autumn 92	34.35	34.38	32.43	49.75	41.90	34.33	37.85	35.83
Mean Spatial (Bulk)	38.09	37.38	32.94	28.20	34.94	30.38	33.65	
Mean Spatial (Surficial)	36.95	41.08	29.75	27.47	34.02	29.20	33.08	

Data derived from Appendix A12

Fig. 5.13.A1

Mean concentrations of Nickel in sediments at the six sampling sites

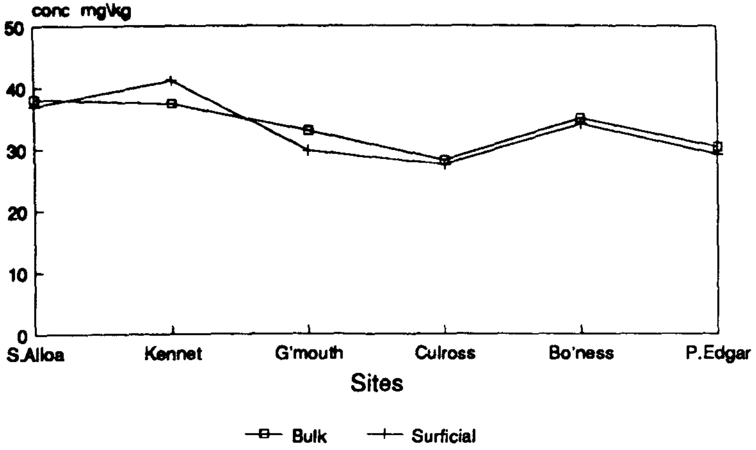


Fig. 5.13.A2

Seasonal variations of Nickel in sediments at the six sampling sites

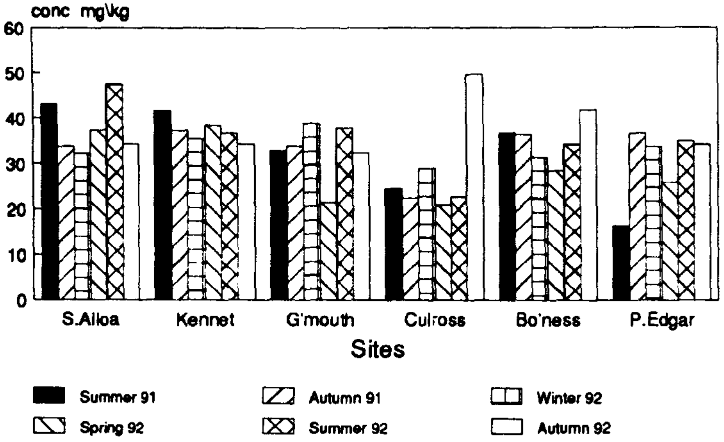


Fig. 5.13.B1

Mean concentrations of Nickel in sediments on the six sampling seasons

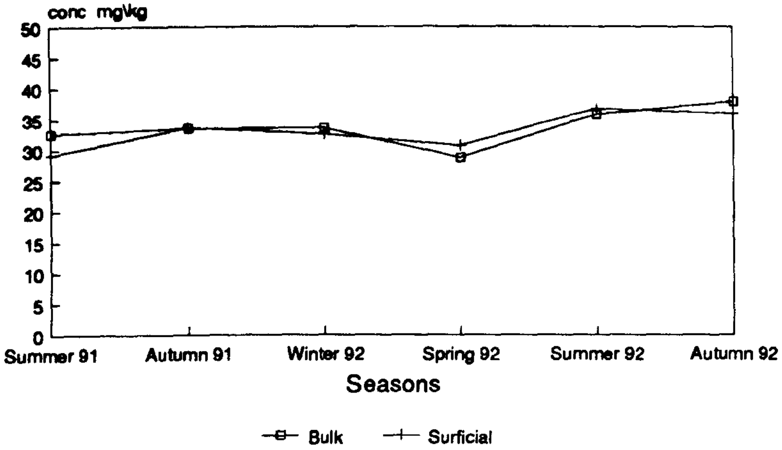


Fig. 5.13.B2

Spatial variations of Nickel in sediments on the six sampling seasons

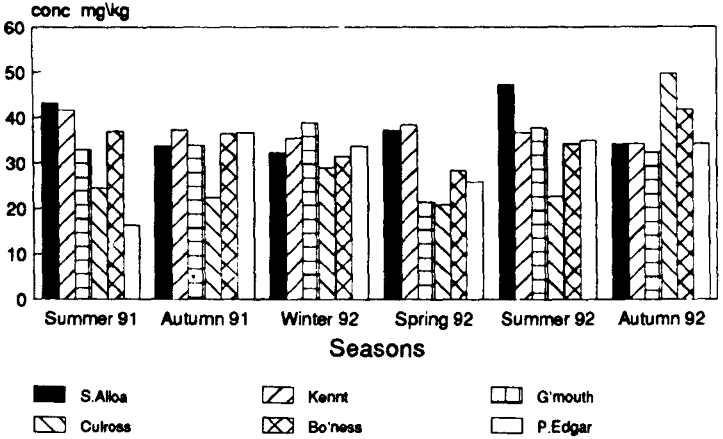


Table 5.15

Mean concentrations of Mercury in the sediment mg\kg

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	3.08	2.88	2.40	0.98	2.65	1.35	2.22	2.18
Autumn 91	1.83	1.95	1.93	1.03	4.25	3.08	2.34	2.68
Winter 92	2.15	2.40	2.18	1.85	2.73	2.13	2.24	2.27
Spring 92	2.20	1.10	2.10	1.05	1.40	1.85	1.62	1.77
Summer 92	1.96	0.94	1.35	1.50	2.22	1.10	1.51	1.71
Autumn 92	1.39	0.75	0.59	1.43	2.25	1.07	1.25	1.35
Mean Spatial (Bulk)	2.10	1.67	1.76	1.31	2.58	1.76	1.86	
Mean Spatial (Surficial)	2.03	2.52	2.04	1.43	2.29	1.66	1.99	

Data derived from Appendix A13

Fig. 5.14.A1

Mean concentrations of Mercury in sediments at the six sampling sites

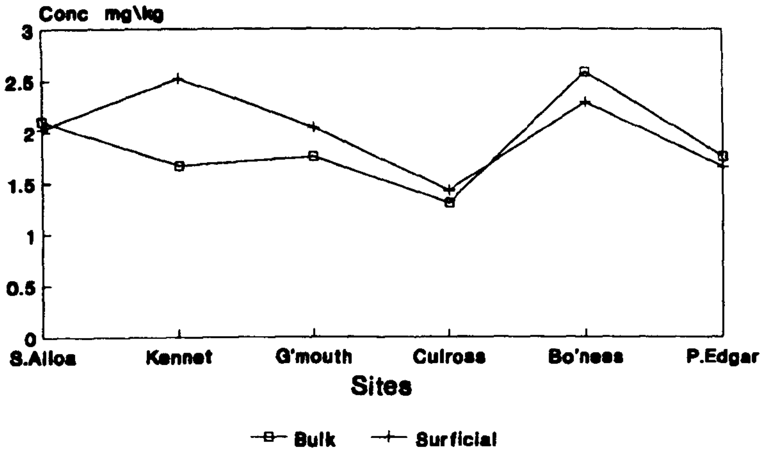


Fig. 5.14.A2

Seasonal variations of Mercury in sediments at the six sampling sites

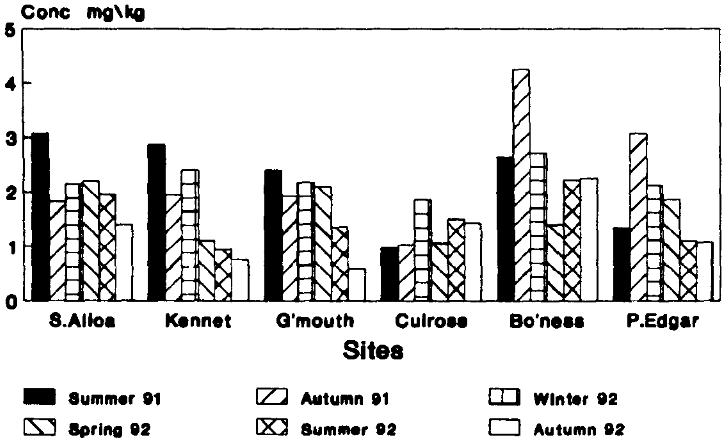


Fig. 5.14.B1

Mean concentrations of Mercury in sediments on the six sampling seasons

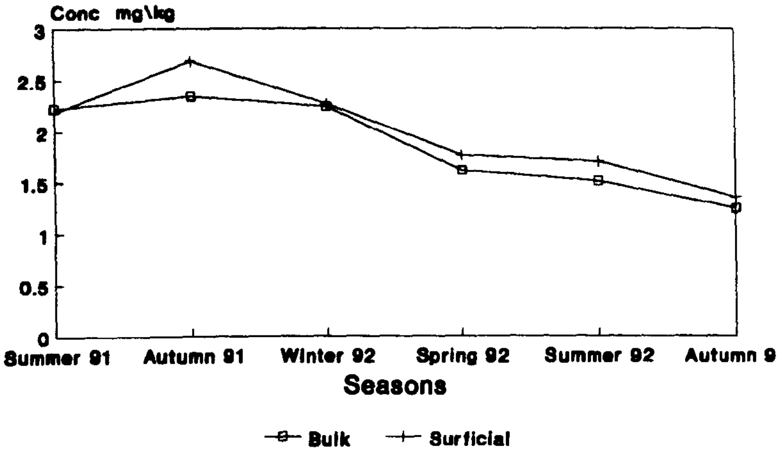
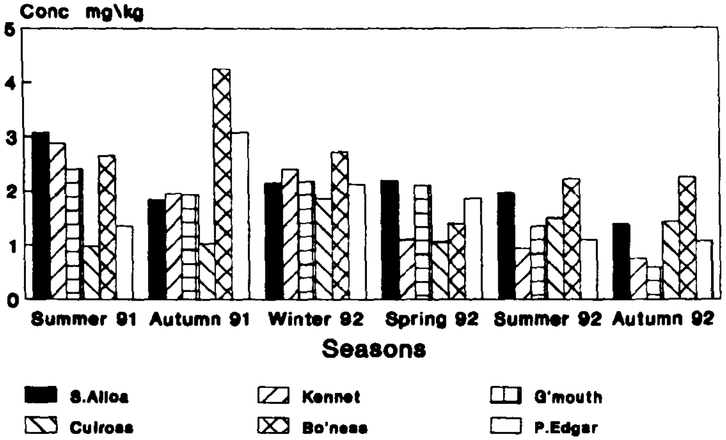


Fig. 5.14.B2

Spatial variations of mercury in sediments on the six sampling seasons



5.1.1.7 Summary of spatial and temporal variations in the sediment parameters

The mean redox potential at each station (see table 5.32) suggests that sediments at stations A (S.Alloa), B (Kennet), E (Bo'ness) and F (P.Edgar) were reducing in that their mean values are negative (-19.75, -16, -19.92 and -13.63 mV respectively). The sediments of stations C (G'mouth) and D (Culross) were oxidizing having positive mean values (11.92 and 18.7 mV).

Particle size and organic matter were the most dominant features controlling the behaviour of trace metals in the sediments of Forth estuary. In general, station B (Kennet) was characterised by a fine-grained sediment with 91.3% < 63 µm and organic matter of 9.88%, followed by station E (Bo'ness) with particle size 77.0% < 63 µm and 10.9% organic matter, station A (S.Alloa) with 75.9% < 63 µm and 11.3% organic matter. The other three stations (C,D and F) were roughly similar in their characteristics. The overall mean values for the different stations in terms of % particles < 63 µm in descending order is B > E > A > C > D > F, while that of organic matter is A > E > B > F > C > D.

Total organic carbon and total organic nitrogen shared similar distribution patterns. Aluminium and iron in the sediment showed close correlation with particle size and organic matter. Manganese also shows some correlation with particle size.

Trace metals distributions were similar to those of particle size and organic matter in the study area. Strong correlation were observed between cadmium, copper, nickel, mercury or lead and organic matter (r = 0.76, 0.8, 0.88, 0.79 and 0.59 respectively).

Stations A (S.Alloa), B (Kennet) and E (Bo'ness) were the most polluted stations in the Forth estuary. This was verified by the high trace metal concentrations in the bulk sediments. The less polluted stations were station C (G'mouth) and Station D (Culross) in the middle of the estuary, and station F (Port Edgar) in the lower reaches of the estuary which showed the lowest trace metal concentrations in the bulk sediments.

Temporally, particle size and organic matter also played a major role in determining the distribution of the trace metals. The overall trend was a decline of the concentrations of trace metals as the cold seasons approached, with some exceptions.

Particle size and organic matter showed the same distribution pattern with strong correlation (r = 0.84). Their highest values were recorded in the winter while the lowest values were in the spring.

Tables 5.32 and 5.33 summarise the ranges and mean values of sediment parameters.

Table 5.32

Ranges and mean values of organic matter of the sediments in the Forth estuary

Stations		*Eh* mV	% < 63 µm	LOI %	TOC %	TON %	C:N
S.Alloa A	mean	-19.75	75.85	11.3	4.93	0.32	17.95
	range	-260 - +100	63.5-95	7-14	3.0-9.3	0.14-0.74	6.81-37.95
Kennet B	mean	-16.0	91.25	9.88	3.52	0.27	16.43
	range	-135 - +91	77.5-98	5-15	1.46-6.48	0.13-0.57	6.51-62.57
G'mouth C	mean	11.92	59.19	7.83	3.37	0.25	17.41
	range	-160 - +360	15.5-95.5	3-14	1.8-5.3	0.10-0.68	4.95-37.95
Culross D	mean	18.75	58.35	7.29	2.94	0.21	16.49
	range	-120 - +290	27-77.5	3-10	0.68-4.35	0.07-0.35	4.16-44.60
Bo'ness E	mean	-19.92	77.04	10.9	4.16	0.31	15.53
	range	-215 - +260	35-92.5	6-14	2.8-5.8	0.09-0.54	7.6-31.89
P.Edgar F	mean	-13.63	57.92	8.25	3.18	0.28	13.40
	range	-200 - +325	20-87.5	4-12	1.66-4.92	0.10-0.43	6.52-32.51
Overall mean		-6.44	70.0	9.25	3.68	0.28	16.20
Overall range		-260 - +360	15.5-98	3-15	0.68-9.27	0.07-0.74	4.16-62.57

Table 5.33

Ranges and mean concentrations of trace metals of the sediments in the Forth estuary

Station		Cd mg\kg	Cu mg\kg	Ni mg\kg	Pb mg\kg	Hg mg\kg	Al %	Fe g\kg	Mn g\kg
S.Alloa A	mean	0.35	48.8	38.1	65.8	2.1	7.3	30.7	0.6
	range	0.25-0.58	38.8-72.8	29.4-51.2	53.8-80.0	1.2-3.2	6.4-8.4	24.3-44	0.35-1.0
Kennet B	mean	0.24	36.2	37.4	48.4	1.7	7.98	32.4	0.57
	range	0.08-0.7	8.7-65.2	24.4-43.9	8.0-82.8	0.2-3.2	6.4-8.9	26.7-38	0.23-0.79
G'mouth C	mean	0.17	29.1	32.9	50.1	1.8	7.11	31.2	0.75
	range	0.08-0.6	3.3-46.5	17.4-42.6	28.3-68.9	0.47-4.9	4.6-8.9	21-42	0.46-1.2
Culross D	mean	0.19	24.5	28.2	44.3	1.3	6.18	24.3	0.48
	range	0.07-0.32	6.6-43.0	18.3-52.3	14.7-78.1	0.5-2.1	5-7	16-30	0.27-0.8
Bo'ness E	mean	0.21	49.7	34.9	65.7	2.6	7.5	32.1	0.78
	range	0.09-0.37	30.9-67.0	23.7-43.3	48.2-80.9	1.2-4.3	6.5-8.4	26-39.3	0.54-1.13
P.Edgar F	mean	0.17	45.9	30.5	67.3	1.8	6.41	26.2	0.59
	range	0.08-0.38	17.3-267	16.6-40.3	38.9-174	0.5-4.0	4.3-7.9	16-34	0.34-0.89
Overall mean		0.22	39.0	33.7	56.9	1.9	7.1	29.5	0.63
Overall range		0.07-0.7	3.3-267	16.6-52.3	8.0-179	0.2-4.9	4.3-8.9	16-44	0.23-1.2

5.1.1.8 Results of trace metals concentration in the less than 63 μm particle size

To investigate the association of trace metals with fine grain sediments, a small portion of the < 63 μm sediment fraction was separated using a plastic sieve and digested (digestion method in section 4.5.2).

Table 5.31 shows the mean values of trace metals concentrations in the < 63 μm fraction and also those of the whole sediment in the 1992 summer season. Figure 5.30 illustrates the effect of grain size on the concentrations of trace metals. There was a clear trend in which trace metal concentrations tended to increase in the less than 63 μm fraction. However, station A (S.Alloa) behaved differently because the concentrations of trace metals were higher in the whole sediment fraction than those of the < 63 μm. Cadmium has also shown higher concentrations on the bulk sediments in all stations except station F (P.Edgar) and mercury was found to be higher in the whole sediment in station B (Kennet). This could be as a result of the presence of coal fragments in the sediments high in trace metals, it is believed that the coal particles led to increase in the the concentrations of trace metals at this particular station.

In view of these results, decision was taken to correct for trace metals against particle size < 63 μm fraction. This will be the topic of the next section.

Table 5.31

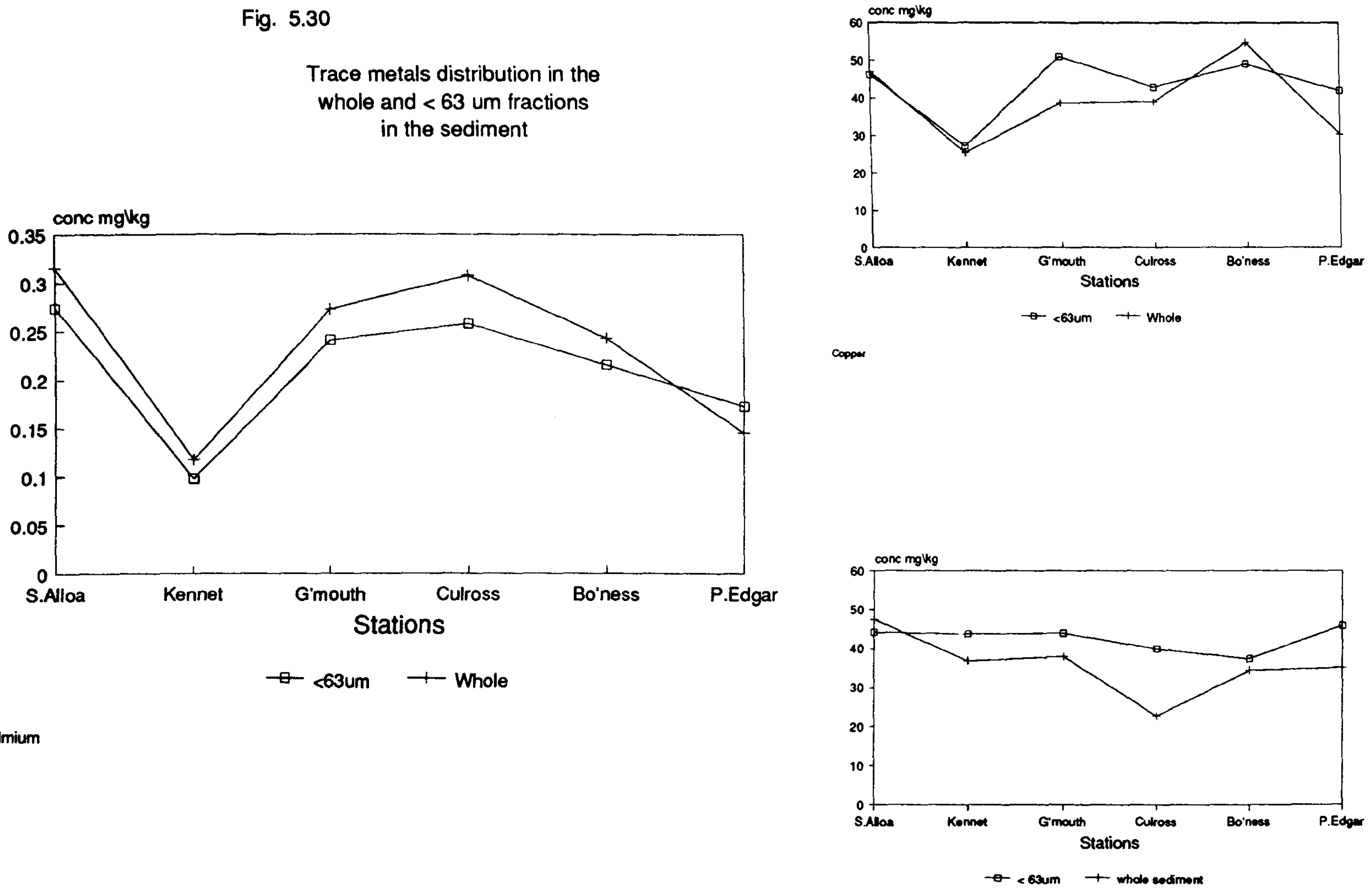
Mean concentrations of trace metals in the < 63 um and in the whole sediment fractions mg\kg

Fraction	Stations Metals	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
< 63 um	Lead	58.13	41.35	69.70	73.58	82.03	77.53
	Cadmium	0.27	0.10	0.24	0.26	0.22	0.17
	Copper	46.10	27.15	51.00	42.88	48.93	41.93
	Nickel	44.15	43.73	43.93	39.80	37.30	45.83
	Mercury	1.75	0.77	1.55	1.87	2.21	1.40
Whole Sediment	Lead	64.15	24.05	63.40	52.28	64.73	45.70
	Cadmium	0.32	0.12	0.27	0.31	0.24	0.15
	Copper	46.95	25.40	38.58	38.95	54.63	30.40
	Nickel	47.43	36.78	37.95	22.70	34.33	35.08
	Mercury	1.96	0.94	1.35	1.50	2.22	1.10

data derived from Appendix A29

Fig. 5.30

Trace metals distribution in the whole and < 63 um fractions in the sediment

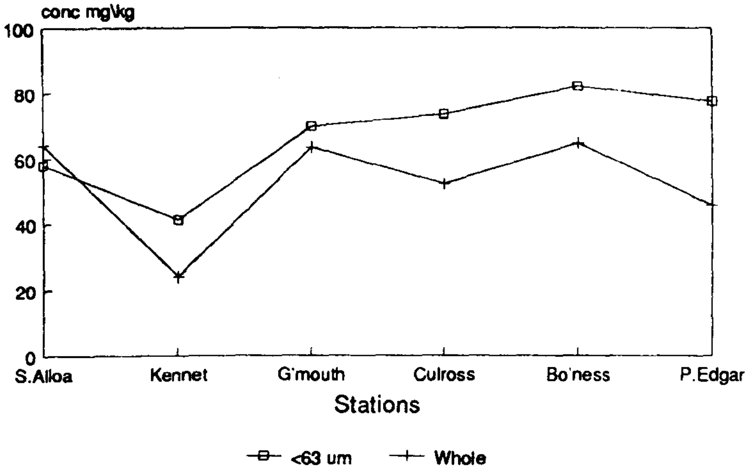


Cadmium

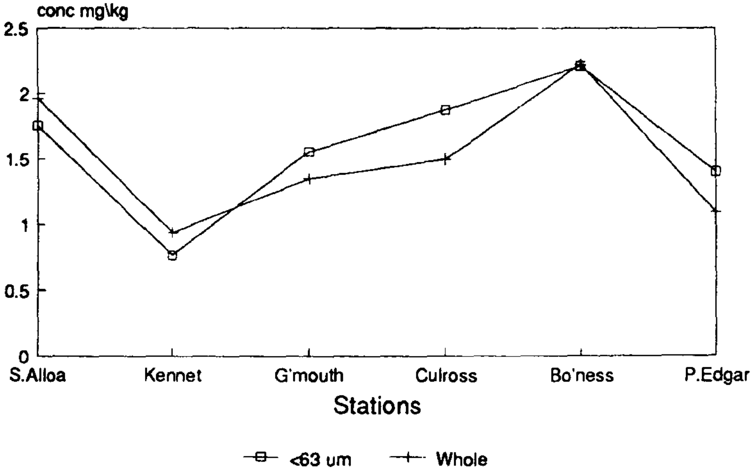
Copper

Nickel

Fig. 5.30 continued



Lead



Mercury

5.1.1.9 Results of the normalization against the < 63 µm grain size

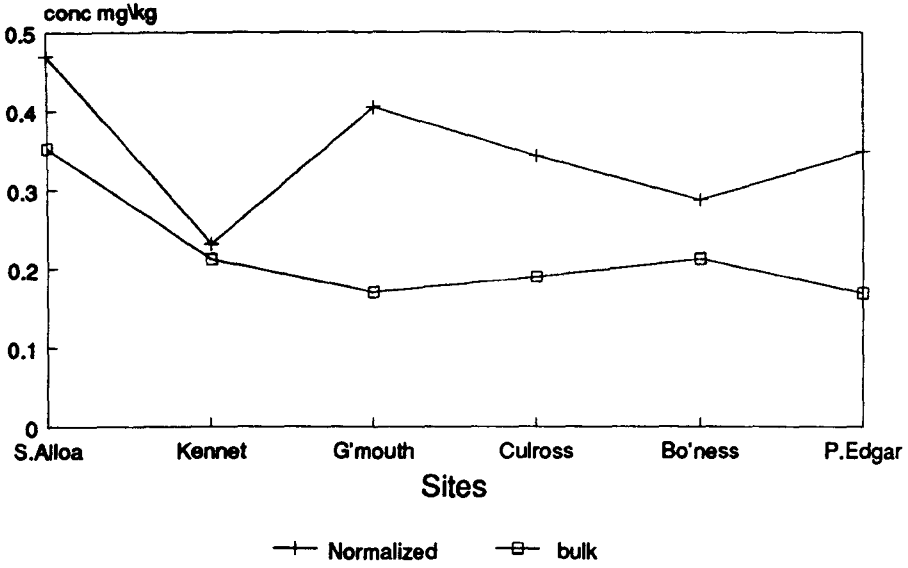
The normalisation procedure used here has been outlined in section 4.5.5. The mean dilution factors calculated for each station were as follows: for station A 1.33, station B = 1.09, station C = 2.38, D = 1.81, E = 1.35 and for station F = 2.06. The above mentioned dilution factors were multiplied by the mean concentration for each metal in the bulk sediments to give the normalised value. These dilution factors were derived from Appendix A 32.

The mean values of the spatial distributions of trace metals in the normalised data are shown in Fig. 5.31.
It depicts that for all the trace metals, the distributions were uniform and it also reveals the presence of high concentrations of trace metals in the normalized data.
The normalized data give a clearer picture of spatial variations in trace metal concentrations. Specifically the Grangemouth site (Station C) shows clear evidence of trace metal pollution. Cd, Cu, Hg, Pb and Ni are higher as shown in figure 5.31.

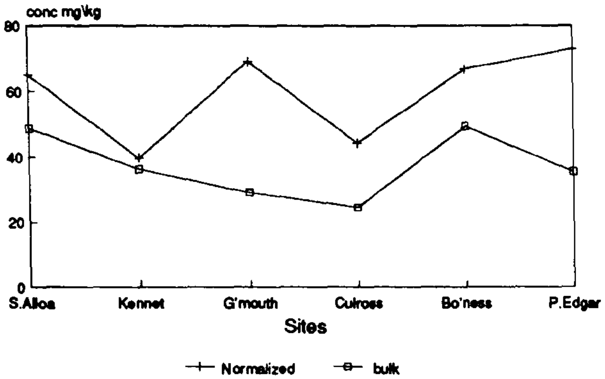
Station B (Kennet) remained unchanged before and after the correction. This could be as a result of the sediment being characterized by fine grain particles mainly silt and clay.

Fig. 5.31

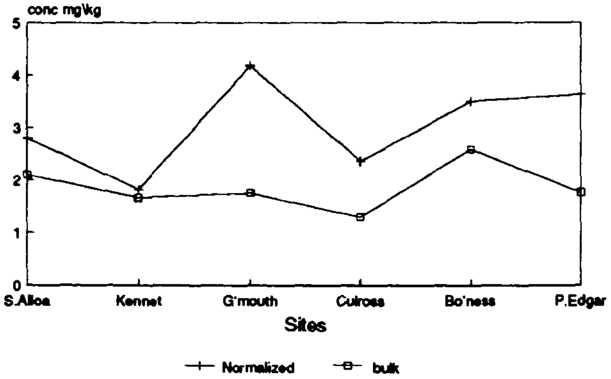
Comparison of trace metal concentrations in the bulk and in the normalized sediment



Cadmium

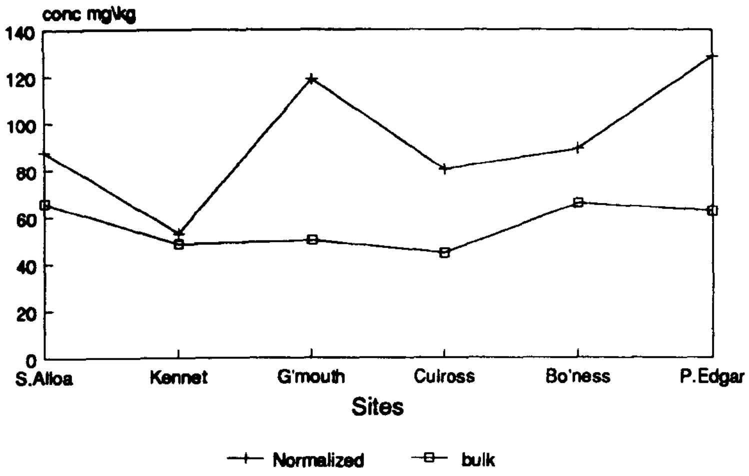


Copper

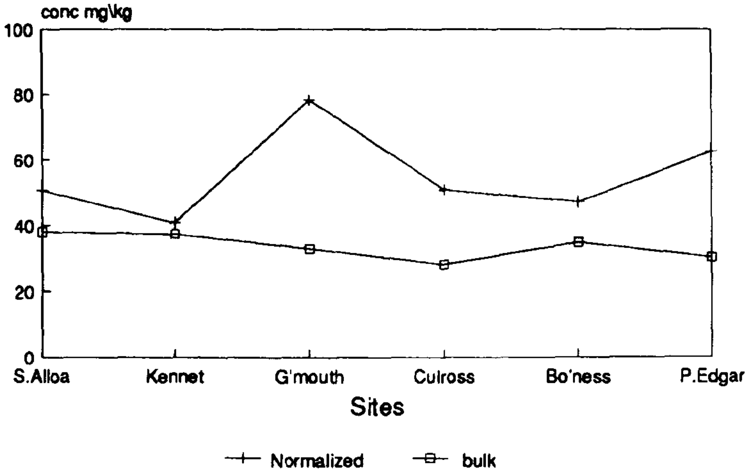


Mercury

Fig. 5.31 continued



Lead



Nickel

5.1.2 Pore water parameters

5.1.2.1 pH and alkalinity

Table 5.16 shows the mean spatial and temporal distributions of hydrogen ion concentration. Spatially, Fig 5.15.A illustrates that low values were recorded in station B (Kennet) while high values showing slightly alkaline conditions, were recorded at station C (G'mouth). The overall mean was 7.78 and the overall range was between 6.7 and 8.3. Spatially, pH and alkalinity were highly correlated (r = 0.73). A gradual increase with depth was observed for both pH and alkalinity.

Temporally, low pH values were recorded in the winter while high values were recorded in the summer and autumn seasons (Fig. 5.15.B). Temporally pH and mercury concentrations in the pore water were highly correlated (r = 0.9).

Table 5.17 shows the mean values of the distributions of alkalinity in the study area. Spatially, Fig. 5.16.A shows that station E (Bo'ness) recorded the highest value while alkalinity fluctuation in the other stations was the predominant feature. The overall mean value for alkalinity was 6.1 meq/l and the range was between 2.0 and 18.0 meq/l.

Seasonally, Fig. 5.16.B indicates a gradual decrease in alkalinity as the cold seasons approached. Alkalinity values showed an increase with depth in all the stations (Fig. 5.16.A1).

Table 5.16

Mean concentrations of Hydrogen Ion pH

Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar	Mean
Seasons	A	B	C	D	E	F	Temporal
Summer 91	7.53	7.43	7.83	7.70	7.73	7.88	7.68
Autumn 91	7.85	7.53	8.20	7.88	8.20	7.63	7.88
Winter 92	7.43	7.25	7.60	7.43	7.75	7.75	7.53
Spring 92	7.83	7.68	7.93	8.00	7.85	7.68	7.83
Summer 92	8.03	7.84	7.99	7.72	7.87	7.70	7.86
Autumn 92	7.86	7.85	8.19	7.80	7.90	8.01	7.93
Mean Spatial	7.75	7.59	7.95	7.75	7.88	7.77	7.78

Data derived from Appendix A14

Fig. 5.15.A1

Mean values of pH in pore water at the six sites

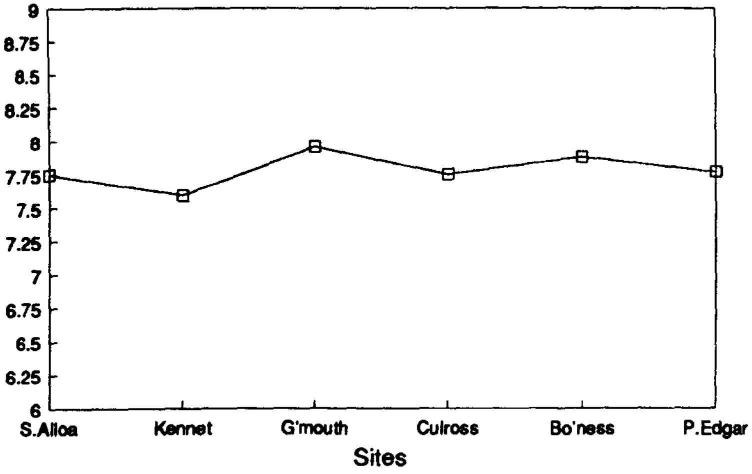


Fig. 5.15.A2

Seasonal variations of pH values in porewater at the six sites

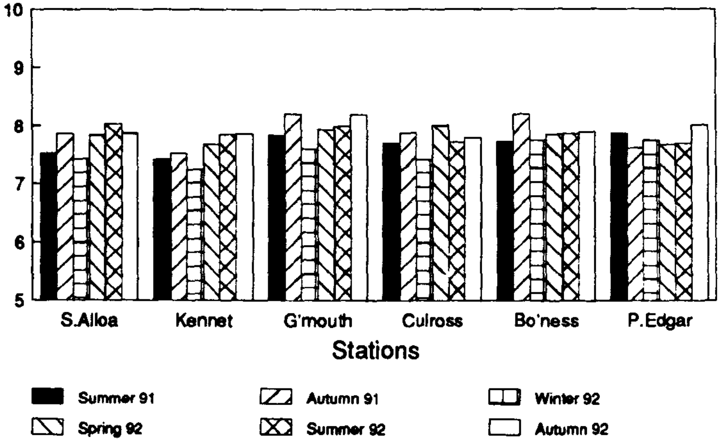


Fig. 5.15.B1

Mean values of pH in pore water on the six seasons

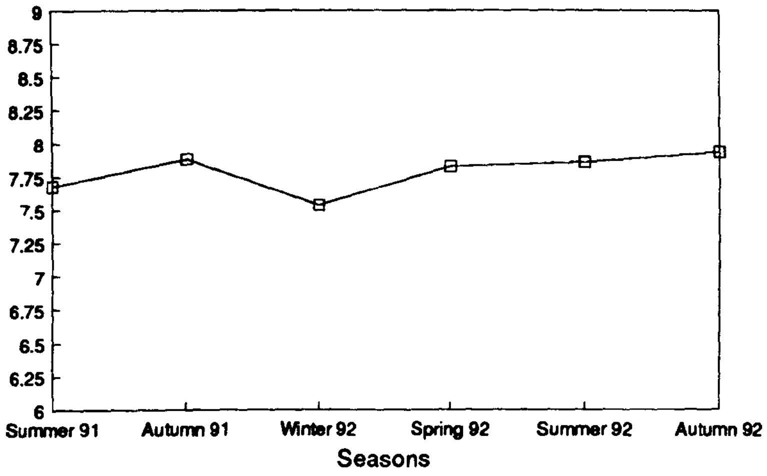


Fig. 5.15.B2

Spatial variations of pH in pore water on the six seasons

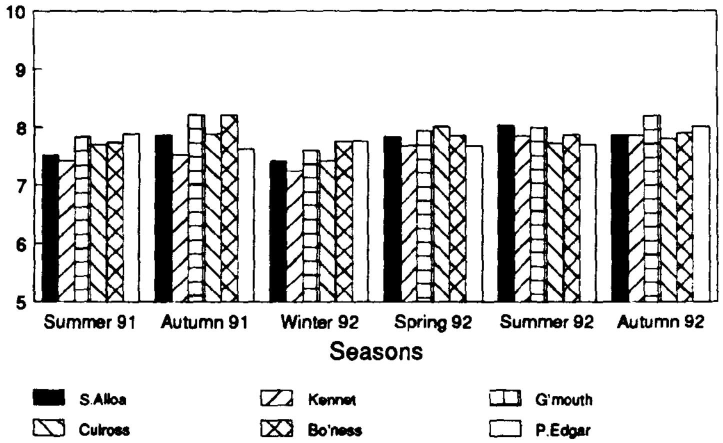


Table 5.17

Mean values of Alkaliniy in the pore water meq\l

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	10.00	6.50	4.75	2.75	13.25	2.75	6.67	3.83
Autumn 91	5.00	5.25	8.75	4.50	9.75	7.25	6.75	4.50
Winter 92	5.25	4.25	6.25	6.25	6.50	5.75	5.71	4.00
Spring 92	6.00	2.75	4.75	3.00	7.00	5.25	4.79	3.17
Summer 92	5.25	5.50	12.50	6.25	9.00	7.25	7.63	5.50
Autumn 92	4.25	3.25	3.75	5.75	8.50	3.25	4.79	3.17
Mean Spatial (Bulk)	5.96	4.58	6.79	4.75	9.00	5.25	6.06	
Mean Spatial (Surficial)	3.33	3.33	4.83	3.17	5.50	4.00	4.03	

Data derived from Appendix A15

Fig. 5.16.A1

Mean values of Alkalinity in pore water at the six sites

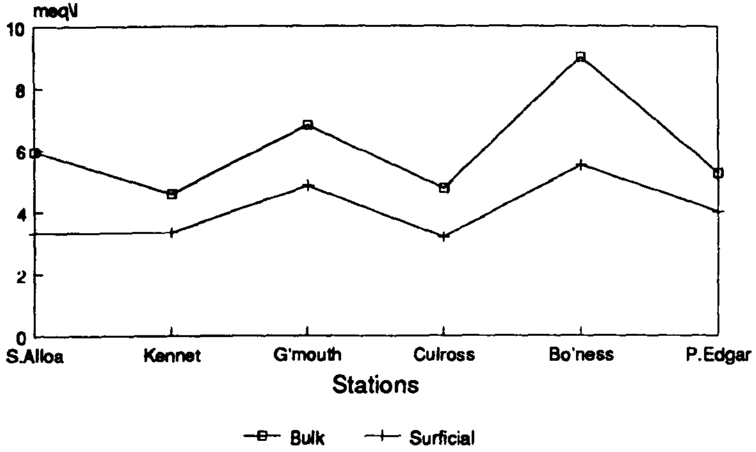


Fig. 5.16.A2

Seasonal variations of Alkalinity in pore water at six sites

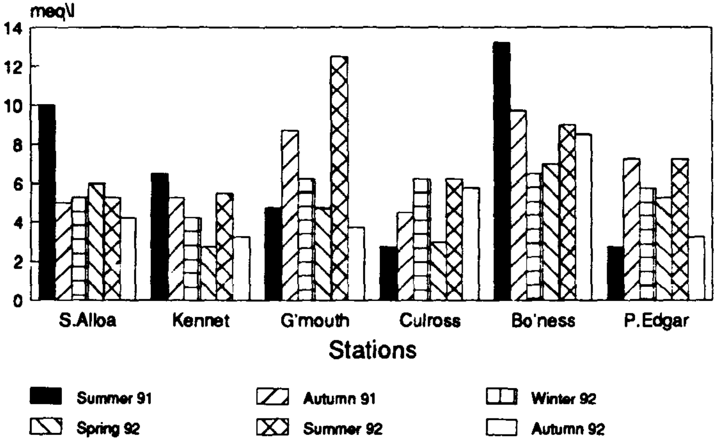


Fig. 5.16.B1

Mean values of Alkalinity in pore water on the six sampling seasons

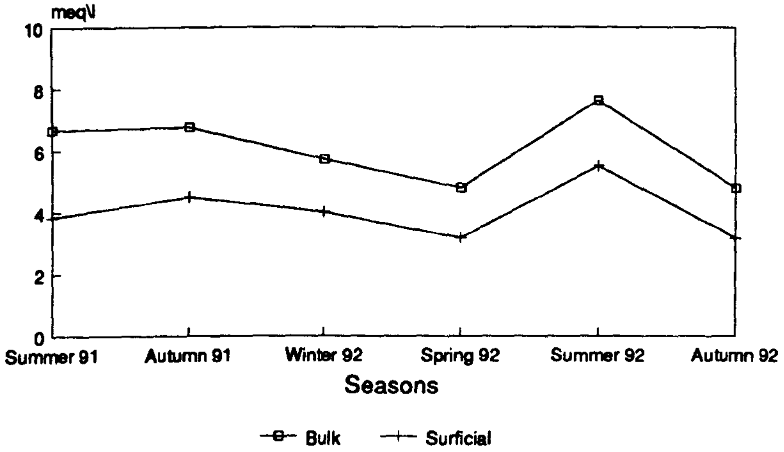
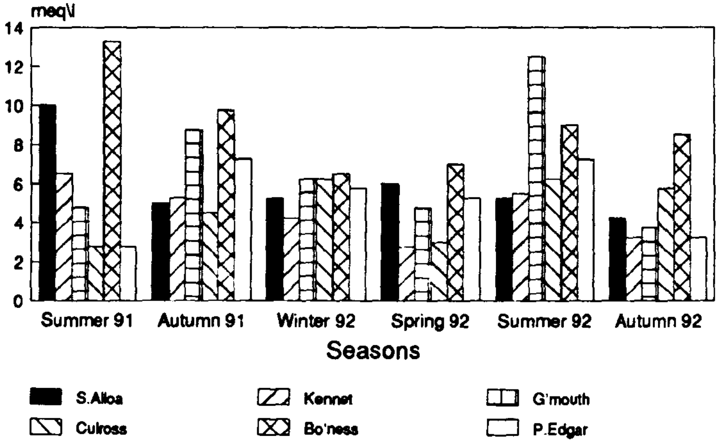


Fig. 5.16.B2

Spatial variations of Alkalinity in pore water on the six seasons



5.1.2.2 Chloride, sulphate and conductivity

Tables 5.18, 5.19 and 5.20 show the average spatial and temporal variations of chloride, conductivity and sulphate respectively. These three parameters showed similar trends and variations. Spatially, Figures 5.17.A1, 5.18.A1 and 5.19.A1 indicate a gradual sea-ward increase in their values. Station A (S.Alloa) represents the river end member recorded the lowest values of 177 meq/l for chlorides, 10.86 mS/cm for conductivity, and 4.92 meq/l for sulphates while station F (P.Edgar) represents the sea end member showed the highest values of 791.5 meq/l for chlorides, 49.9 mS/cm for conductivity and 42.18 meq/l for sulphates.

The overall mean values were found to be for chlorides, 606.5 meq\l; sulphates, 28.7 meq\l and conductivity, 39.0 mS/cm. The overall ranges were between 57 and 1246 meq\l for chlorides, 0.0 and 65.0 for sulphates, and 4.6 and 64 mS\cm for conductivity (Appendices A16-A18).

Similar trends for all the three parameters were observed seasonally especially between sulphates and conductivity, and chlorides and conductivity. Chlorides recorded the highest value in the autumn season. Sulphate showed a decrease with depth, indicating bacterial sulphate reduction (Fig.20.A1).

Table 5.18

Mean concentrations of chloride in the pore water meq\l

Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar	Mean
Seasons	A	B	C	D	E	F	Temporal
Summer 91	441.8	778.8	755.3	761.3	814.5	806.8	726.4
Autumn 91	222.3	818.8	926.5	954.8	988.8	1172.0	847.2
Winter 92	107.5	446.8	729.8	754.3	844.8	853.3	622.7
Spring 92	103.8	472.8	583.0	544.3	727.5	765.8	532.8
Summer 92	111.3	466.0	569.5	580.8	542.0	655.8	487.5
Autumn 92	75.3	444.3	454.8	528.3	536.0	495.8	422.4
Mean Spatial	177.0	571.2	669.8	687.3	742.3	791.5	606.5

Data derived from Appendix A16

Fig. 5.17.A1

Mean concentrations of Chloride in pore water at the six sites

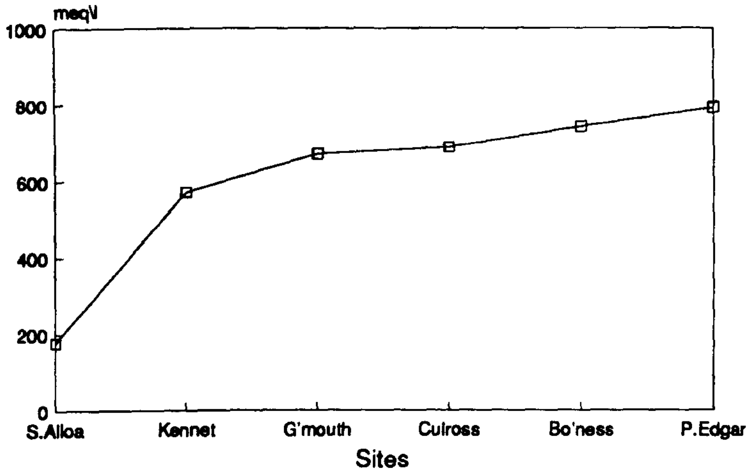


Fig. 5.17.A2

Seasonal variations of chloride in Pore water at the six sites

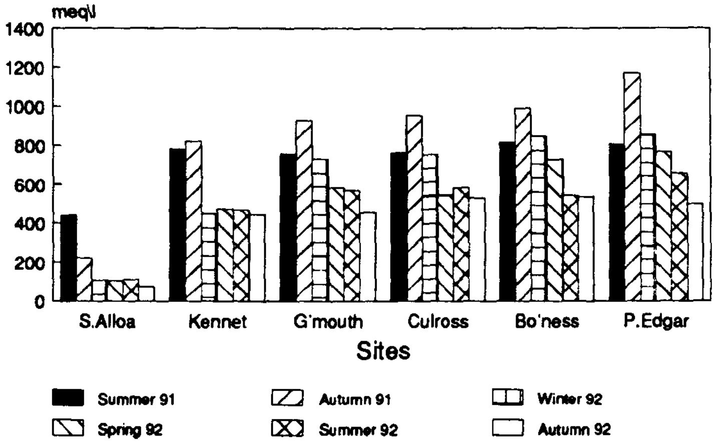


Fig. 5.17.B1

Mean concentrations of Chloride in
pore water on the six sampling seasons

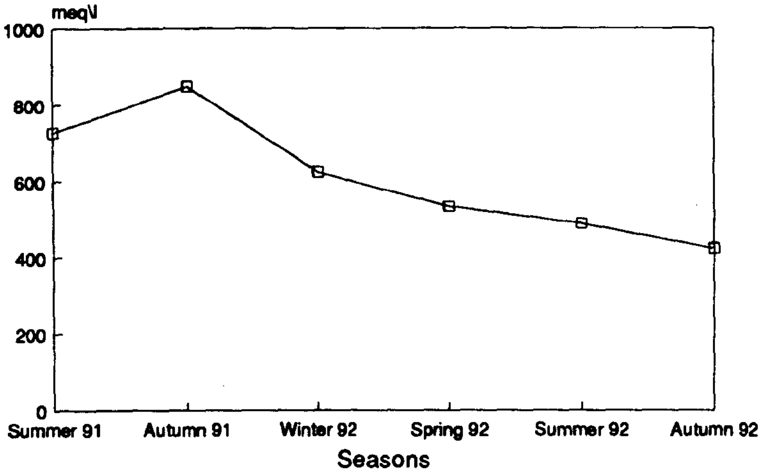


Fig. 5.17.B2

Spatial variations of Chloride in
pore water on the six samplig seasons

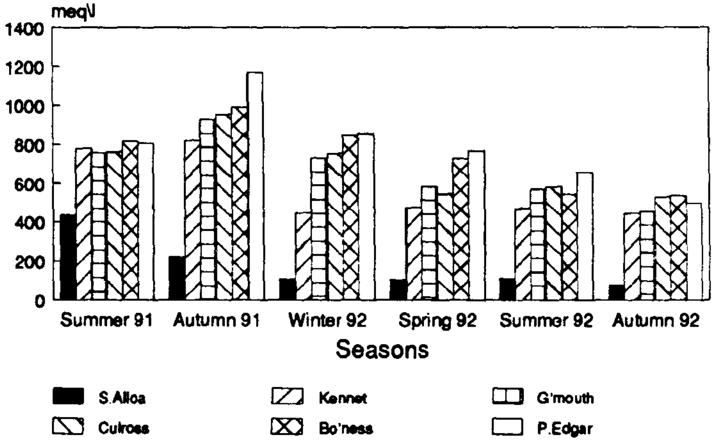


Table 5.19

Mean values of conductivity in the pore water mS/cm

Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar	Mean
Seasons	A	B	C	D	E	F	Temporal
Summer 91	21.75	51.00	53.50	57.00	58.25	57.25	49.79
Autumn 91	9.50	38.50	41.25	45.50	49.25	52.00	39.33
Winter 92	7.63	35.75	47.75	49.00	51.50	54.00	40.94
Spring 92	10.10	31.75	39.00	38.50	42.75	44.50	34.43
Summer 92	9.98	36.45	39.43	45.40	47.05	49.45	37.96
Autumn 92	6.23	29.25	36.63	41.05	42.15	42.18	32.91
Mean Spatial	10.86	37.12	42.93	46.08	48.49	49.90	39.23

Data derived from Appendix A17

Fig. 5.18.A1

Mean values of conductivity in Pore water at the six sites

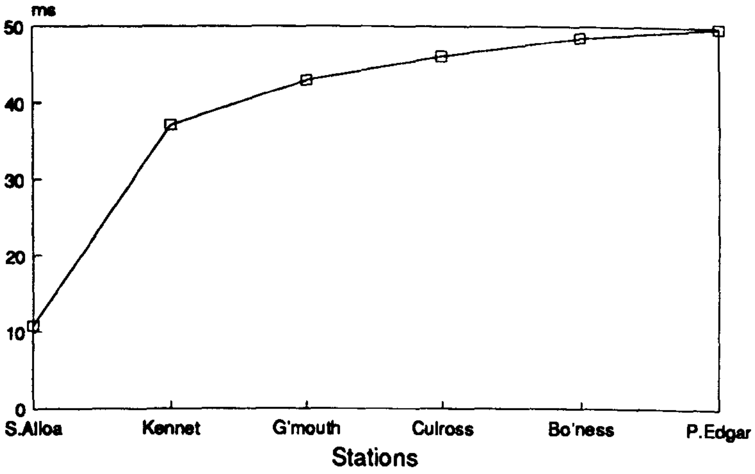


Fig. 5.18.A2

Seasonal variations of conductivity in pore water at the six sites

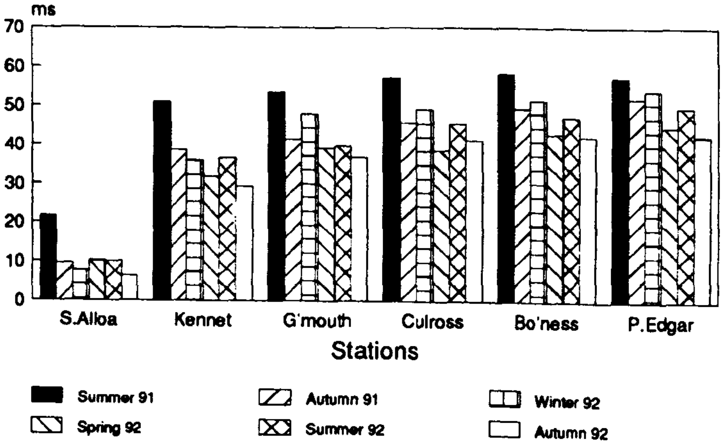


Fig. 5.18.B1

Mean values of conductivity in the Pore water at the six seasons

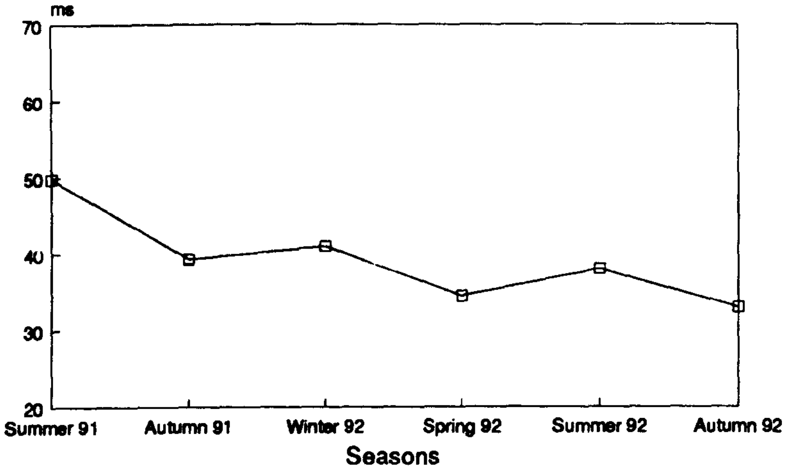


Fig. 5.18.B2

Spatial variations of conductivity in Pore water at the six seasons

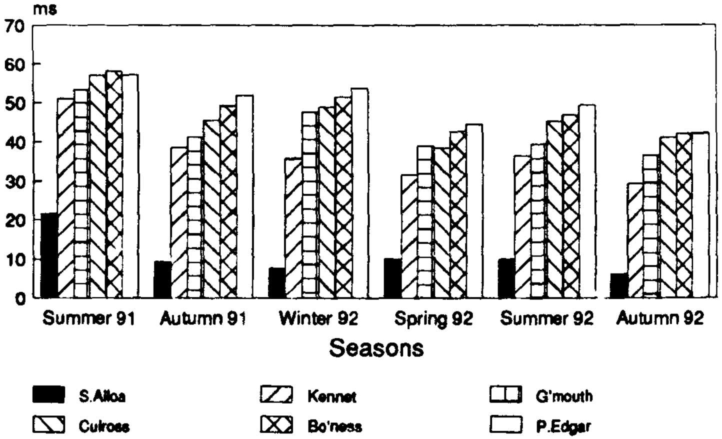


Table 5.20

Mean concentrations of Sulphate in the pore water meq\l

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	11.75	34.00	37.00	46.75	24.00	50.75	34.04	44.33
Autumn 91	5.83	26.00	22.25	41.00	29.75	41.25	27.68	32.83
Winter 92	1.25	26.50	29.75	33.50	45.50	52.50	31.50	36.23
Spring 92	2.38	26.00	27.50	32.00	35.13	30.65	25.61	33.67
Summer 92	6.68	33.05	26.55	25.00	24.88	38.35	25.75	28.40
Autumn 92	1.63	28.85	34.80	32.05	29.18	39.60	27.68	31.57
Mean Spatial (Bulk)	4.92	29.07	29.64	35.05	31.40	42.18	28.71	
Mean Spatial (Surficial)	9.50	32.55	35.95	40.07	39.62	49.35	34.51	

Data derived fron Appendix A18

Fig. 5.19.A1

Mean concentrations of sulphate in pore water at the six sites

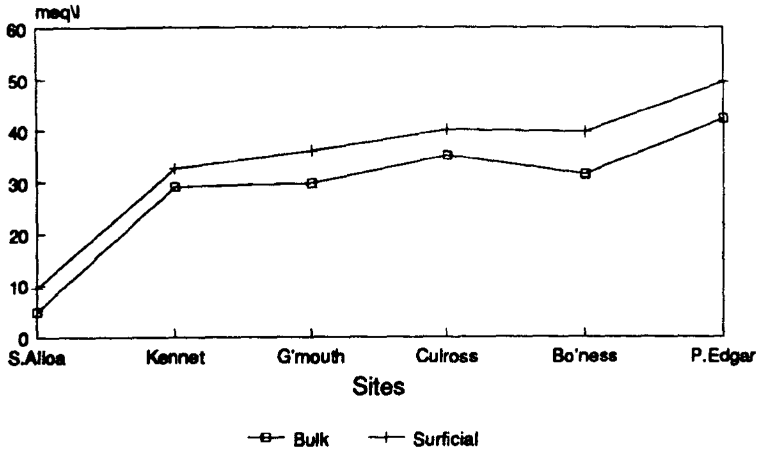


Fig. 5.19.A2

Seasonal variations of sulphate in pore water at the six sites

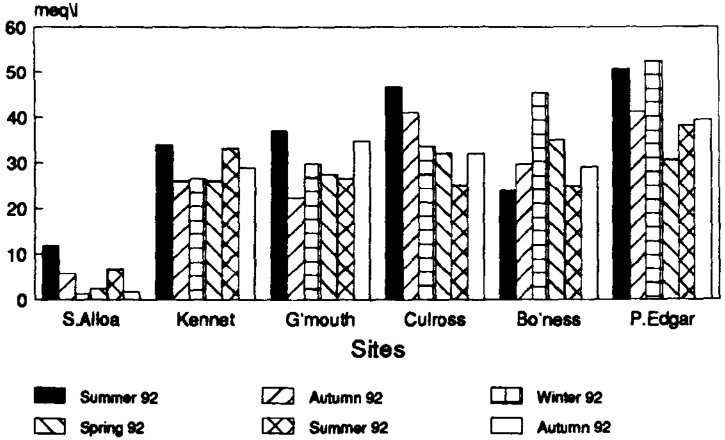


Fig. 5.19.B1

Mean concentrations of Sulphate in pore water on the six seasons

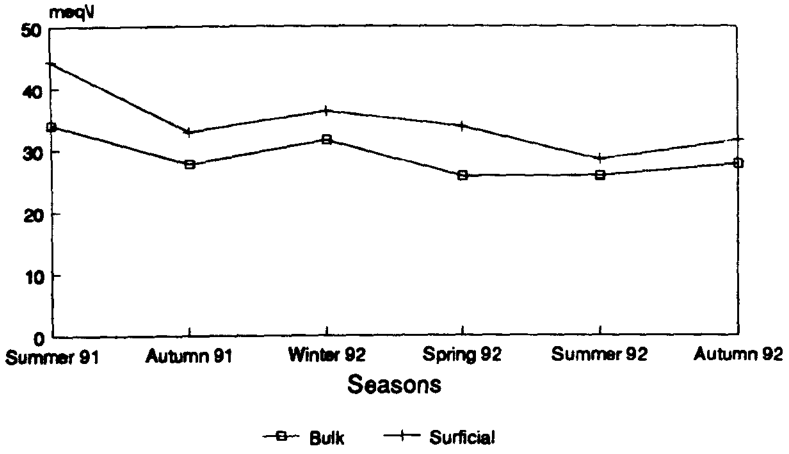
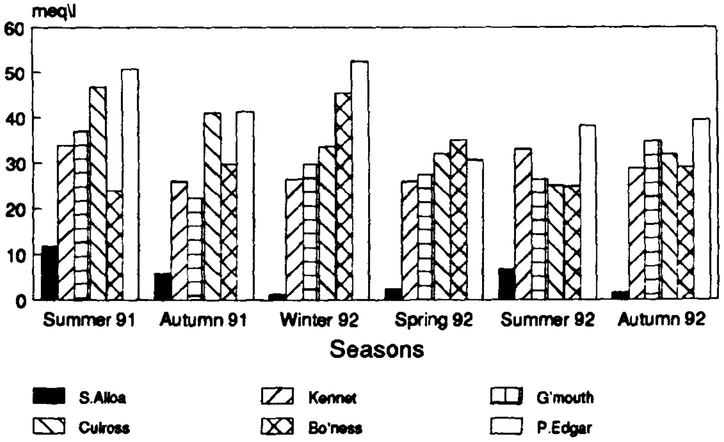


Fig. 5.19.B2

Spatial variations of Sulphate in pore water at the six seasons



5.1.2.3 Nitrates, phosphate and dissolved organic carbon

Table 5.21 shows the distribution of nitrates in the study area. Figure 5.20.A1 illustrates the mean spatial distribution of nitrates with elevated concentration of nitrates in station D (Culross) with a mean value of 203 μmol l^{-1}. The slightly high concentrations of nitrates in stations C (G'mouth) and E (Bo'ness) could be the result of the high nitrates concentration at Station D.

The overall mean concentration of nitrates was found to be 75.1 μmol l^{-1} and the overall range was between 1.0 and 1065 μmol l^{-1}. No overall trend with depth was observed.

Seasonally, Fig. 5.20.B1 shows high nitrates concentration in the spring and summer 1992 seasons. Sandy particles and oxidizing conditions were observed in station D (Culross) during this time. This explains the elevated mean concentration of nitrates observed at station D (Culross).

Table 5.22 shows the average variation in phosphate concentration. Fig. 5.21.A1 depicts the mean spatial distribution of phosphates. It is clear that stations E (Bo'ness) and F (P.Edgar) recorded the highest values. The overall mean concentration for phosphate was found to be 15.5 μmol l^{-1} and the overall range was between 0.0 and 102 μmol l^{-1}. Seasonally, phosphate concentration showed a marked increase in summer and autumn, 1991 (Fig. 5.21.B1). An overall increase with depth was the dominant feature

($p < 0.05$).

Table 5.23 and Fig. 5.22.A1 and B1 show the average spatial and temporal variations of dissolved organic carbon (DOC). There was no overall significant spatial trend. The overall mean concentration was found to be ~40.0 mg/ and the overall range was between 10 and 97 mg/l.

Seasonally, Fig. 5.22.B indicates a remarkable decrease of DOC concentrations in the summer and autumn, 1991. An overall decrease with depth was observed except at station A (S.Alloa) that had an increase in concentration with depth and station E (Bo'ness) without variation in concentration with depth Fig. (5.22.A1).

Table 5.21

Mean concentrations of Nitrate in the pore water umol/l

Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar	Mean	Mean
Seasons	A	B	C	D	E	F	Temporal (Bulk)	Temporal (Surficial)
Summer 91	4.43	1.60	14.63	27.15	20.10	9.68	12.93	9.68
Autumn 91	11.55	10.05	7.68	1.60	1.60	2.83	5.88	6.72
Winter 92	47.25	35.75	22.75	38.75	15.78	23.20	30.58	37.68
Spring 92	65.00	16.45	287.25	658.25	161.00	23.35	201.88	72.50
Summer 92	49.00	87.50	63.25	470.25	352.75	116.50	189.88	365.33
Autumn 92	14.00	3.95	6.25	22.25	7.00	3.00	9.41	13.73
Mean Spatial (Bulk)	31.87	25.88	66.97	203.04	93.04	29.76	75.09	
Mean Spatial (Surficial)	26.32	17.47	44.33	211.53	144.28	61.72	84.28	

Data derived from Appendix A19

Fig. 5.20.A1

Mean concentrations of Nitrate in Pore water at the six sites

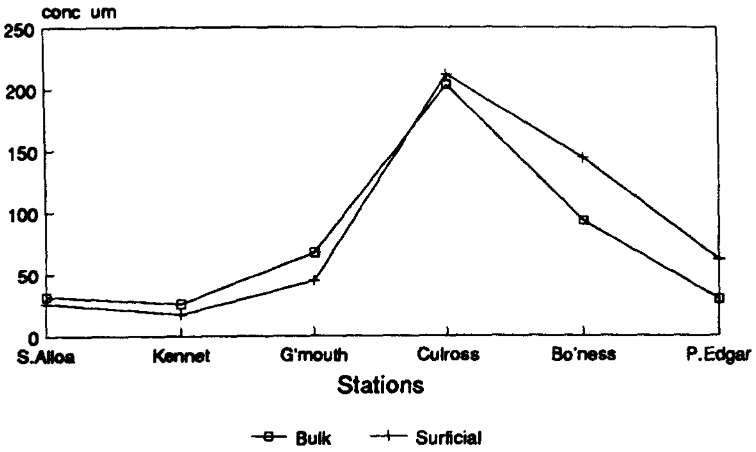


Fig. 5.20.A2

Seasonal variations of Nitrate in Pore water at the six sites

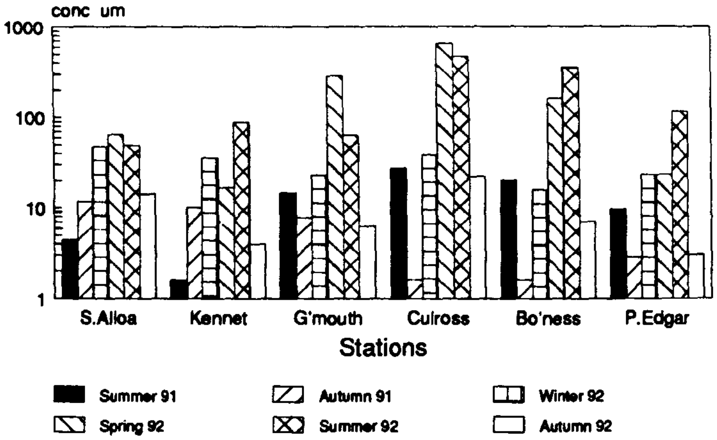


Fig. 5.20.B1

Mean concentrations of Nitrate in Pore water on the six seasons

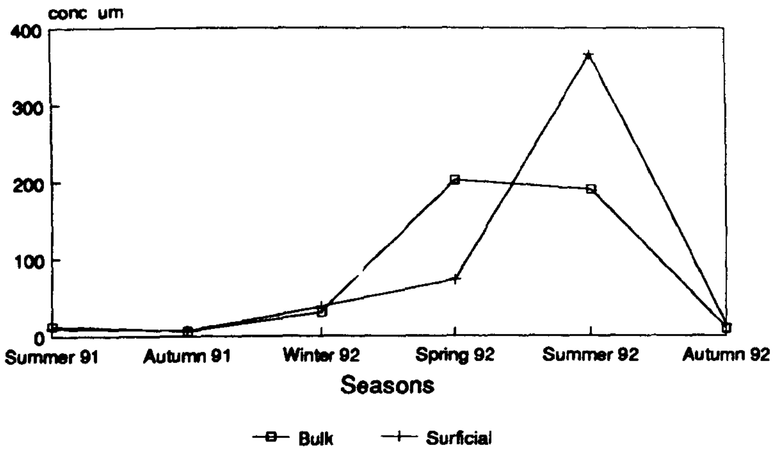


Fig. 5.20.B2

Spatial variations of Nitrate in pore water on the six seasons

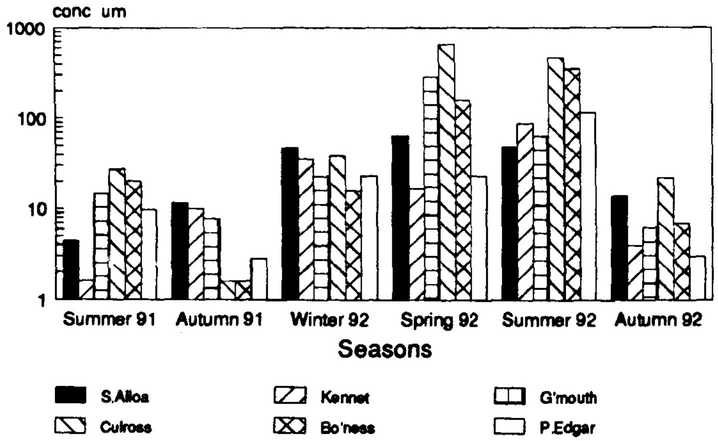


Table 5.22

Mean concentrations of Phosphate in the pore water umol/l

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	6.05	43.00	16.95	1.10	72.25	17.15	26.08	25.15
Autumn 91	3.70	5.80	24.50	11.23	75.75	39.00	26.66	12.78
Winter 92	8.43	4.23	31.30	2.40	21.35	7.43	12.52	2.85
Spring 92	4.48	14.43	5.80	8.43	6.05	54.00	15.53	12.72
Summer 92	9.25	12.00	0.88	7.50	14.85	15.00	9.91	5.32
Autumn 92	2.20	0.55	0.98	3.30	3.75	1.25	2.00	1.37
Mean Spatial (Bulk)	5.68	13.33	13.40	5.66	32.33	22.30	15.45	
Mean Spatial (Surficial)	5.58	9.97	5.05	4.83	19.00	15.75	10.03	

Data derived from Appendix A20

Fig. 5.21.A1

Mean concentrations of Phosphate in pore water at the six sites

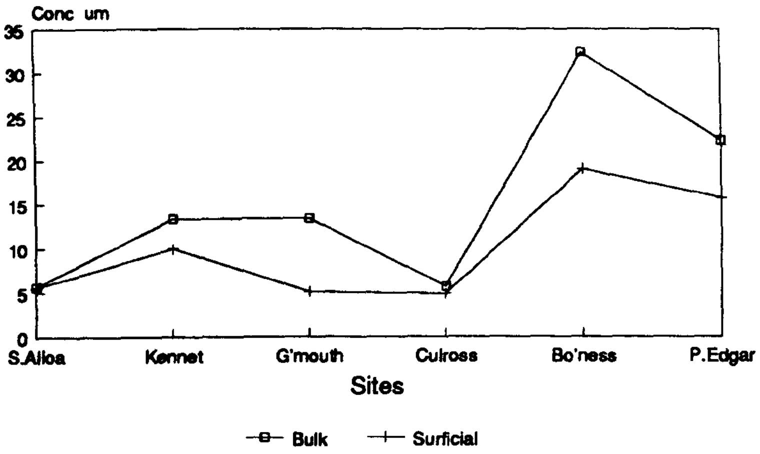


Fig. 5.21.A2

Seasonal variations of Phosphate in Pore water at the six sites

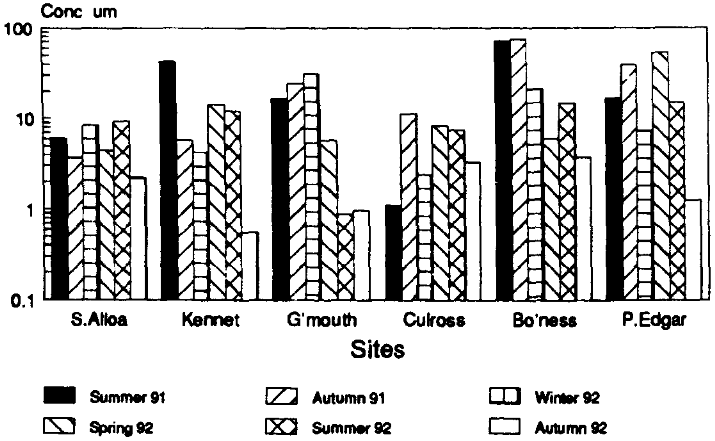


Fig. 5.21.B1

Mean concentrations of Phosphate in Pore water on the six seasons

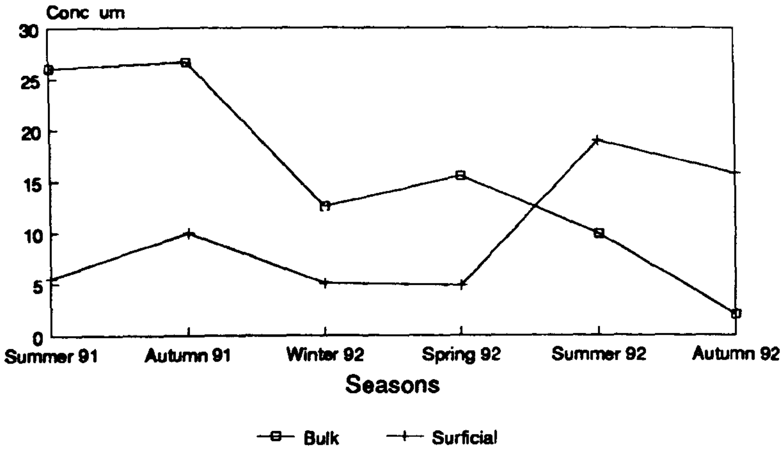


Fig. 5.21.B2

Spatial variations of Phospate in Pore water on the six sampling seasons

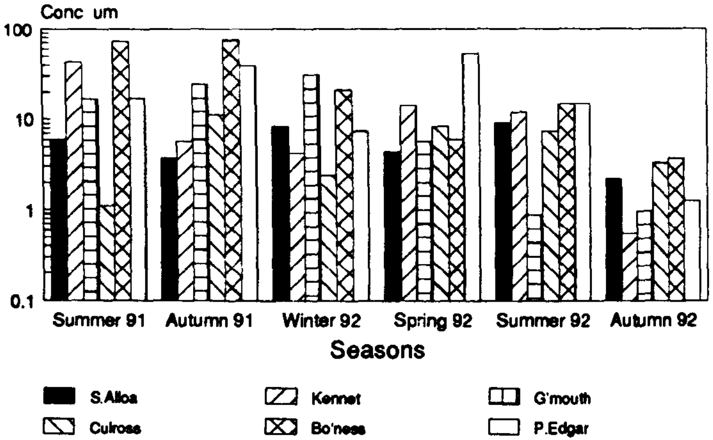


Table 5.23

Mean concentrations of dissolved organic carbon in the pore water mg\l

Stations	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Seasons								
Summer 91	34.25	48.25	20.75	17.25	29.75	15.75	27.67	29.50
Autumn 91	17.50	21.50	27.75	28.25	29.25	24.00	24.71	23.83
Winter 92	27.50	49.75	57.25	61.25	50.75	50.25	49.46	56.67
Spring 92	36.25	14.00	41.50	39.75	69.50	54.25	42.54	56.67
Summer 92	54.25	40.00	59.75	33.00	33.50	29.25	41.63	49.00
Autumn 92	43.00	31.00	53.00	53.75	65.25	72.00	53.00	54.33
Mean Spatial (Bulk)	35.46	34.08	43.33	38.88	46.33	40.92	39.83	
Mean Spatial (Surficial)	27.33	51.33	48.17	44.83	46.17	52.17	45.00	

Data derived from Appendix A21

Fig. 5.22.A1

Mean concentrations of DOC in pore water at the six sites

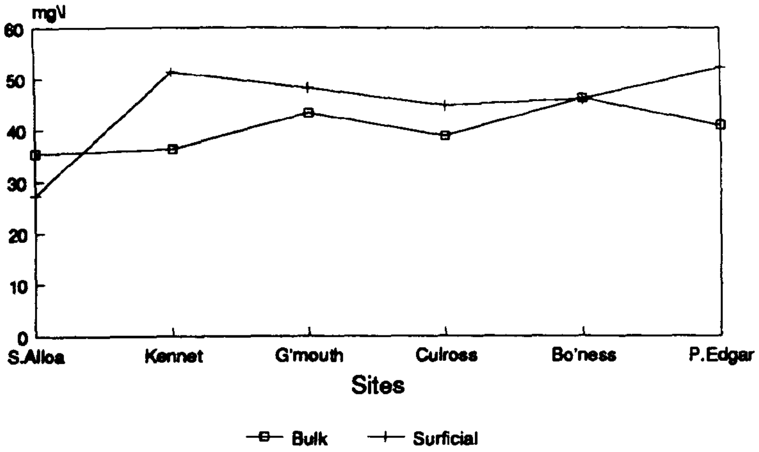


Fig. 5.22.A2

Seasonal variations of DOC in pore water at the six sites

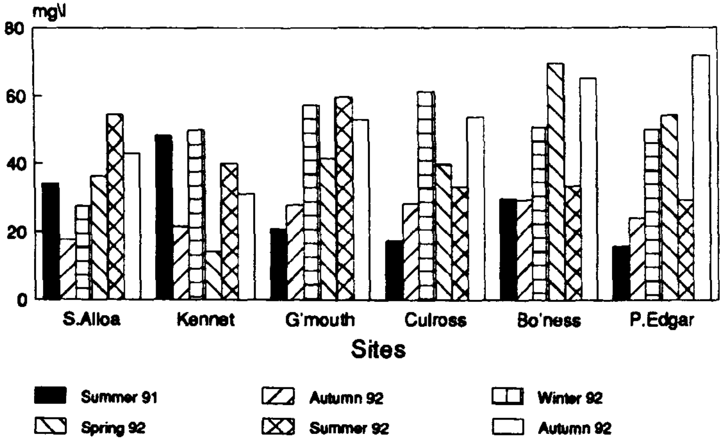


Fig. 5.22.B1

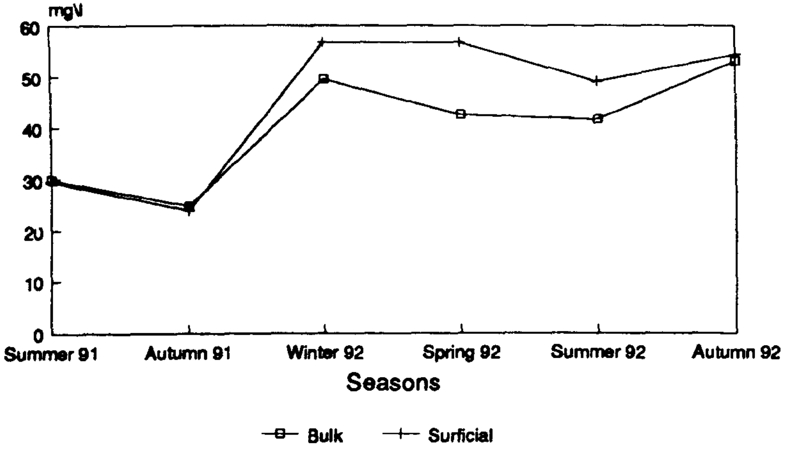
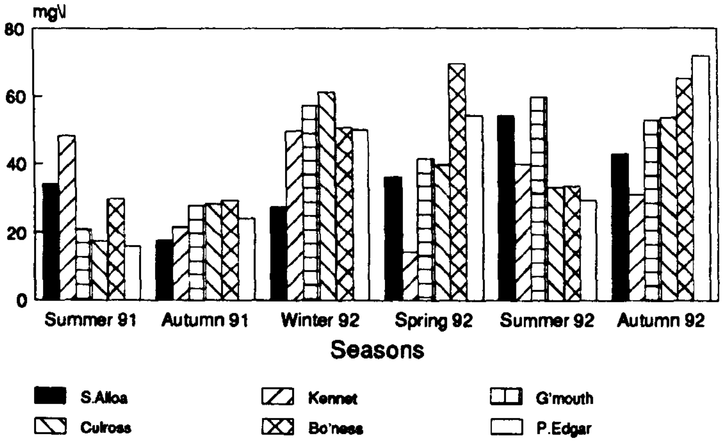

Mean concentrations of DOC in pore water
on the six sampling seasons

Fig. 5.22.B2


Spatial variations of DOC in pore water
on the six sampling seasons

5.1.2.4 Major elements (iron and manganese)

Mean concentrations of iron and manganese in the pore water are shown in Tables 5.24 and 5.25.

Spatially, iron concentration (Fig. 5.23.A) shows a distinctive distribution by which the intertidal stations (stations A and B) recorded the highest concentrations of 13.33 and 11.83 mg/l. The tidal stations (Stations C-D) had similar distribution. Their mean values ranged between 3.38 and 4.46 mg/l. Spatially, manganese showed a random distribution and recorded its highest concentration at station E (Bo'ness) of 8.77 mg/l and its lowest concentration at station D (Culross) with a value of 3.15 mg/l (Fig. 5.24.A).

In all stations except station A (S.Alloa), iron and manganese showed decrease in concentrations with depth (Figs. 5.23.A1 and 5.24.A1).

The overall mean concentration of iron was 6.85 mg/l and the range was between 0.1 and 36.0 mg/l. The overall mean concentration of manganese was 5.5 mg/l and the range was 0.5-20 mg\l.

Seasonally, iron and manganese shared a similar variation with lowest concentrations in the spring season (Figs. 5.23.B1 and 5.24.B1).

Table 5.24

Mean concentrations of Iron in the pore water mg\l

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	21.75	19.00	3.60	2.25	4.18	0.25	8.50	10.40
Autumn 91	9.33	16.33	9.55	4.23	0.53	8.85	8.13	9.78
Winter 92	12.30	20.90	4.03	9.75	3.10	3.95	9.00	10.43
Spring 92	17.50	6.63	3.80	1.75	9.23	3.30	7.03	7.73
Summer 92	2.80	4.05	3.68	3.73	0.65	4.15	3.18	3.58
Autumn 92	16.33	4.08	2.10	4.95	2.63	1.53	5.27	3.05
Mean Spatial (Bulk)	13.33	11.83	4.46	4.44	3.38	3.67	6.85	
Mean Spatial (Surficial)	6.23	17.02	7.05	5.05	5.02	4.62	7.50	

Data derived from Appendix A22

Fig. 5.23.A1

Mean concentrations of Iron in pore water at the six sites

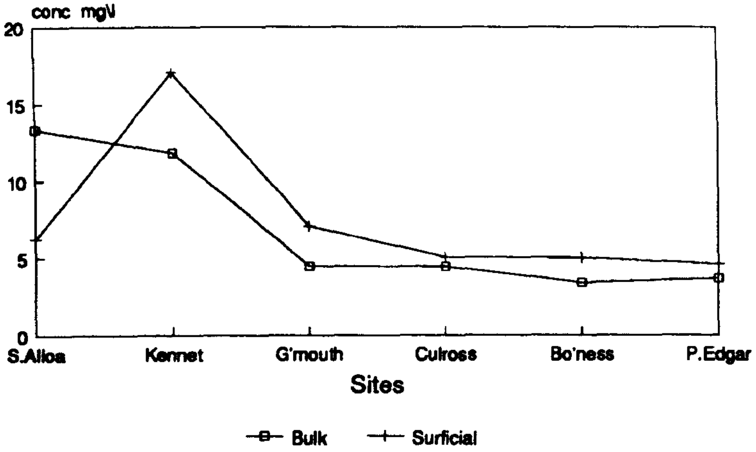


Fig. 5.23.A2

Seasonal variations in Iron in pore water at the six sites

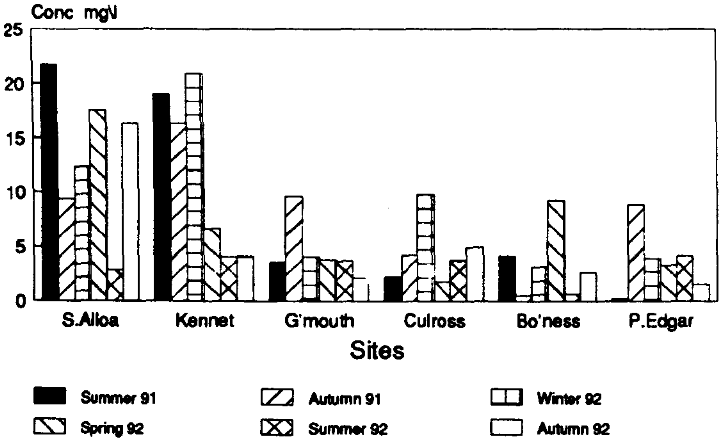


Fig. 5.23.B1

Mean concentrations of Iron in pore water on the six seasons

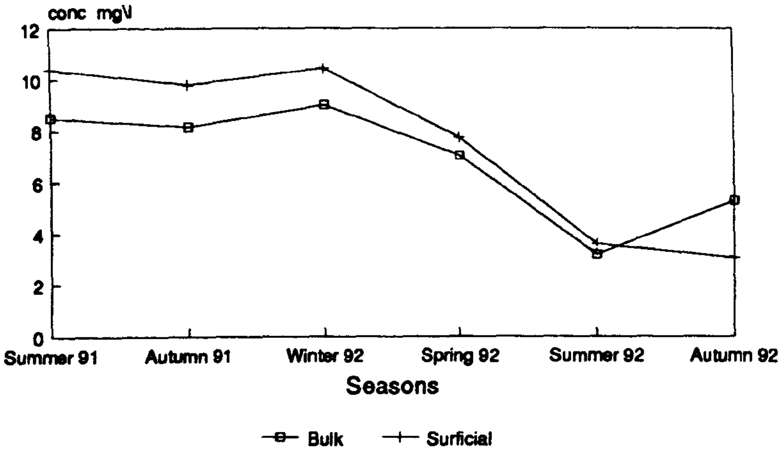


Fig. 5.23.B2

Spatial variations of Iron in pore water on the six seasons

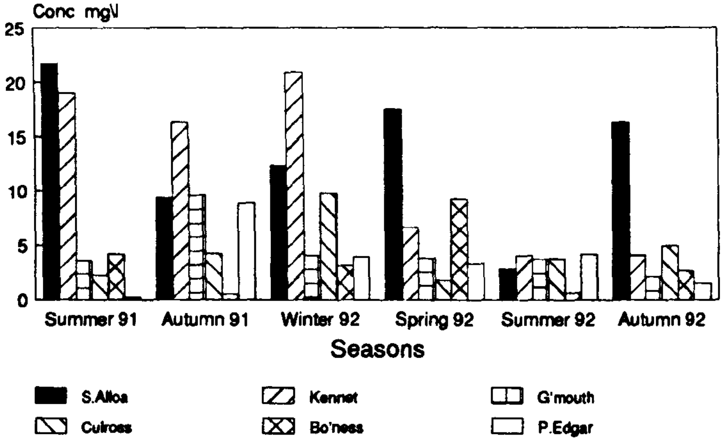


Table 5.25

Mean concentrations of Manganese in the pore water mg\l

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	9.75	9.55	2.78	3.80	9.68	2.00	6.26	8.35
Autumn 91	4.08	7.48	6.40	2.23	7.80	10.90	6.48	8.88
Winter 92	4.13	7.63	7.33	4.78	10.05	6.63	6.75	7.80
Spring 92	6.35	2.53	4.03	1.93	10.50	5.83	5.19	6.35
Summer 92	3.04	2.87	11.77	3.31	5.81	3.92	5.12	5.87
Autumn 92	3.34	2.33	0.74	2.87	8.79	1.35	3.24	2.84
Mean Spatial (Bulk)	5.11	5.40	5.51	3.15	8.77	5.10	5.51	
Mean Spatial (Surficial)	4.30	9.46	6.78	3.60	8.75	7.20	6.68	

Data derived from Appendix A23

Fig. 5.24.A1

Mean concentrations of Manganese in pore water at the six sites

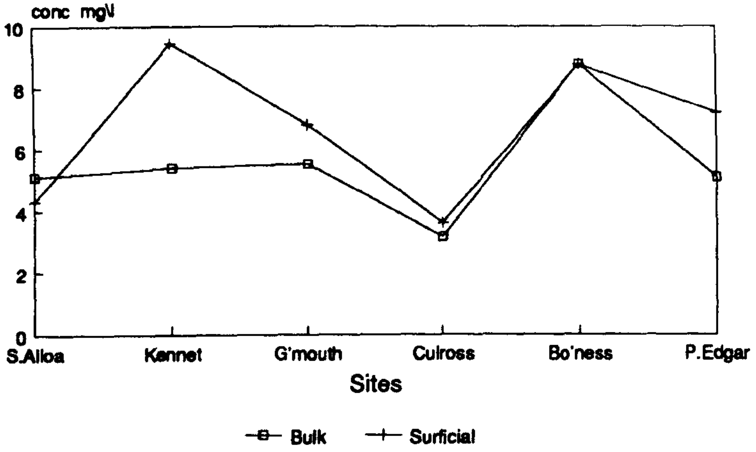


Fig. 5.24.A2

Seasonal variations of Manganese in pore water at the six sites

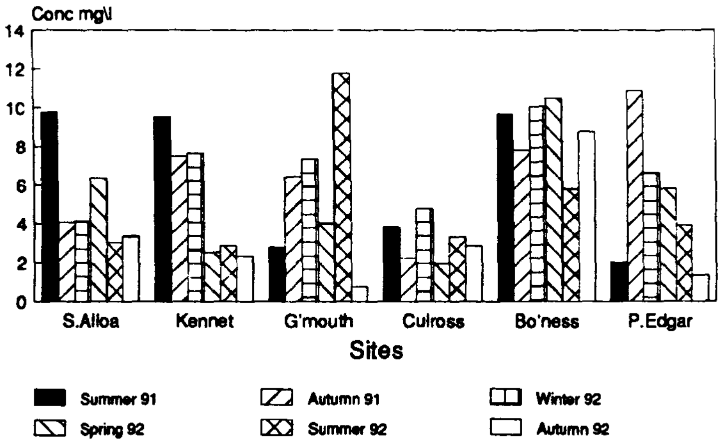


Fig. 5.24.B1

Mean concentrations of Manganese in pore water on the six seasons

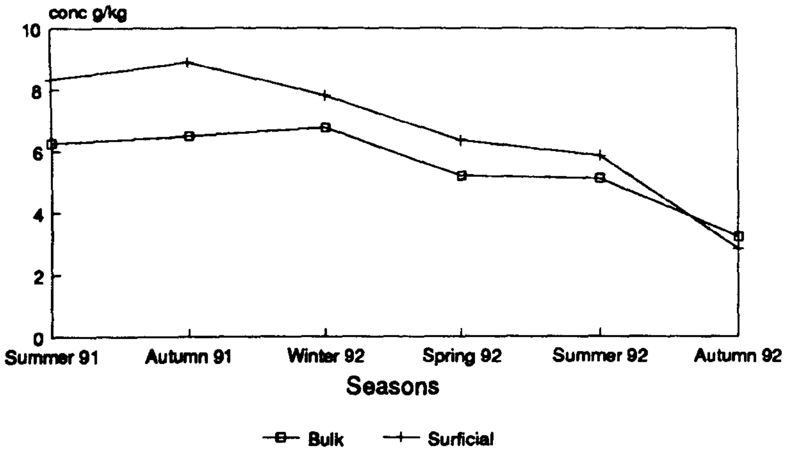
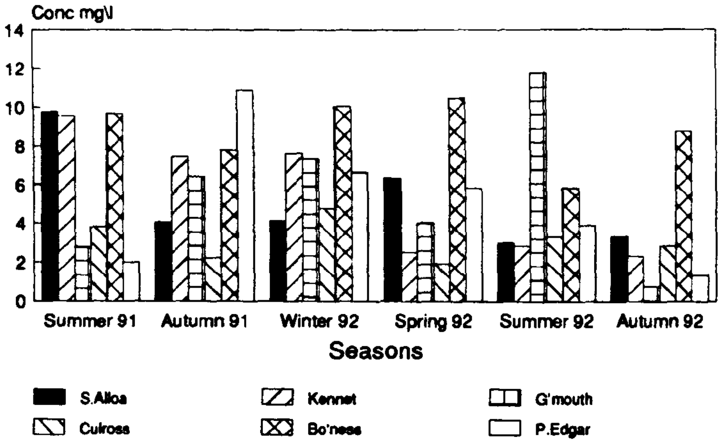


Fig. 5.24.B2

Spatial variations of Manganese in pore water on the six seasons



5.1.2.5 Trace metals (Pb, Cd, Cu, Ni and Hg)

Table 5.26 presents the mean spatial and temporal distributions of lead in the pore water. Spatially, lead shows no distinctive distributions throughout the sampling sites (Fig. 5.25.A). The overall mean concentration was 3.14 µg/l with an overall range of 0.1-9.1 µg/l.

No obvious vertical trend was observed. The results revealed a general decrease in concentration with depth in the summer and winter seasons. Seasonally, Fig. 5.25.B shows a decline in the concentration of lead in the winter. Lead had an inverse relationship with iron and manganese, r = - 0.8 and - 0.9 respectively, and a positive correlation with cadmium in the pore water (r = 0.6).

The mean spatial and temporal distributions of cadmium in the pore water are presented in Table 5.27.

Fig. 5.26.A shows that cadmium had similar average spatial distribution with lead. The overall mean concentration was 1.86 µg/l with a range of 0.0-5.91 µg/l.

Seasonally, Fig. 5.26.B indicates that the highest concentration was in the spring season with a value of 2.45 µg/l. Obvious increase in cadmium concentration with depth was observed in stations B and C, and vice versa for stations A and F. This is shown in Fig. 5.26.A1. depicting the variation between the surficial and bulk concentrations.

Table 5.28 shows the mean distributions of copper at different seasons and stations. Fig. 5.27.A shows no obvious spatial trend. The overall mean concentration was 31.88 μg/l and the range was between 7.7 and 98.0 μg/l. Random fluctuations with depth were observed. However, there was an increase in concentrations with depth in stations A and B (intertidal stations) and the reverse was the case in the tidal stations. Seasonally, a decrease towards the cold seasons was observed. Summer, 1991 recorded the highest concentration (Fig. 5.27.B).

Table 5.29 shows the mean distributions of nickel in the pore water. Spatially, there was a uniform distribution in all the stations. However, station A (S.Alloa) had the lowest value (Fig. 5.28.A). The overall mean was 24.7 μg/l and the range was between 2.2 and 72.0 μg/l.

Seasonally, nickel decreased in concentration in the spring season (Fig. 5.28.B). Nickel in the pore water was found to be strongly correlated with iron and manganese in the pore water (r = 0.9 each). Nickel showed an overall increase with depth both spatially and temporally (Fig. 5.28.A1 and Fig. 5.28.B1).

Mercury distribution is shown in Table 5.30. Spatially, station A recorded the highest concentration (Fig. 5.29.A). Mercury in the pore water inversely correlated with chlorides (r = - 0.8). The overall mean concentration was 74.7 ng/l and the overall range was between 0.0 and 1108 ng/l.

Seasonally, a decrease in mercury concentrations in the winter season was observed (Fig. 5.29.B). Mercury in the pore water were found to correlate negatively with dissolved organic carbon and positively with hydrogen ion concentration, r = - 0.75 and 0.9 respectively.

Table 5.26

Mean concentrations of Lead in the pore water ug\l

Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Seasons	A	B	C	D	E	F		
Summer 91	4.80	3.73	3.43	2.92	4.01	2.85	3.62	4.06
Autumn 91	3.43	2.32	2.65	4.52	1.41	2.41	2.79	2.51
Winter 92	2.48	2.38	2.17	2.40	3.10	1.61	2.36	3.03
Spring 92	3.00	5.50	4.34	5.34	3.33	2.89	4.06	3.61
Summer 92	3.70	3.65	3.55	2.30	4.93	4.34	3.74	4.10
Autumn 92	2.90	2.04	1.21	2.18	2.71	2.57	2.27	2.56
Mean Spatial (Bulk)	3.39	3.27	2.89	3.28	3.25	2.78	3.14	
Mean Spatial (Surficial)	4.39	2.56	3.32	3.02	4.16	2.41	3.31	

Data derived from Appendix A24

Fig. 5.25.A1

Mean concentrations of Lead in pore water at the six sampling sites

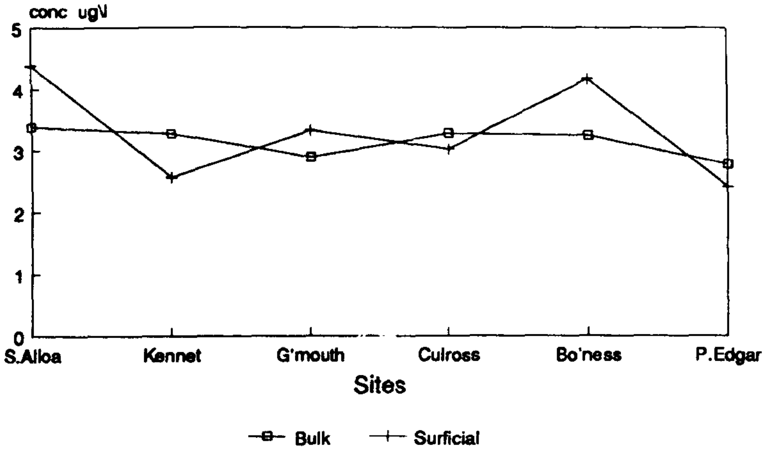


Fig. 5.25.A2

Seasonal variations of Lead in pore water at the six sampling sites

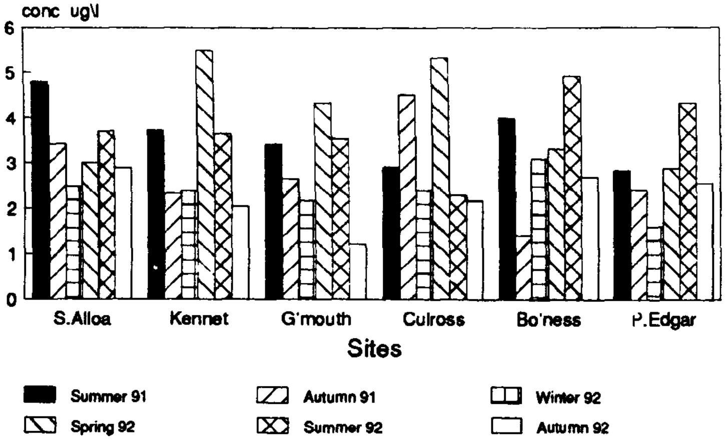


Fig. 5.25.B1

Mean concentrations of Lead in pore water on the six sampling seasons

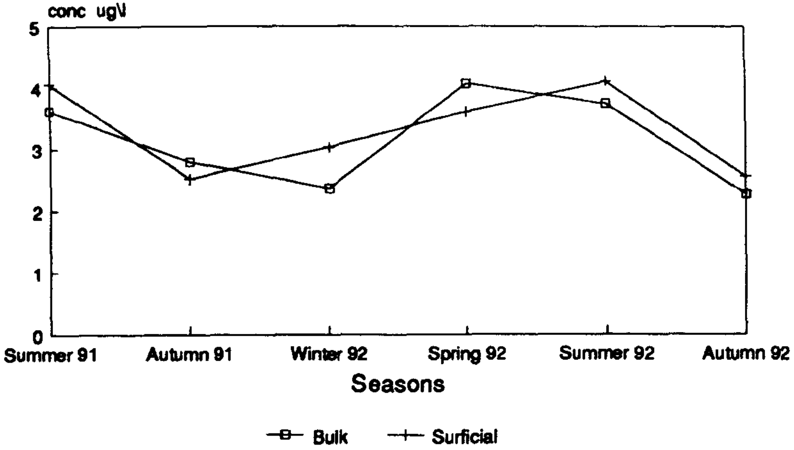


Fig. 5.25.B2

Spatial variations of Lead in pore water on the six sampling seasons

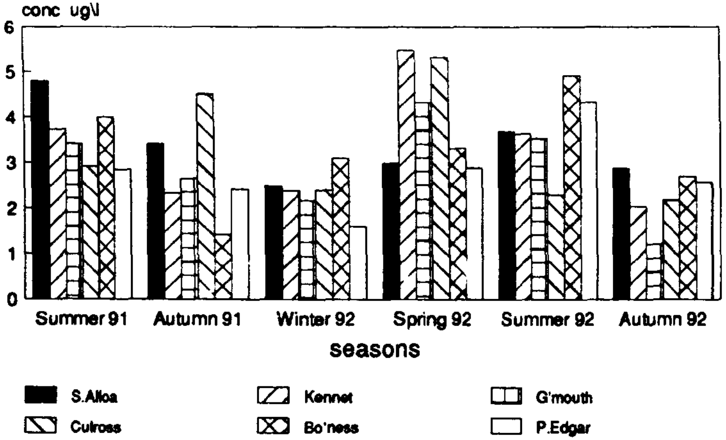


Table 5.27

Mean concentrations of Cadmium in the pore water ug\l

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	2.43	2.25	1.98	1.54	1.85	0.52	1.76	1.56
Autumn 91	1.77	2.39	1.76	3.24	1.55	1.13	1.97	1.75
Winter 92	1.30	0.93	1.16	0.37	2.28	4.70	1.79	1.91
Spring 92	2.60	3.55	1.67	3.09	1.43	2.35	2.45	2.22
Summer 92	2.31	2.14	2.26	3.32	1.68	1.60	2.22	2.26
Autumn 92	1.54	1.12	0.94	1.15	0.62	0.57	0.99	0.81
Mean Spatial (Bulk)	1.99	2.06	1.63	2.12	1.57	1.81	1.86	
Mean Spatial (Surficial)	2.46	1.50	1.29	2.10	1.66	1.49	1.75	

Data derived from Appendix A25

Fig. 5.26.A1

Mean concentrations of Cadmium in pore water at the six sampling sites

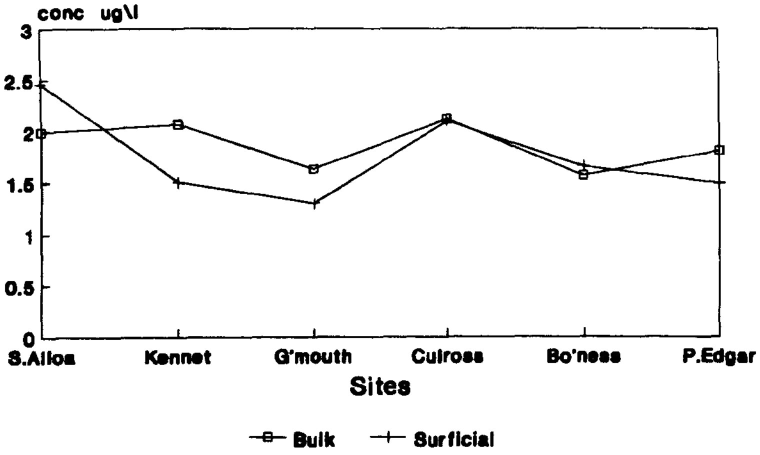


Fig. 5.26.A2

Seasonal variations of Cadmium in pore water at the six sampling sites

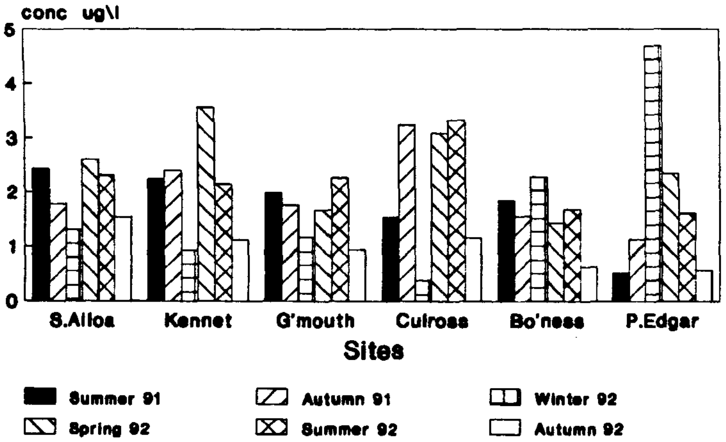


Fig. 5.26.B1

Mean concentrations of Cadmium in pore water on the six sampling seasons

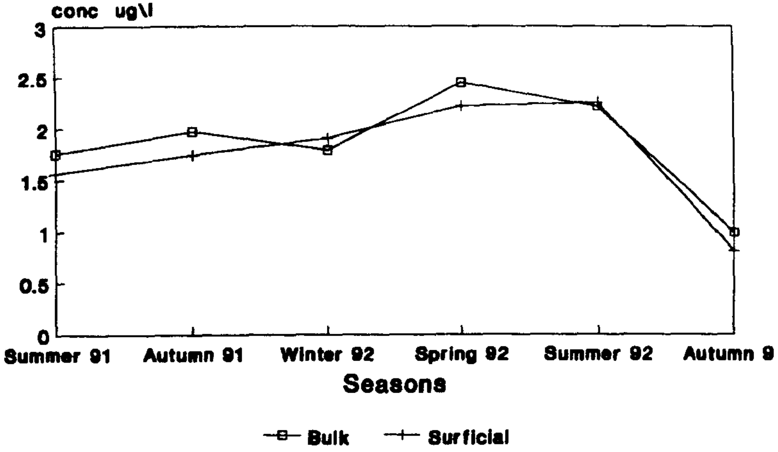


Fig. 5.26.B2

Spatial variations of Cadmium in pore water on the six sampling seasons

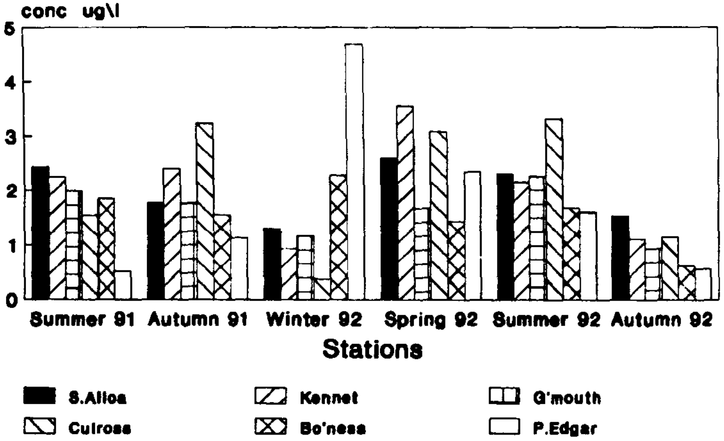


Table 5.28

Mean concentrations of Copper in the pore water ug\l

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	33.00	53.50	67.00	71.00	63.75	38.25	54.42	57.00
Autumn 91	39.50	33.00	26.50	45.50	33.00	20.25	32.96	35.17
Winter 92	27.43	18.28	19.75	16.05	62.50	18.10	27.02	30.25
Spring 92	29.38	36.00	21.75	24.75	23.00	23.35	26.37	22.38
Summer 92	27.19	29.40	27.78	26.30	20.03	21.61	25.38	23.11
Autumn 92	23.73	26.23	27.73	26.78	21.50	24.88	25.14	24.98
Mean Spatial (Bulk)	30.04	32.73	31.75	35.06	37.30	24.41	31.88	
Mean Spatial (Surficial)	25.49	26.73	36.65	37.07	44.75	22.21	32.15	

Data derived from Appendix A26

Fig. 5.27.A1

Mean concentrations of Copper in pore water at the six sampling sites

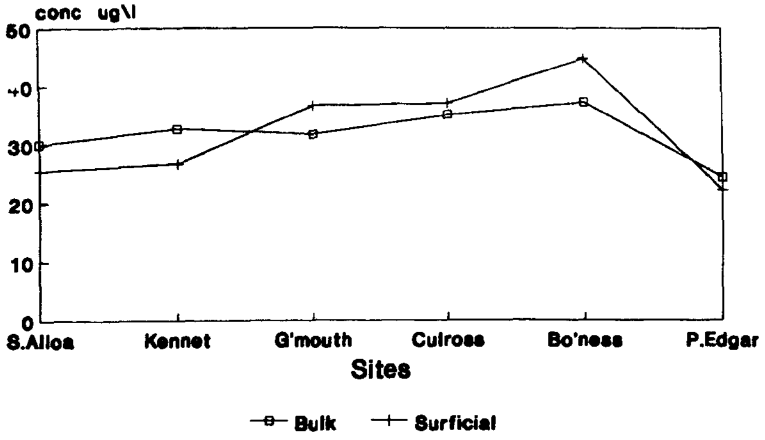


Fig. 5.27.A2

Seasonal variations of Copper in pore water at the six sampling sites

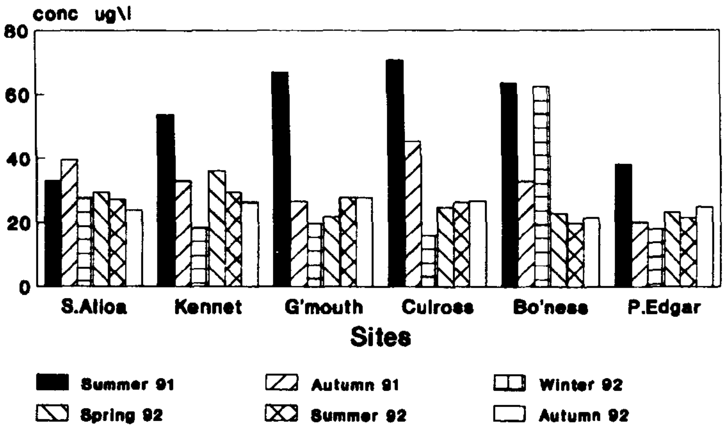


Fig. 5.27.B1

Mean concentrations of Copper in pore water on the six sampling seasons

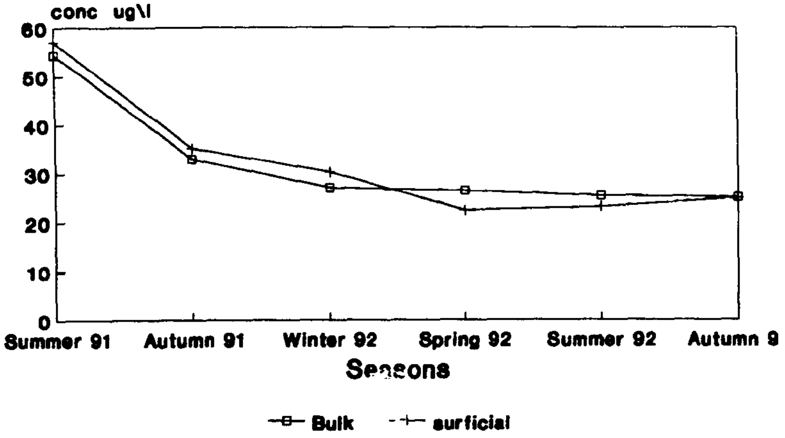


Fig. 5.27.B2

Spatial variations of Copper in pore water on the six sampling seasons

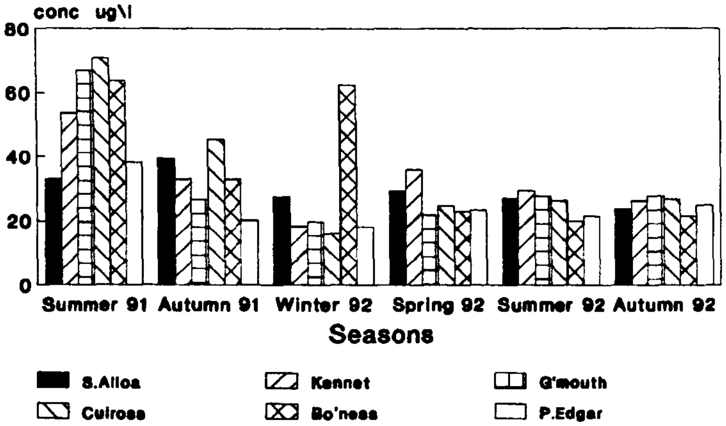


Table 5.29

Mean concentrations of Nickel in the pore water ug\l

Stations Seasons	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F	Mean Temporal (Bulk)	Mean Temporal (Surficial)
Summer 91	22.25	62.00	50.75	27.75	16.75	22.75	33.71	35.33
Autumn 91	31.00	42.50	17.75	38.00	21.75	35.50	31.08	24.17
Winter 92	21.03	21.45	40.80	21.83	51.50	34.50	31.85	22.72
Spring 92	23.78	34.18	25.98	28.58	9.28	13.15	22.49	14.28
Summer 92	14.23	11.63	17.18	15.25	17.93	28.20	17.40	13.57
Autumn 92	11.53	9.75	13.03	7.88	15.45	10.70	11.39	11.87
Mean Spatial (Bulk)	20.63	30.25	27.58	23.21	22.11	24.13	24.65	
Mean Spatial (Surficial)	15.97	22.75	23.52	21.32	18.45	19.93	20.32	

Data derived from Appendix A27

Fig. 5.28.A1

Mean concentrations of Nickel in pore water at the six sampling sites

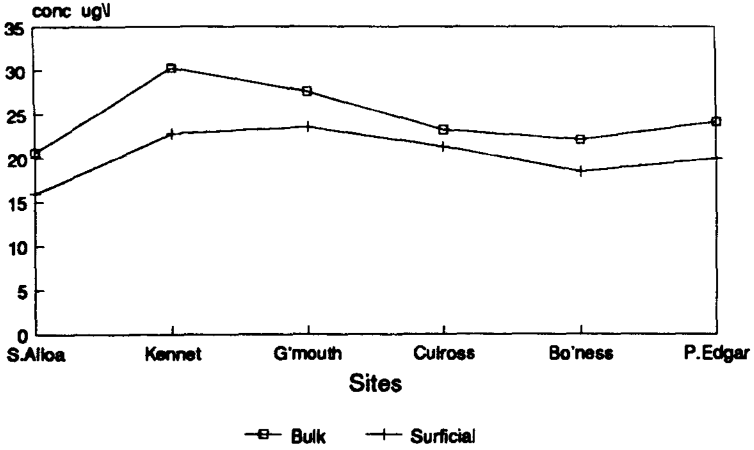


Fig. 5.28.A2

Seasonal variations of Nickel in pore water at the six sampling sites

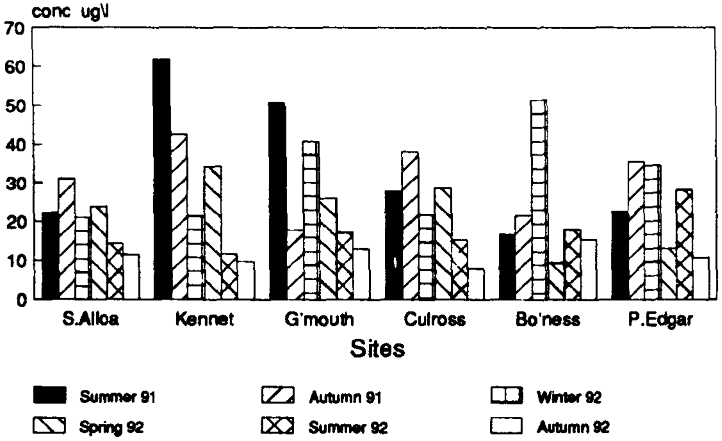


Fig. 5.28.B1

Mean concentrations of Nickel in
pore water on the six sampling seasons

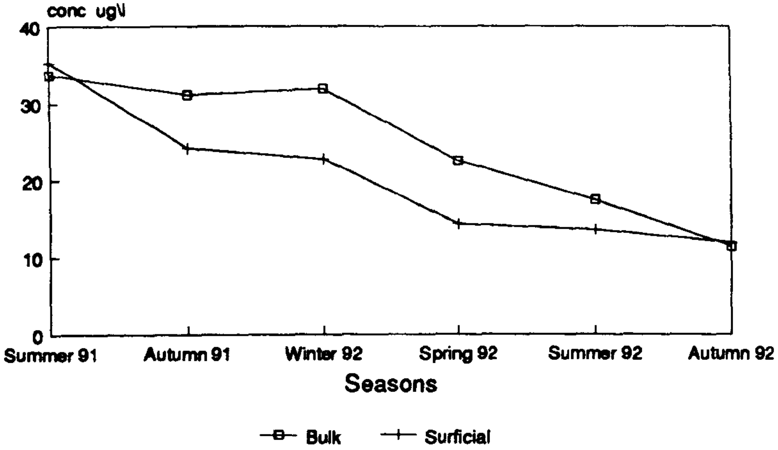


Fig. 5.28.B2

Spatial variiations of Nickel in
Pore water on the six sampling seasons

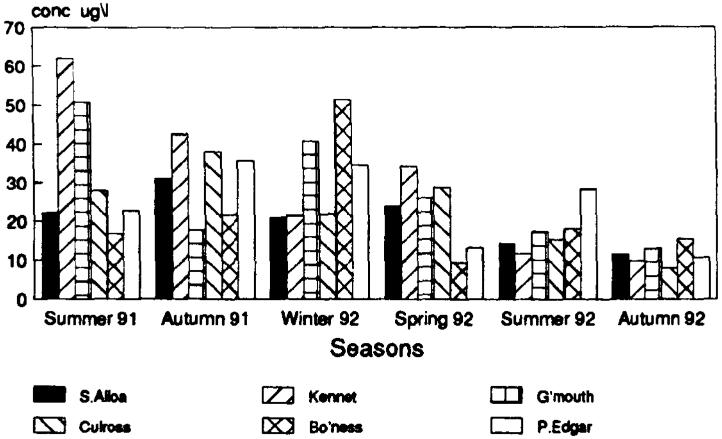


Table 5.30

Mean concentrations of Mercury in the pore water ng\l

Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar	Mean	Mean
Seasons	A	B	C	D	E	F	Temporal (Bulk)	Temporal (Surficial)
Summer 91	157.25	50.75	47.25	46.75	76.00	39.25	69.54	68.17
Autumn 91	396.00	49.00	290.25	53.25	62.00	177.50	171.33	131.50
Winter 92	65.75	18.75	7.25	53.75	33.25	58.75	39.58	36.50
Spring 92	252.00	6.00	43.25	141.75	125.25	5.00	95.54	119.83
Summer 92	38.79	25.24	82.55	76.81	28.88	26.79	46.51	49.90
Autumn 92	53.25	15.89	43.53	17.67	22.55	9.49	27.06	19.33
Mean Spatial (Bulk)	160.51	27.60	85.68	65.00	56.78	53.15	74.73	
Mean Spatial (Surficial)	119.35	13.86	70.31	70.04	58.16	94.88	69.48	

Data derived from Appendix A28

Fig. 5.29.A1

Mean concentrations of Mercury in pore water at the six sampling sites

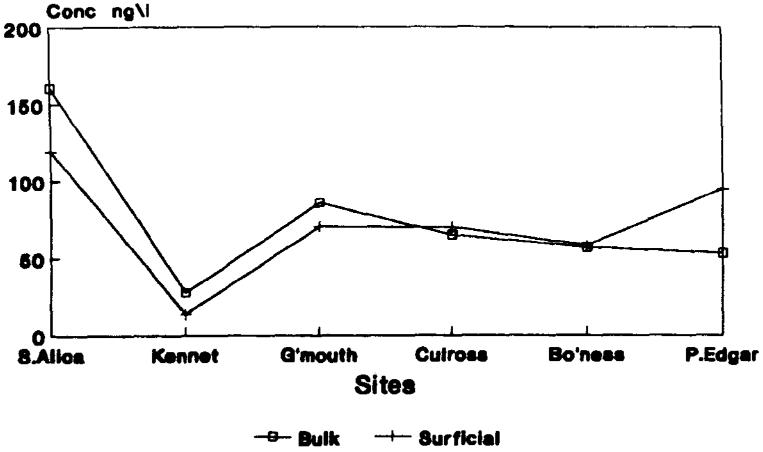


Fig. 5.29.A2

Seasonal variations of Mecury in pore water at the six sampling sites

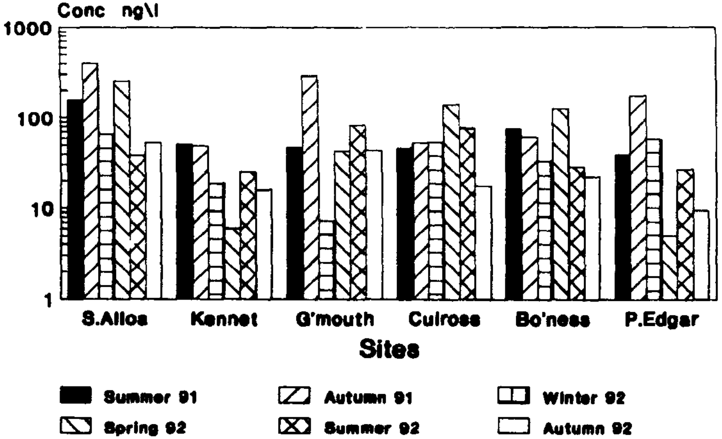


Fig. 5.29.B1

Mean concentrations of Mercury in pore water on the six sampling seasons

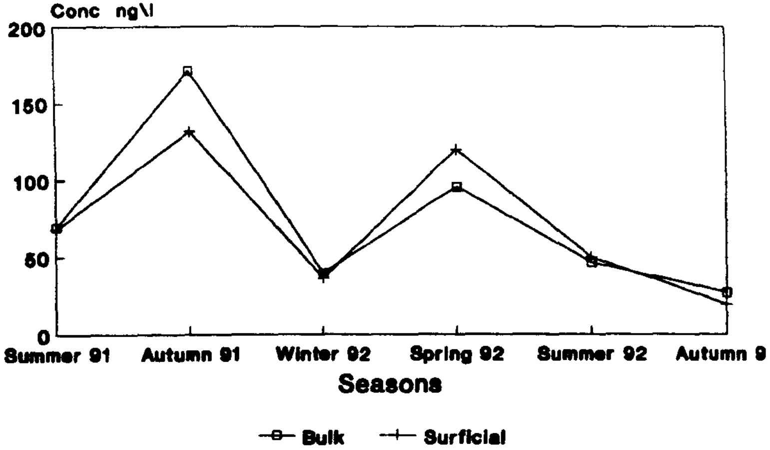
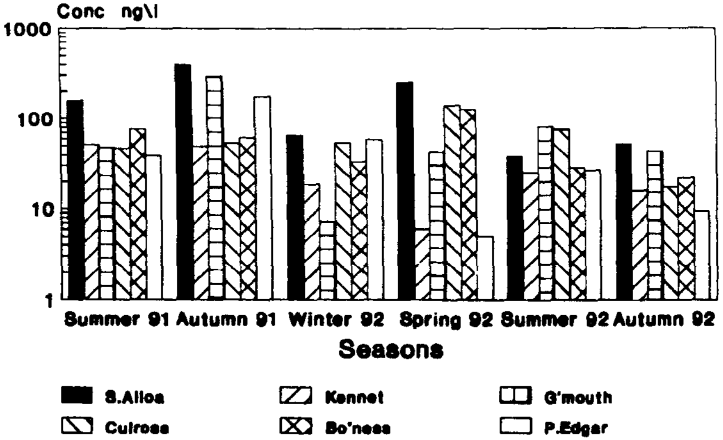


Fig. 5.29.B2

Spatial variations of Mercury in pore water on the six sampling seasons



5.1.2.6 Summary of the spatial and temporal distributions in the pore water parameters

Spatially, chloride, sulphate, conductivity (salinity), dissolved organic carbon and phosphate were observed to increase sea-ward while iron, lead and mercury decreased. Chloride correlated well with sulphate and conductivity, $r = 0.95$ and 0.99 respectively. Chloride and conductivity reflected the salinity in the Forth estuary. The mean values for the different stations in descending order is A > B > C > D > E > F. This is theoretically logical, regarding their locations on the river-sea dilution line.

Spatially, iron and mercury and to some degree lead in the pore water were observed to inversely correlate with chloride ions. Manganese and copper in the pore water correlated positively with a correlation coefficient of + 0.7, suggesting that copper concentrations could be related to manganese content.

Station E (Bo'ness) was characterized by high alkalinity, nitrate, phosphate, manganese, and copper in the pore water.

Temporally, considering the first four seasons, chloride, sulphate, alkalinity, conductivity, phosphate, were found to be decreasing as the wetter seasons approached while dissolved organic carbon and total oxidized nitrogen (nitrate and nitrite) increased.

Tables 5.34 and 5.35 summarises the ranges and means of pore water parameters.

Table 5.34

Ranges and mean concentrations of nutrients in the pore water of the Forth estuary

Station		pH	AlK meq/l	Cl$^-$ meq/l	SO$_4^{2-}$ meq/l	Cond mS.cm^{-1}	PO$_4^{3-}$ µmol	NO$_3^-$ µmol	DOC mg\l
S.Alloa A	mean	7.75	5.96	177	4.92	10.9	5.68	31.9	35.8
	range	7.2-8.3	2.0-15	57-519	0-23	5.6-28	0.4-20.0	1.6-160	12-85.0
Kennet B	mean	7.59	4.6	571	29.0	37.0	13.0	25.9	36.3
	range	6.7-8.1	2-8	423-876	23-44	28.7-58	0-53	1.4-213	10-82
G'mouth C	mean	7.95	6.79	669.8	29.6	42.9	13.4	67.0	43.4
	range	6.9-8.3	3-14	390-956	14-51	34-62	0-78	1.6-497	18-73
Culross D	mean	7.75	4.75	687	35.0	46.0	5.7	203	38.9
	range	7-8.1	2-8	434-971	17.8-48	38-59	1.1-27	1.6-1065	11-97
Bo'ness E	mean	7.88	9.0	742	31.4	46.6	32.3	93.0	46.0
	Range	7.5-8.3	4-18	520-993	10-53	5-62	0.2-102	1.6-710	19-78
P.Edgar F	mean	7.77	5.3	792	42.2	49.9	22.3	29.8	40.9
	range	7.3-8.1	2-9	466-1245	20-65	41.3-64	0-100	1-305	10-94
overall mean		7.78	6.1	607	28.7	38.9	15.5	75.1	40.2
overall range		6.7-8.3	2-18	57-1246	0-65	4.6-64	0-102	1-1065	10-97

Table 5.35

Ranges and mean concentrations of trace metals in the pore water of the Forth estuary

Station		Cd µg/l	Cu µg/l	Ni µg/l	Pb µg/l	Hg ng/l	Fe mg/l	Mn mg/l
S.Alloa A	mean	1.99	30.0	20.6	3.4	161	13.3	5.1
	range	0.5-3.58	16.0-60.0	7.5-48	1.5-6.6	1.9-1108	0.3-32.0	1.1-12
Kennet B	mean	2.06	32.73	30.3	3.27	27.6	11.7	5.4
	range	0.0-5.4	13-68	7.0-72	0.84-7.5	2.7-81	1.0-36	1.8-20
G'mouth C	mean	1.63	31.8	27.7	2.89	85.7	4.46	5.5
	range	0.2-3.6	11.4-98	10.6-70	0.1-6.15	0.0-815	0.6-16	0.5-15
Culross D	mean	2.12	35.1	23.1	3.28	65.0	4.44	3.2
	range	0-5.9	12.0-96	6.5-52	1.32-8.0	11.3-260	0.3-15	1.3-5
Bo'ness E	mean	1.57	37.3	22.1	3.25	56.8	3.38	8.8
	range	0.5-3.2	7.7-88	2.2-67	1.0-9.1	0.0-182	0.3-16.0	5.2-14
P.Edgar F	mean	1.78	24.41	24.1	2.78	53.2	3.67	5.1
	range	0.2-4.99	9.9-49	7.6-55	1.2-6.08	4.0-460	0.1-12.0	0.9-14
overall mean		1.86	31.9	24.7	3.14	74.7	6.85	5.5
overall range		0.0-5.91	7.7-98.0	2.2-72	0.1-9.1	0.0-1108	0.1-36	0.5-20

5.2 Results of the variations with depth

To study the variations with depth, two stations were chosen. Station B (Kennet) was chosen for two reasons; firstly, this station was a unique station, typified by compact sediments. Secondly, it represents the river end member. In addition, this station together with station A (S.Alloa) was sampled by hand and the subsequent relocation of the site was easier than the other stations. Station E (Bo'ness) was chosen to represent the sea end member.

Two seasons were selected to show the temporal variations in the sediment and pore water parameters. These two seasons were summer 1991 and winter 1992.

5.2.1 Sediment depth profiles

5.2.1.1 Station B (Kennet)

Trace metals variations with depth at station B in both summer and winter together with organic matter and particle size are shown in Fig. 5.32.

The distribution of particle size and organic matter were similar in the two seasons. However, their values were higher in the summer season except total organic nitrogen which recorded higher values in the winter season. The particle size slightly decreased with depth (97%-95%) in the summer while in the winter, the decline was sharp (90.5% to 85.0% < 63 µm). This trend was also observed for organic matter (LOI), total organic carbon and total organic nitrogen.

The overall trend was generally a decrease with depth in all the trace metals in the two seasons. In general, trace metal variations with depth were found to be controlled by particle size and organic matter contents in both the summer and winter.

5.2.1.2 Station E (Bo'ness)

Variations with depth at station E (Bo'ness) is illustrated in Fig. 5.35. At this station, total organic carbon distribution rather than organic matter loss on ignition was found to correlate positively with particle size ($p < 0.05$). Sediment particle size and total organic carbon values in the summer season were in striking contrast to the winter season values. This was reflected in the trace metal profiles. In the summer season, all trace metals were found to increase with depth up to 7.5 cm and then decreased thereafter. Total organic nitrogen increased in the first 2.5 cm and then decreased along the sediment core. Trace metals in the summer season were found to correlate positively with particle size and organic matter (LOI) while in the winter they correlated positively with particle size and total organic carbon ($p < 0.05$).

5.2.2 Pore water depth profiles

5.2.2.1 Station B (Kennet)

Nutrients in the interstitial water at station B (Kennet) are shown in Fig. 5.33. Sulphate and dissolved organic carbon showed a similar profile in both summer and winter. The rate of sulphate reduction was higher in the summer profile while winter profile remained constant in the first 5 cm depth and started decreasing afterwards. This trend was also observed for the dissolved organic carbon profile. This could be explained by the higher rate of organic matter decomposition in the summer. Associated with decrease in sulphate were increases in interstitial concentration of HCO_3^- (alkalinity) and phosphate in the summer. The phosphate profile observed was similar to pore water iron profile in this station. This suggests that phosphates were controlled by the amount of iron. This will be discussed later.

Trace metals variations with depth at station B are illustrated in Fig. 5.34. The high values of trace metals in the pore water in the summer compared to winter could be related to the high concentrations of dissolved organic carbon in this season. The interstitial water profiles showed a large surface enrichment of dissolved iron and manganese. Iron slightly increased in the first depth and then decreased rapidly in further depths.

Manganese concentrations showed a progressive decline with depth. Iron and manganese profiles suggested that sediment became reducing after the first depth when redox potential became negative. Trace metals had a unique distribution in the summer as well as in the winter. In winter, the variations with depth seemed to be controlled by redox profile. The concentrations showed a decrease in values when redox values were positive and as soon as the redox profile became reducing after the first depth, concentrations started to increase. The summer profile showed some fluctuations by which concentrations recorded an increase and then decreased thereafter.

Cadmium and lead in the pore water were observed to share similar vertical distributions in both the summer and winter seasons, indicating similar processes controlling their mobilization.

5.2.2.2 Station E (Bo'ness)

Fig. 5.36 summarizes the vertical distribution of nutrients in station E (Bo'ness). Redox potential profile indicated anoxic conditions in the first depth in the summer while in the winter, anoxic conditions started at a lower depth. Sulphate was observed to decrease from its highest value near the sediment water interface of more than 40 meq/l to about 10 meq/l in the summer. Its reduction was much slower in the winter when it decreased from its highest values in the 2.5 cm depth of more than 50 meq/l to about 35 meq/l. As a result of sulphate reduction, increases in carbonate (alkalinity) and phosphate in the winter were observed. Nitrates showed an increase in the first depth and then decreased as the sediment became anoxic. This gradient reflected zones of oxygen reduction, nitrates reduction and sulphate reduction in the sediment. Alkalinity values showed a rapid increase with depth in the summer compared to the winter profile. Winter phosphate profile showed a progressive increase with depth while summer profile showed some fluctuation, in that its values were characterised by a rise in the first 5 cm followed by a decrease down to about 7.5 cm and then an increase thereafter.

Fig. 5.37 illustrates the variations of trace metals with depth in station E (Bo'ness). Iron and manganese were observed to decrease with depth in the summer while in the winter, iron and manganese showed an increase in the top 5 cm and then decreased. Trace metals; Cd, Pb and Hg were found to decrease sharply in the top 5 cm, increased in the middle of the core and then decreased in the last depth.

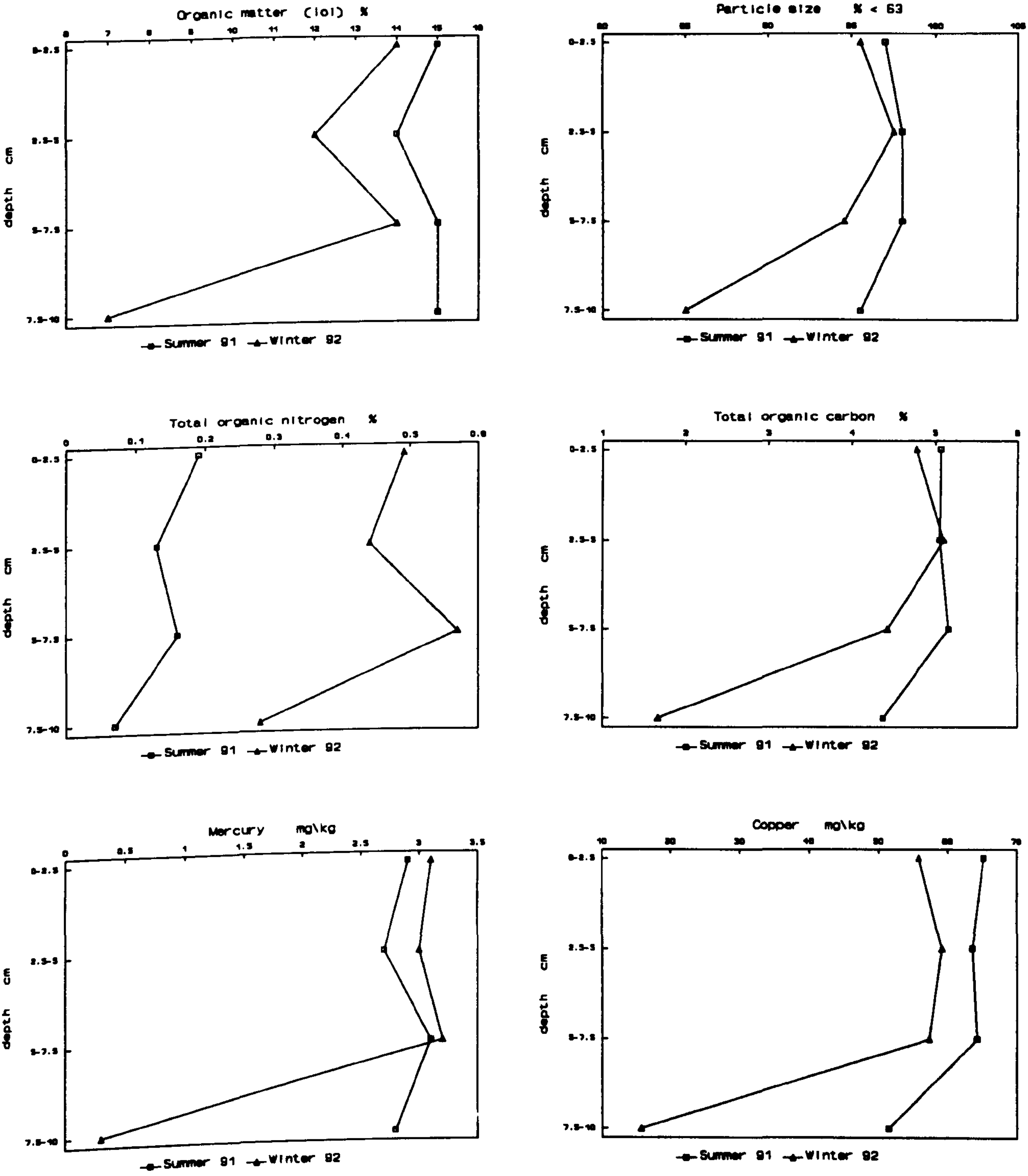


Fig. 5.32 Sediments particle size, organic matter (loi), toc ton, copper and mercury profiles at station B (Kennet) in summer and winter.

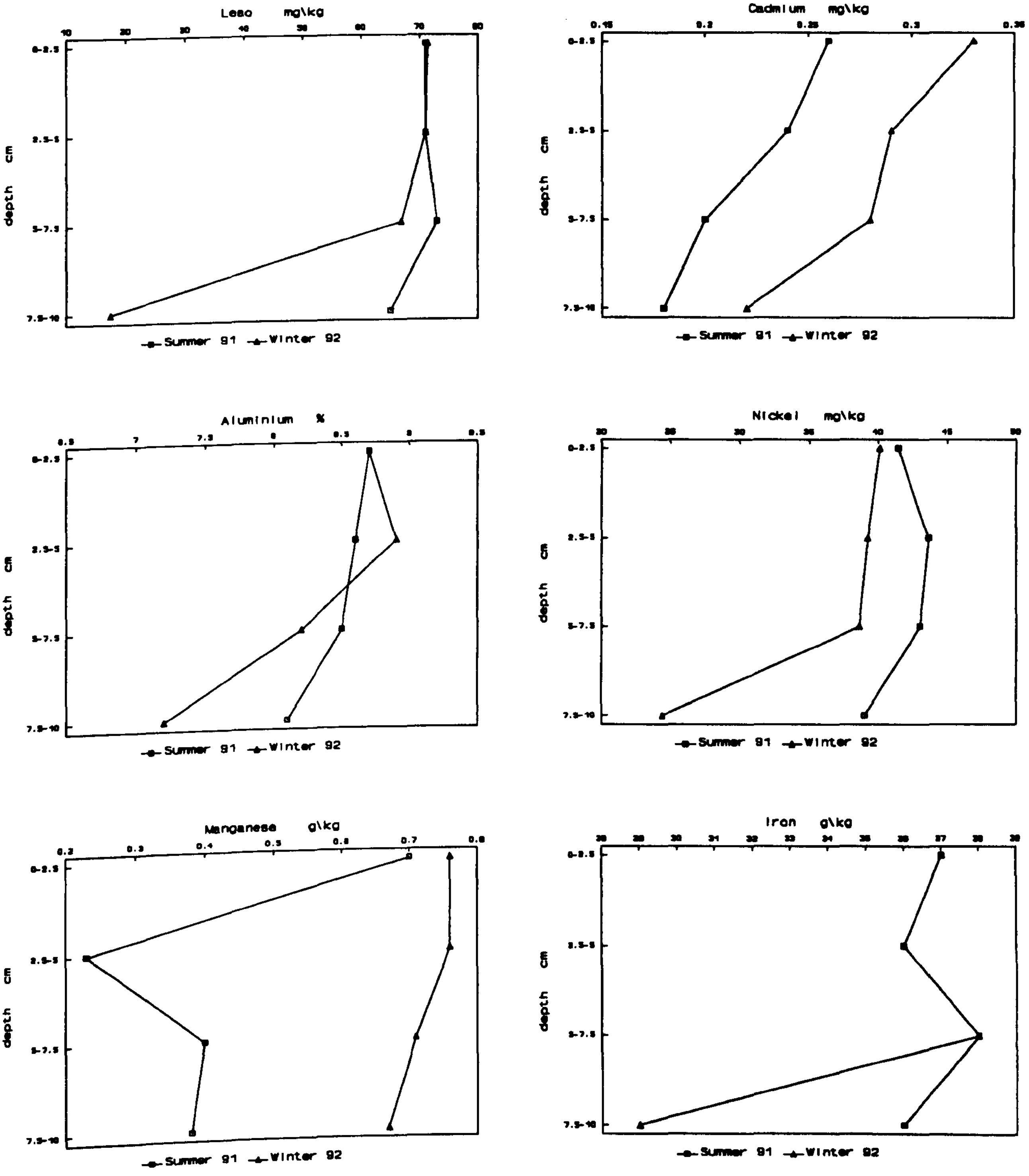


Fig. 5.32 (continued)
sediments cadmium, lead, nickel, aluminium, iron and manganese profiles at station B (Kennet) in summer and winter

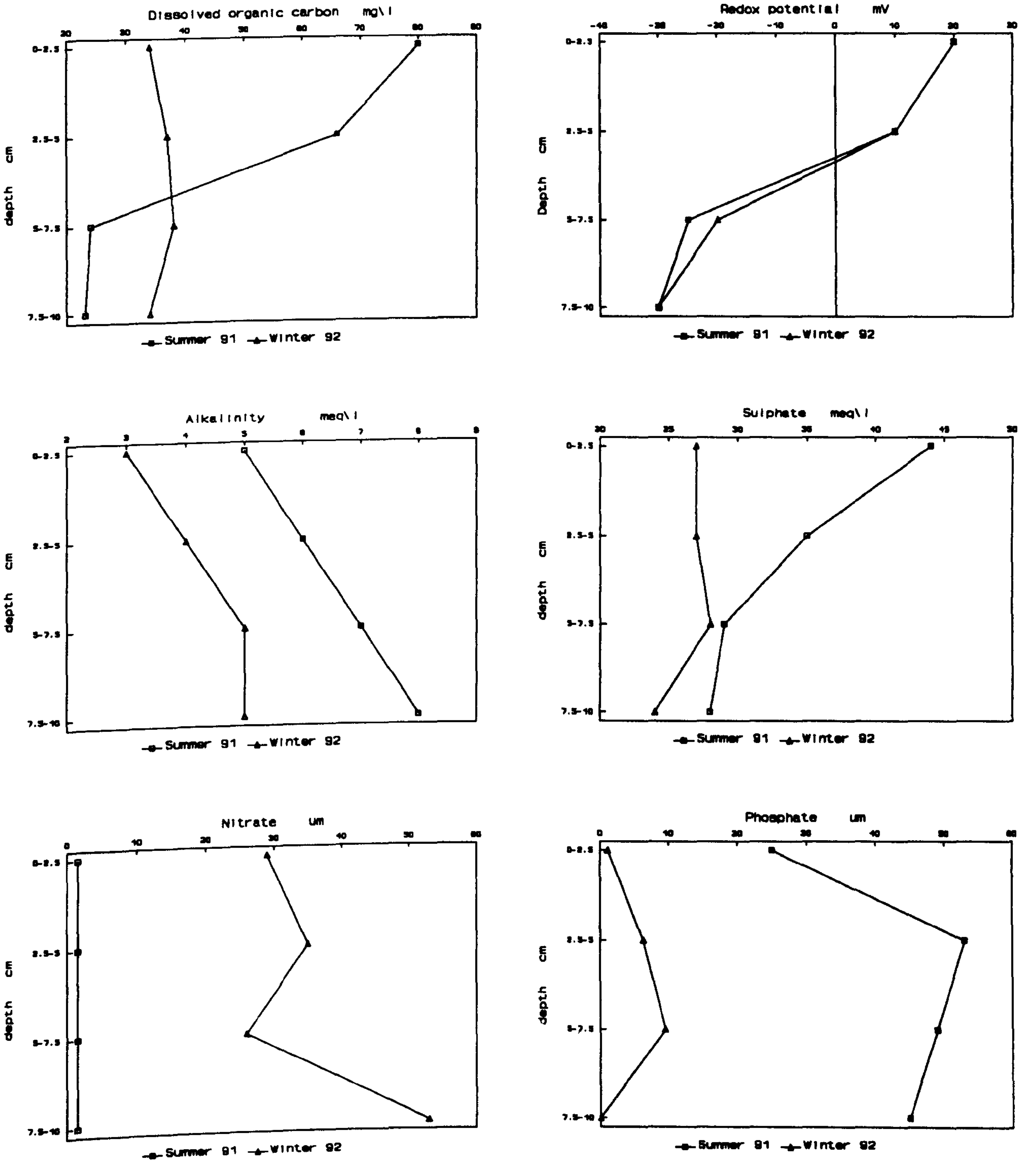


Fig. 5.33 Pore water redox potential, dissolved organic carbon, sulphate, alkalinity, phosphate and nitrate profiles at station B (Kennet) in summer and winter.

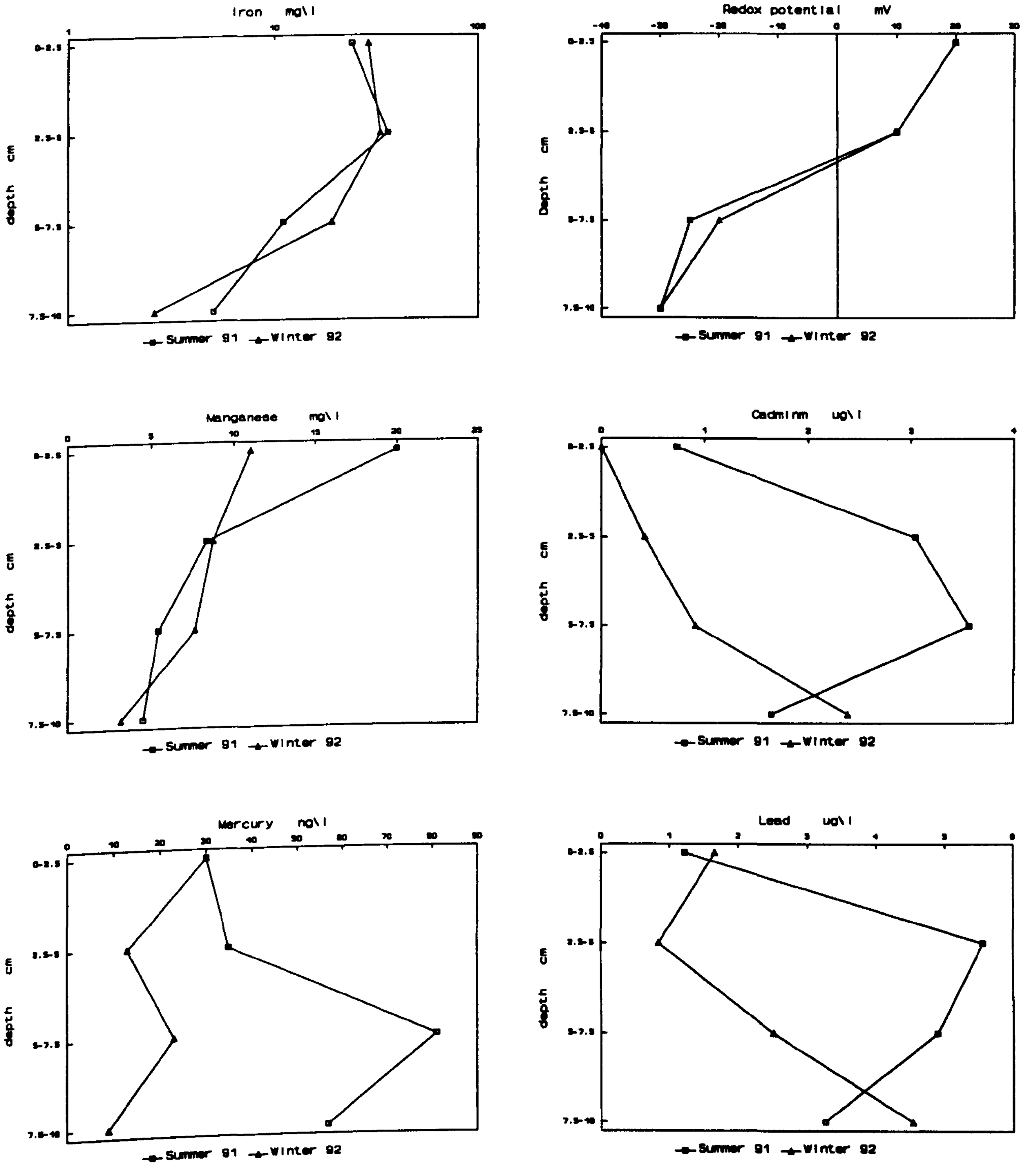


Fig. 5.34 Pore water redox potential, Iron, Manganese, cadmium, lead and mercury profiles at station B (Kennet) in summer and winter.

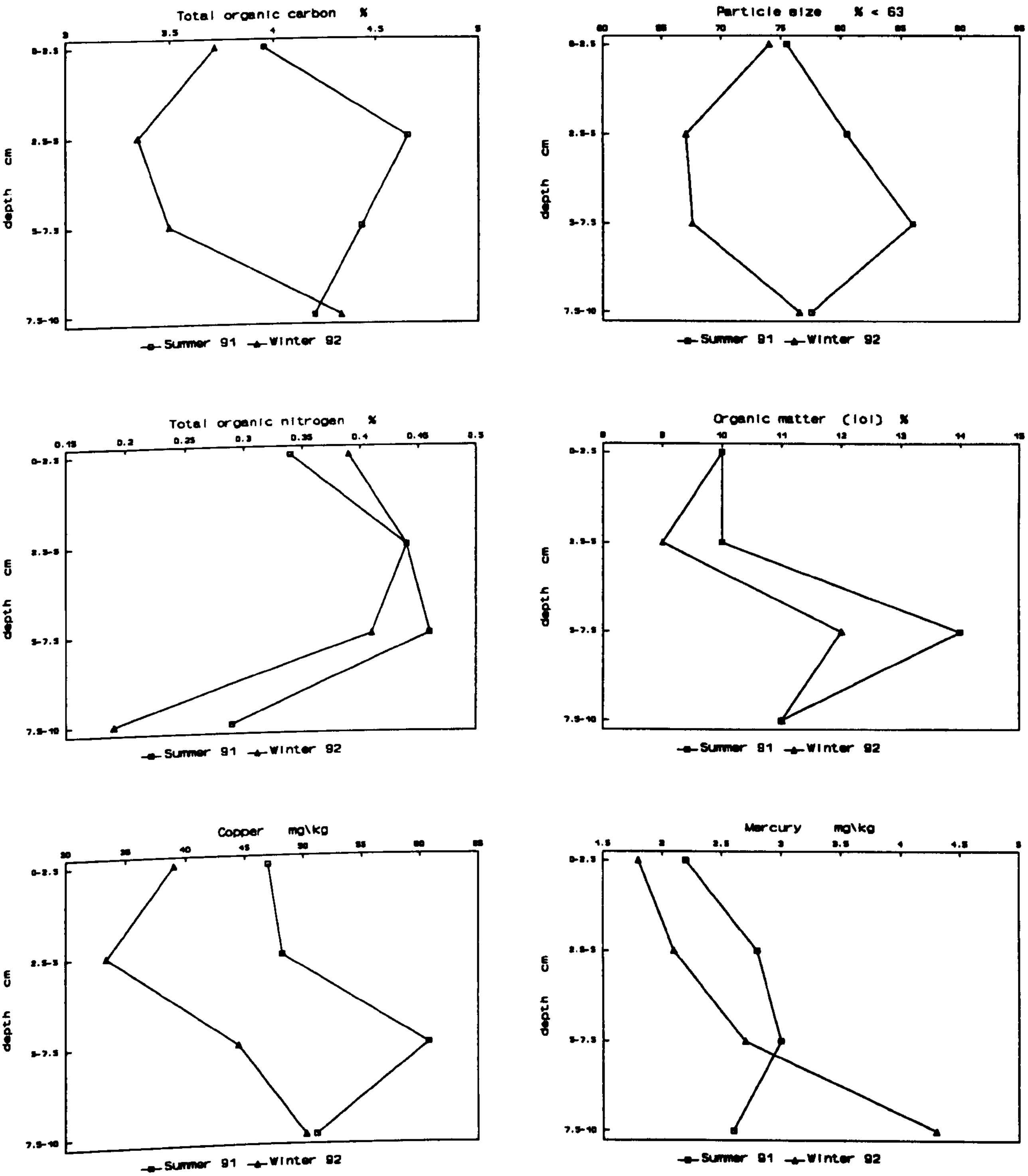


Fig. 5.35 Sediments particle size, organic matter (loi), total organic carbon total organic nitrogen, mercuıy and copper profiles at station E (Bo'ness) in summer and winter.

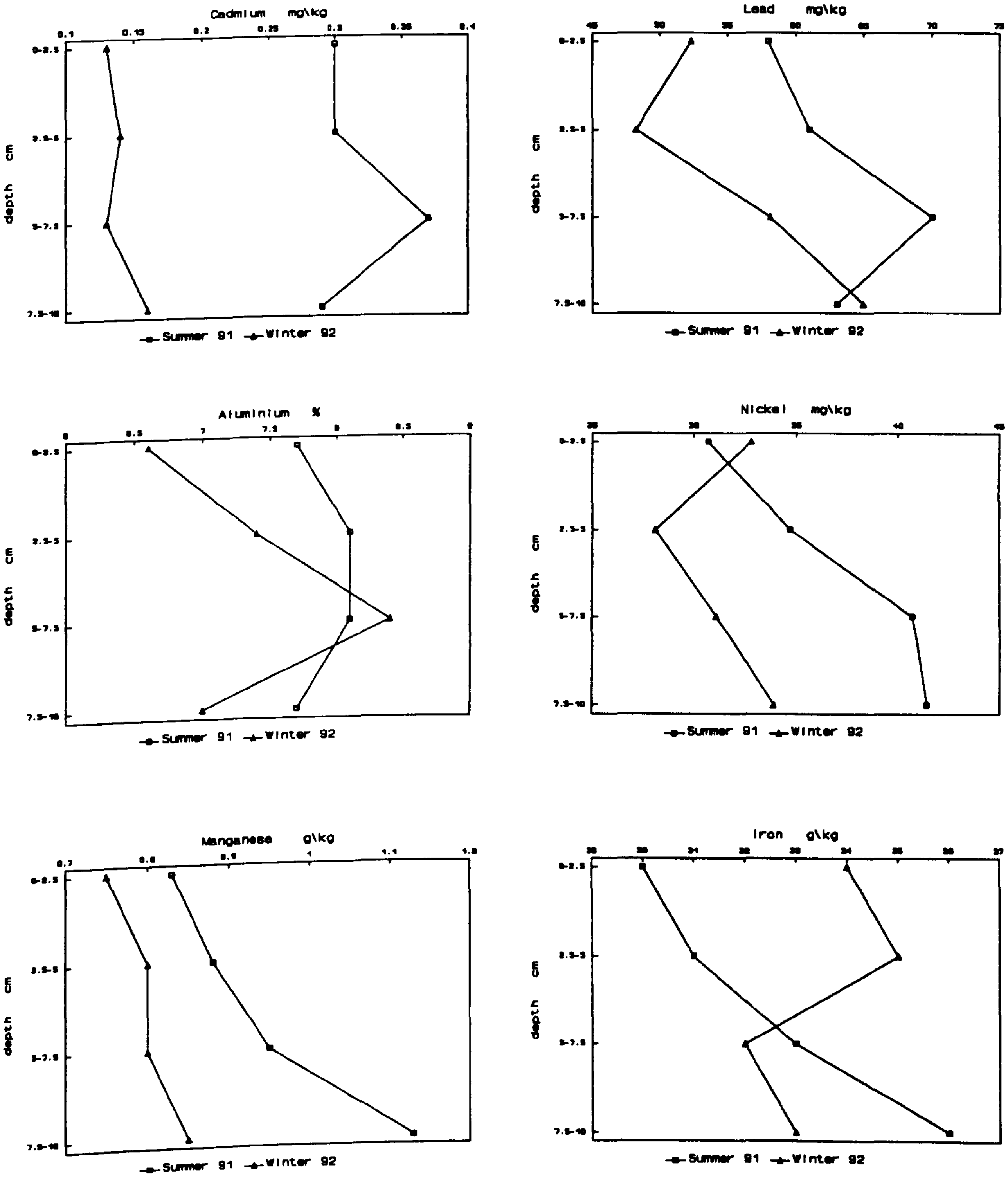


Fig. 5.35 (continued)
sediments lead, cadmium, nickel, aluminium, iron and manganese profiles at station E (Bo'ness) in summer and winter

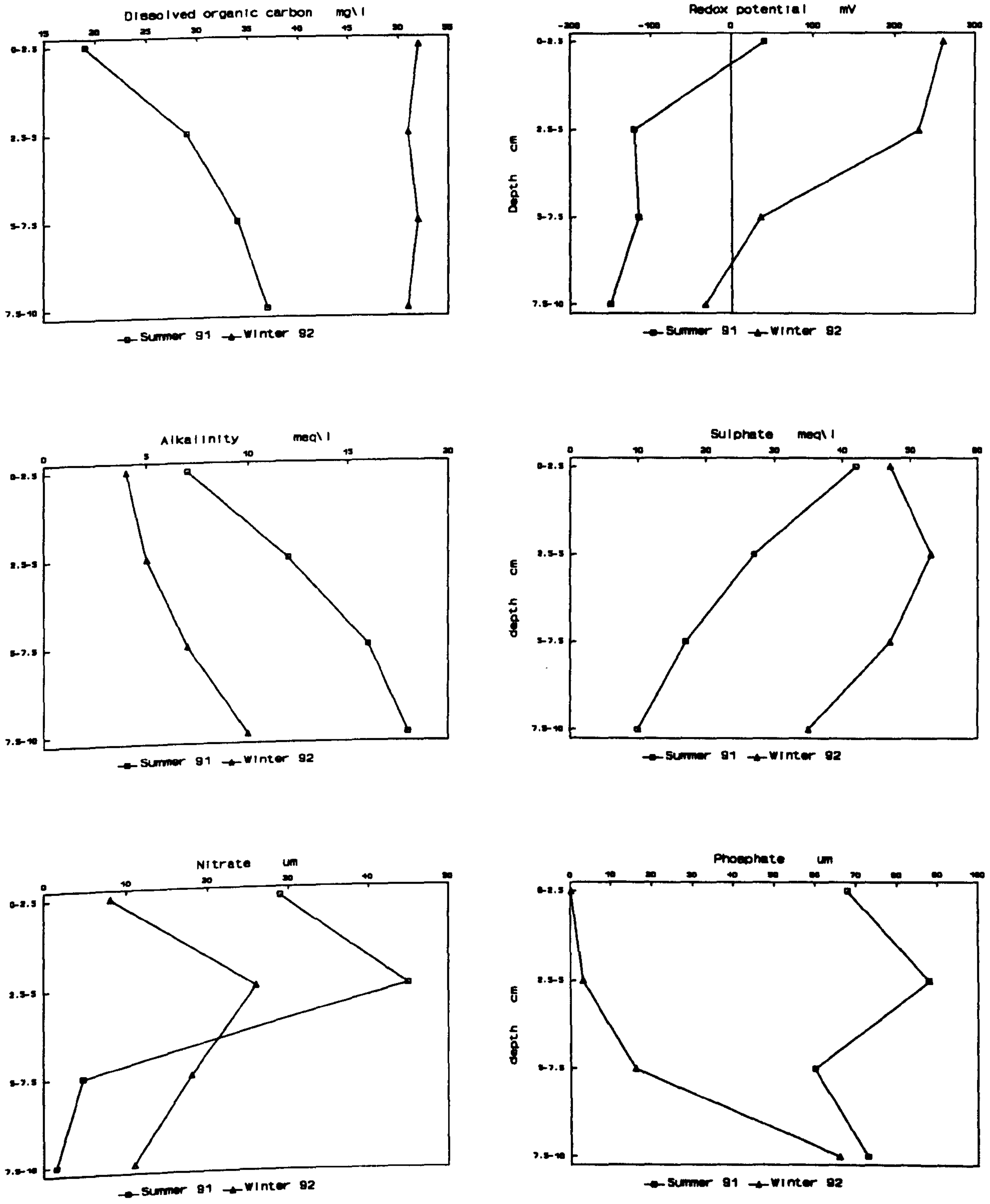


Fig. 5.36 Pore water redox potential, alkalinity, sulphate, Nitrate and phosphate profiles at station E (Bo'ness) in summer and winter

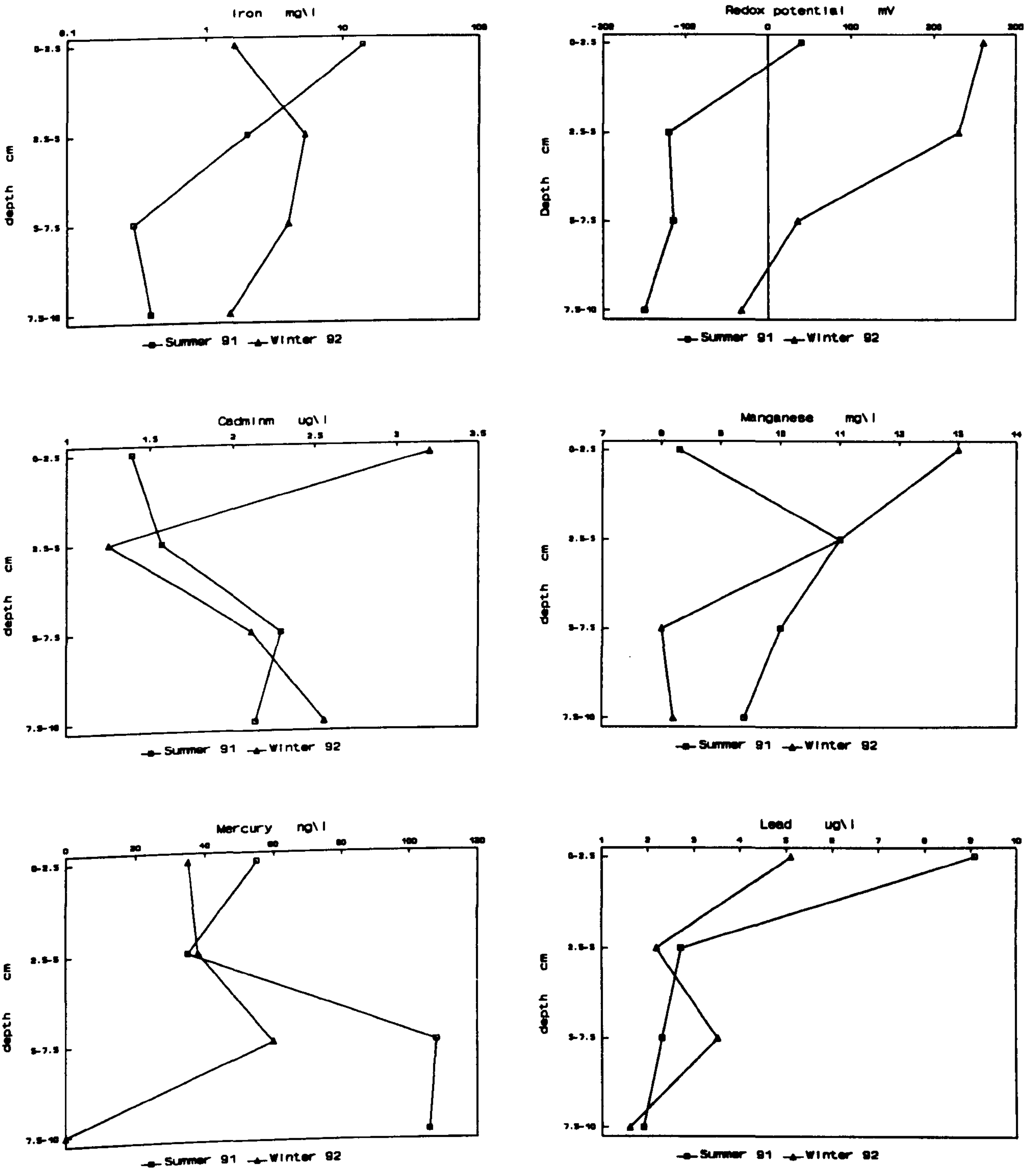


Fig. 5.37 Pore water redox potential, iron, manganese, cadmium, lead, and mercury profiles at station E (Bo'ness) in summer and winter

CHAPTER 6 DISCUSSION

CHAPTER SIX DISCUSSION

6.1 Sediment parameters

6.1.1 General features of the spatial and temporal variations of trace metals in the Forth Estuary

The interpretation of trace metal concentrations is consistently complicated by their dependence on sediment type. The most important aspects of this are the particle size and the organic matter content, hence the results will be discussed in terms of these two parameters. Iron and manganese oxides were also found to play an important role in concentrating certain trace metals at various sites. A reasonably consistent Fe/Al ratio of 0.42 was observed in all stations suggesting that the iron was held in structural position within the aluminusilicates. Calvert (1973), found a ratio of 0.52 between Fe (Fe_2O_3) and Al (Al_2O_3) in some recent sediments from the Gulf of Paria. He concluded, any iron exceeding that represented by the average Fe/Al ratio can therefore be used, to a first approximation, as a measure of the amount of authigenic minerals (non detrital) present in the sediment.

Spatially, metal concentrations varied in sediments at various locations. Certain metals (e.g Pb, Cu and Hg) had fairly similar distribution patterns, indicating the same source of input (anthropogenic inputs). For these metals, the highest concentrations occurred in stations A (S.Alloa), E (Bo'ness) and F (P.Edgar). Exceptionally high concentrations of lead were occasionally found, especially at station

F (P.Edgar) near the Forth bridge. These might be due to the presence in the sediments of relatively large fragments of lead based paints, possibly originating from the Forth rail bridge as suggested by FRPB (TW 89). The mean concentrations of trace metals established in this study were slightly higher than that reported by the FRPB in their reports (FRPB, 89) but compared to other estuaries the Forth estuary was found to be less polluted. However, mercury is still found in the sediments in high concentrations.

The mean value of mercury was found to be 1.9 mg/kg. Natural background of mercury is thought to be between 0.3 and 0.4 mg/kg. This level is 4-5 times higher. A similar pattern can be seen in sediments from Lake Winderemere in England (Aston, et al, 1973) and that from Lake Ontario (Thomas, 1972). Cadmium recorded its highest concentrations in station A (S.Alloa) with a mean value of 0.35 mg/kg. Kershaw (1980) found a marked variations in the concentration distribution with low concentrations of Ni, Cu, Cr and Zn associated with channel areas and high concentrations occurring on the extensive, muddy overbank deposits. The highest concentrations occurred in the vicinity of Alloa Inch and on the north shore at Kennetpans in the Forth estuary. Cadmium and nickel were found to be positively correlated. Nickel was found to be strongly and positively associated with iron and aluminium in the sediments ($p < 0.05$). This could be a reflection of the lithology of the Forth estuary. Investigations on sediments from 87 lakes situated in different climatic and lithogenic environments by Forstner (1981b) showed a high degree of positive correlations between the elements Fe, Cr, Ni, Co and Mn. This was interpreted as an indication of the influence of lithology of the lake catchment.

Temporally, the overall mean trace metals distributions in the sediments were found to be similar, in that they tended to decrease in concentrations in the spring season except lead that showed no trend. This overall trend could the result of the distribution of particle size and organic matter. The difficulty of site relocation could be partly responsible for the observed seasonal variability of trace metal concentrations in the tidal stations (C, D, E and F). As a conclusion, particle size and organic matter controlled the behaviour of trace metals both spatially and temporally.

Vertical variations of trace metals were also affected by the variations in particle size and organic matter (sections 5.1 and 5.2). The overall downward decrease could be due to a decline in organic matter with depth resulting from the biological decomposition of organic matter.

Redox potential measurements in the sediments of the Forth estuary disclosed the following: sediments in the middle of the estuary at stations C (G'mouth) and D (Culross) were oxidizing, having positive mean values (11.9 and 18.7 mV) while stations A (S.Alloa), B (Kennet) in the upper estuary and stations E (Bo'ness), F (P.Edgar) in the lower estuary were reducing in nature having negative mean values (Table 5.32).

6.1.1.1 Role of particle size

The results of the present investigation revealed strong relationships between all trace metals and the particle size (Table 6.1).

Generally, stations A, B and E were characterised by fine-grained sediments mainly silt and clay having 75.9, 91.3 and 77.0 % < 63 µm respectively while stations C, D and F were typified by coarser particles having 59.2, 58.4 and 57.9 % < 63 µm respectively. The distribution of particle size was reflected on the distribution of trace metals in the study area. The fine-grained sediments stations showed elevated concentrations of trace metals in contrast to the coarser particles stations which showed lower values.

To further investigate the association of trace metals with fine-grained sediments, a small portion of the < 63 µm sediment fraction was separated and chemically analyzed.

Generally, separation of grain size is advantageous because only few samples from a particular locality are needed. However, separation of fraction less than 2 µm in settling tubes is time consuming (Jenne, et al. 1980). The fraction less than 173 µm and 204 µm contains considerable percentage of large grains which are usually low in trace metals. The fraction less than 63 µm is recommended for many reasons (Forstner, 1984); (i) trace metals have been found to be adsorbed on clay\silt particles; (ii) this fraction was almost equivalent to the material carried in suspension; (iii) sieving did not alter metal concentrations; and (iv) numerous metal studies have already been performed on the

< 63 µm fraction, allowing better comparison of results (Salomons and Forstner, 1984).

The results are summarized in section 5.1.7. As shown in the figures, there was a clear indication that trace metals were found to be associated with fine-grained sediment particles (silt and clay). In station A (S.Alloa), this association was not established. This could be due to the presence of coal fragments which was observed during sampling, as also reported elsewhere (Kershaw, 1980). The finer-grained fraction consisting mainly of clay minerals showed high trace metal content, i.e trace elements concentrations tended to increase as grain size decreased. This increase could be due to the increase in specific area and to the surface properties of clay minerals (Mayer and Fink, 1980; Jones and Bowser, 1978; Forstner and Wittmann, 1981; Forstner et al., 1982 and Salomons and Forstner, 1984). High concentrations of trace metals in the < 63 µm fraction of the sediment in the intertidal mudflats of the Scheldt estuary compared to bulk sediments were observed (Panturak-ul, et al. 1991).

Enrichment factor for different metals in the < 63 µm fraction compared to total (Bulk) sediment was calculated. The result showed that each metal exhibited a different behaviour, with an average enrichment factor for: Pb, 1.4 ; Ni, 1.3; Cu, 1.13 and Hg, 1.1. Cadmium did not show any enrichment in the fine fraction. Station A (S.Alloa), was excluded from calculating the average because at this particular station, trace metals concentrations showed higher values in the whole sediment than the fine fraction values.

Correction for particle size effects

To further support the fact that trace metals tend to accumulate in the finer particles, correction for the trace metals data against particle size less than 63 µm was performed.

The result of the corrected data revealed an obvious strong relationship between grain size and trace elements concentrations (Fig. 5.31). Generally, as pointed earlier, trace elements tend to concentrate on finer-grained sediments. Therefore, the addition of coarser-grained materials which typically have lower trace elements concentrations to trace element rich finer-grained sediments could be viewed as a dilution process. The addition of coarser diluents can possibly conceal a significant trace element dispersion pattern (deGroot, et al., 1982; Horowitz and Elrick, 1988).

Different methods have been proposed to allow for the effect of grain size on trace metals concentrations: (i) separation of different grain size fractions (generally < 63 µm) (Thornton et al., 1975; Jenne et al., 1980), (ii) correction for inert material (Thomas, 1972; Williams, et al., 1978); Salomons and Mook (1977), (iii) correction for organic material (Williams et al., 1978) and (iv) comparison with conservative element (Al, Sc) (Bertine, et al., 1977; Bruland, et al., 1977; Thomass and Marten, 1982; Klinkhammer and Bender, 1981; Windom, et al.,1984; Trefrey, et al. 1985;

Kaouadio and Trefry 1987).

The correction procedure used in this investigation was according to the recommendation of Horowitz (1991). It became clear that these data suggested that all trace metals studied were concentrated in the fine-grained sediments.

In station B (Kennet), the sediment was typically fine-grained. There was little or no variation between the concentrations of trace metals in the bulk compared to the normalised sediments. In station C (G'mouth), which was suspected to have a high trace metals concentration due to the presence of several sources of pollution including chemical industries, the trace metals content in the normalised data was much higher than that of the bulk sediment. This was supported by the conclusion of Reinson (1975), that variations in mineralogy, particularly of the clay mineral content, had an influence on the concentration of several trace metals, including copper, zinc, chromium and nickel, in fine-grained estuarine sediments. Strong correlations between the metals Fe, Mn, Cu, Zn were not evident in the Tamar estuary sediments. However, the normalisation procedure, in which the total metal data set was standardised to 100% < 63 µm grain size, eliminated bias created by the grain size distribution and produced relationships amongst all the metals (Ackroyd, et al 1987).

6.1.1.2 Role of organic matter

As shown in Table 6.1 , the trace metals were found to be strongly correlated to organic matter ($p < 0.05$). Stations A (S.Alloa), B (Kennet) and E (Bo'ness) were characterised by high organic matter concentrations. However, at station B, the high values were in the surface sediment. These were reflected in the trace metals concentration. The remaining stations were observed to have low organic matter concentrations with low trace metals.

The mean value of organic matter (LOI) found in this study 9.25% was slightly higher than that reported by the FRPB of 8.7% (FRPB, 1989). This could explain the higher observed trace metals concentrations.

The close association amongst trace metals, e.g Cu, Ni, Pb, and Zn, and organic matter in many sediments, especially from reducing environments, was often interpreted as being due to the existence of metal-organic matter bonding (Price and Calvert, 1973a). Most of the reactions and processes in the sediment are related directly or indirectly to the degradation of organic matter.

The capacity of organic matter to concentrate various trace metals appears to be related to several factors, including: large surface area, high cation exchange capacity, high negative surface charge (Horowitz and Elrick, 1987; Hirner et al., 1990).

The analysis of the constituents of sedimentary organic matter was previously used to evaluate the nutritional value of sediment (Buchanan and longbottom, 1970) and to discriminate between the organic compounds which are readily biodegradable and those which are non biodegradable (Liu, 1976). The organic carbon present in the sediment is often considered to be resistant to decomposition (Marshall, 1972; Wilson et al., 1985; Grant and Hargrave, 1987).

The general decrease of organic compounds with depth observed in the study area especially in station B (Kennet) could be the result of aerobic and anaerobic microbial decomposition processes. However, a significant portion approximately 4-5% as total organic carbon resisted decomposition. A ratio of ~16 for C/N was found in the sediments of the Forth estuary implies that the sediments are rich in organic matter contents. In general a low C/N ratio in sediments is characteristic of those poor in organic matter. This has been interpreted on the basis that the percentage of nitrogen as fixed ammonium will be highest where organic matter has been highly depleted through biological activity. Others have reached the same conclusion for some sediment depth profiles and they believe that this may account for the low C/N ratios of < 5.0 (compared with the more normal values of > 7.0 (Price, N. 1976).

The major factors affecting the early stages of the diagenesis of organic matter in aquatic and sedimentary environments are: (i) biological degradation; (ii) organic-metal interactions; (iii) organic minerals interactions and (iv) increasing temperature (Degens, E.T. et al, 1976).

Table 6.1

A correlation matrix of the particle size, organic matter and trace metals in all stations

Station A (S.Alloa)

	% < 63	LOI	Cu	Ni	Pb	Fe
Loi	0.508					
Cu	0.665	0.513				
Ni	0.678	0.525	0.763			
Pb	0.804	0.611	0.809	0.834		
Fe	0.685	0.704	0.832	0.680	0.801	
Hg	0.641	0.689	0.786	0.616	0.762	0.818

Station B (Kennet)

	% < 63	LOI	Cu	Ni	Pb	Fe
Loi	0.722					
Cu	0.727	0.951				
Ni	0.571	0.653	0.760			
Pb	0.728	0.818	0.909	0.782		
Fe	0.671	0.944	0.906	0.651	0.746	
Hg	0.651	0.938	0.969	0.732	0.883	0.879

Station C (G'mouth)

	% < 63	LOI	Cu	Ni	Pb	Fe
Loi	0.806					
Cu	0.770	0.785				
Ni	0.664	0.636	0.381			
Pb	0.784	0.700	0.728	0.706		
Fe	0.609	0.528	0.288	0.726	0.393	
Hg	0.601	0.662	0.784	0.134	0.413	0.087

Station D (Culross)

	% < 63	LOI	Cu	Ni	Pb	Fe
Loi	0.597					
Cu	0.606	0.809				
Ni	0.803	0.746	0.634			
Pb	0.651	0.753	0.671	0.659		
Fe	0.799	0.588	0.364	0.871	0.125	
Hg	0.610	0.749	0.821	0.647	0.626	0.452

Station E (Bo'ness)

	% < 63	LOI	Cu	Ni	Pb	Fe
Loi	0.765					
Cu	0.746	0.747				
Ni	0.853	0.693	0.640			
Pb	0.689	0.741	0.693	0.655		
Fe	0.585	0.452	0.231	0.732	0.219	
Hg	0.511	0.616	0.702	0.322	0.677	0.069

Station F (P.Edgar)

	% < 63	LOI	Cu	Ni	Pb	Fe
Loi	0.822					
Cu	0.718	0.716				
Ni	0.862	0.623	0.547			
Pb	0.660	0.603	0.586	0.332		
Fe	0.926	0.724	0.682	0.829	0.704	
Hg	0.633	0.827	0.615	0.352	0.864	0.620

Significance level 0.46 at 95% confidence

6.2 Pore water parameters

6.2.1 Chloride, conductivity, alkalinity, pH and sulphate

Chloride and conductivity shared similar variations and trends in the present investigation in that they both increased gradually towards the sea. Data for chloride and conductivity reflected the mean salinity of the Forth estuary. The low values of chlorides in the spring season could be attributed to the high volume of fresh water discharged into the estuary, while the high autumn values reflected decrease in river discharge and increase in evapo-transpiration.

The pH values reported in this study were similar to those reported in the literature. Almost no pH values could be found outside the range of 6.7 - 8.3 . The constancy of pore water pH, in spite of the potentially disturbing conditions of CO_2, NH_3, etc., could be partially explained by the calculation of Nissenbaum et al., (1972), stating that a pH of 7.0 should be obtained whenever the products of marine organic decomposition equilibrate with water.

Overall mean *Eh* values ranging between 360.0 and -260.0 mV were found in the sediment of the Forth estuary. However, higher redox potential values were observed in stations C, D, E and F in the middle and lower reaches of the estuary compared to stations A and B in the upper estuary. The rapid reduction in oxygen level below the top centimetres of the sediment is typical of muddy estuarine sediment rich in organic matter. The profiles at all six stations differed in shape. This was probably due to a variation in the intensity of reduction of sulphate. In many sediments, anoxic conditions may be produced beneath a surface oxidized layer. This often occurs in fine grain sediments which accumulate rapidly and contain a relatively high concentration of organic material. Because of its rapid deposition, this organic material is utilized by bacteria and other microorganisms within the sediments, resulting in oxygen depletion in the pore waters. After all oxygen has been removed, production of H_2S by sulphate-reducing bacteria leads to anoxic conditions. The upper oxidized layer is generally pale brown in colour and is easily distinguished from the underlying grey to green reduced layer.

As a very general rule, the pH tends to increase and the *Eh* decreases with depth in a sediment and these result in more alkaline and more reducing conditions at depth respectively.

The increase of alkalinity values with increasing depth emanates primarily from a progressive sulphate depletion with depth in the sediments. The main component of carbonate alkalinity is the bicarbonate ion. It is produced mainly from the oxidation of organic matter by sulphate reducing bacteria, described by the equation below. Therefore, an inverse relationship between sulphate and alkalinity would be expected if the alkalinity is primarily produced by bacterially mediated oxidation of organic matter.

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$$

An inverse relationship between these two parameters was found in the present investigation indicating progressive oxidation of organic matter. Troup, (1974) and Bray, (1973) have shown a similar relationship exists in the Chesapeake Bay.

The result of sulphate distribution in the Forth estuary emphasised the fact that the rate of sulphate reduction by bacteria is dependent on the concentration of sulphate in the pore water. Stations like A (S.Alloa) and B (Kennet) were characterised by low sulphates. Therefore, the rate of sulphate reduction was also low. In stations C, D, E and F the amount of sulphates was higher. Hence, the rate of sulphate reduction was also higher.

As mentioned in the literature review (section 2.4.2.1), it is generally agreed that the rate of sulphate reduction varies with geographic location and depth. The factors that affect this process are many. Some of the most important factors are: (i) temperature (Vosjan, 1974; Jorgensen, 1977; Nedwell and Abram, 1978; Aller and Yingest, 1980; Westrich, 1983); (ii) pressure (Goldhabber and Kaplan, 1975); (iii) amount of reactive organic carbon entering the sediment and the extent to which it could be metabolised (Berner, 1964, 1981; Goldhaber and Kaplan 1975; Jorgensen, 1978b; Westrich and Berner, 1984) and (iv) the concentration of dissolved sulphates in the pore water. Some confusions exist with regard to the dependence of the sulphate reduction process on the concentration of dissolved sulphate. A number of investigators believe that the concentration of dissolved sulphate in the sediment pore water could exert a major controlling influence on the rate of sulphate reduction (Nakai and Jensen, 1964, Kaplan and Rittenberg, 1964; Vanderborght et al., 1977, Gunnarson and Ronnov, 1982).

6.2.2 Nutrients and dissolved organic carbon

Nutrients and dissolved organic carbon concentrations in the pore water are closely related to some of the parameters discussed above, especially; alkalinity, *Eh* and sulphate.

Discussing nutrient pore water profile in the upper 10 cm of a sediment core is extremely difficult. The difficulty arises from the interaction of chemical, physical and biological processes taking place. Two processes played an important role in creating the observed pore water profiles. These were bioturbation and bacterial sulphate reduction. An important impact of these two processes on pore water chemistry results usually when an infaunal organism drains overlying estuarine water through its burrow in order to renew its oxygen or food supply. This activity (bioturbation) is sometimes called irrigation. The net effect of irrigation is to decrease concentration differences between solutions contained within the burrow and the overlying water. For closely spaced burrows, this may in turn potentially affect overall sediment pore water chemistry due to diffusional exchange (Aller, 1980). Additionally, the activities of infaunal organism could ventilate large volumes of sediment during their feeding or burrowing activities. This second process is often referred to as mixing. Typically, the increased mixing of the sediment by faunal activity results in heterogeneous distributions of both the dissolved components and the particulate matter (Aller, 1980). Martens et al (1977) concluded that where sulphate reduction is incomplete, dissolved N_2 and Ar concentrations in the upper 10-30 cm of Long Island Sound sediments appear to be controlled by macroinfaunnal irrigation activities and vary in accordance with overlying water condition. Physical exchange processes, mainly wave and current action have been shown to lower interstitial water nutrient concentrations to a depth of about 10 to 15 cm in a shallow sandy area in the Wadden Sea (Rutgers, L. 1980).

Dissolved organic carbon in the pore water of the Forth estuary was found to be higher compared to the overlying water reported for sea water. The mean concentration was around 40 mg/l. Carbon is usually found in the sediment pore water as a result of decomposition of organic matter and is usually present as $CO_{2\,(aq)}$ and $H_2CO_{3\,(aq)}$ (Berner, 1971).

In sea water, dissolved organic matter values are relatively constant at 2-3 mg/l, but Nissenbaum et al., (1971) found 50-150 mg/l in pore water from Saanich Inlet. Dissolved organic carbon in the pore water of the Forth sediment showed a closer correlation to pH and phosphate.

As a result of mineralization, nutrients (phosphate and ammonia) increase with depth. However, at some stations the top layer showed higher values of nutrients than the layers underneath. This could be probably due to the mineralization of recently deposited fine-grained material rich in organic matter. This has been observed by (Rutgers, M. 1980) in the Southern Bight of the North Sea.

Goldhaber and others (1977) have shown that interstitial water profiles of alkalinity, sulphate, ammonia, and phosphate varied temporally in Long Island Sound sediments with depth independent profiles within the upper 8 cm during the summer. This was caused by bioturbation and diffusion controlled profiles during the winter when the bioturbating activity of the infauna decreased.

Spatially, nitrates and phosphates concentrations were found to increase towards the sea in the middle and lower reaches of the estuary. The fluctuation of nitrate concentrations with depth could be due to the oxygen penetration in the sediment depth profile resulting from the relatively sandy particle especially in station D (Culross) when particle size recorded a low value of 58.4 less than 63 μm because the presence of oxygen in the sediments favours nitrification while it stops nitrate reduction as shown in the equation:

$$NH_4 + O_2 \rightarrow NO_3$$

The low organic matter contents are usually associated with sandy sediments, so denitrification does not develop. In pelagic sediments the amount of degradable organic material is often too low for denitrification to develop (Suess, 1976a). Billen suggested that this situation occurred also in some North Sea sediments poor in organic matter. In two 15 cm cores he did not find a decrease of nitrate concentration with depth. Generally, denitrification take place in aerobic-anaerobic interfaces, and some researchers consider this process as a strictly anaerobic metabolism pathway. However, there has been a long controversy in the literature concerning the lowest oxygen concentration that permits denitrification (Robertson and Kuenen, 1984b). Recent reports have shown the occurrence of aerobic denitrification (Bonin et al, 1989, 1990). Others have described how denitrification is blocked in the presence of low oxygen concentration, which inhibits and/or prevents the synthesis or the enzymes associated with denitrification (Kapralek et al, 1982).

A survey carried out between Kincardine and Queensferry during 1981 indicated that the major inputs of ammonia were located on the south shore and sublittorally around Grangemouth. The gradients that were produced by these inputs were shown to persist many kilometres down the Forth estuary (Griffith A.H. 1987). Among the phosphorus phases buried in marine sediments that directly affect dissolved phosphorus availability in the overlying water, organic phosphorus is quantitatively one of the most important (Froelich et al., 1982).

6.2.3 Trace metals in the pore water

6.2.3.1 Iron and manganese

The geochemistry of iron and manganese in the pore waters is well known. As a result of the reducing conditions beneath the sediment-water interface, these metals are reduced and become more soluble (Berner, 1980; Presley and Trefry, 1980).

In the present study the concentrations of iron and manganese decreased with depth at all stations while increasing gradient was observed at station A (S.Alloa). The likely mechanism is that at depth in the sediment, iron and manganese oxides were reduced and then diffused upwards to be reoxidized and trapped within the sediment column. Their profiles were generally typical of many recorded for anoxic sediments (Calvert and price, 1972; Holdren, Bricker and Matissof, 1975; Aller, 1980), indicating that oxygen was rapidly removed from interstitial water. Li et al., (1969) were the first to show that there are pore water Mn gradients reflecting dissolution at depth and upward diffusion.

It was also observed that concentrations of iron and manganese in the surficial sediment compared to the average bulk sediment were higher in the summer and autumn, 1991 than those of spring and winter. This suggests that flux was higher in the summer and lower in the winter. In addition, this could have resulted from the high rate of bacterial sulphate decomposition in the hot seasons. Iron concentrations in the pore waters were found to be higher in stations A and B than stations C,D,E and F by three orders of magnitude. This could be due to a significant contribution from clay minerals (Salomons, 1987).

6.2.3.2 Trace metals (Pb, Cd, Cu, Ni and Hg)

The concentrations of pore water trace metals reported in this study showed some fluctuations both spatially and temporally. Generally, with the exception of lead, trace metals tended to decrease in the cold periods of the spring. This trend was also observed in the concentrations of trace metals in the sediment. In addition, particle size and organic matter showed the same trend. This suggests that these two parameters played a major role in determining the distributions of trace metals both spatially and temporally.

The result suggests that pore water trace metals varied significantly according to sediment type and environmental conditions. These variations could be as a result of variability in the rate of oxidation of organic matter. The vertical variation observed was probably due to bioturbation in the summer season when the infaunal organisms were active. In the winter season, variations with depth seemed to be controlled by redox potential. The concentrations of trace metals showed an increase when redox conditions became reducing.

The observed trace metals concentrations were up to 10 times higher for mercury and lead, and 50 times higher for nickel, copper and cadmium than the concentrations in the overlying water.

Investigations of trace metals in the pore water of coastal marine sediments have shown enrichment relative to the bottom water of: copper (Elderfieled et al., 1981; Heggie and Burrell 1982; Emerson et al., 1984) and nickel (Elderfield et al., 1981; Emerson et al., 1984). Bothner et al., (1980) observed interstitial mercury concentration up to 3.8 µg/l, from 16 to 126 times higher than the concentration in overlying sea water. It has been suggested that, in general, higher fluxes are associated with low oxygen or reducing condition in the overlying sea water. Very high metals concentrations between 8 and 380 µg/l for copper have been found in pore water of sediments from Loch Fyne, Scotland (Duchart et al., 1973). Klinkhammer, G.P.(1980) suggests that the pore water profiles of copper and nickel are controlled by processes involving the major oxidants (O_2, NO_3^-, Mn and Fe oxides).

The behaviour of heavy metals is usually seen in context with precipitation and organometallic complexes complexing reactions. However, chlorides under certain conditions, may also be of great significance in determining heavy metals distribution in the environment. Under high rainfall condition, leaching is more pronounced and aquatic systems usually have lower pH values, promoting solubility of heavy metal compounds. In areas where higher salinity and pH values prevail, formation of insoluble compounds are usually expected (Hahne, et al. (1973).

In the present investigation, iron and mercury concentrations of pore water were found to be inversely correlated with chloride (mercury, r = -0.81; iron, r = -0.873). This suggests that desorption of iron and mercury from sediments was hampered by chloride ions.

6.3 Benthic fluxes and potential release of trace metals and nutrients

The Forth is a highly turbid estuary with a well established turbidity maximum in the upper reaches. This turbidity maximum shows a pattern of upstream migration into the water of the upper reaches, particularly under low flow conditions. The migration of the turbidity maximum has a significant impact on water quality, through the resuspension of fine sedimentary materials. This has been shown to exert an oxygen demand in addition to that from direct discharges of effluents (FRPB, 1986). An estimate of its effect based on tidal stream data and the extent of re-suspension resulting from it, have been undertaken (FRPB 1986). The results of the survey work showed that the oxygen demand from different sediment types varied from 7.7 to 30 mg O_2 m^{-2} hr^{-1} (Griffith 1987).

In the light of the foregoing facts, a quantification of nutrient fluxes would help in understanding the nutrient mass balance in the area. The average gradient of < 0.1 % per cm depth would produce in global terms fluxes of many constituents (Mg, K, Na, SO_4^{2-} etc.) that almost matches the total river input of these elements to the sea (Sayles et al., 1973b). Dissolved chemicals transported across the sediment-water interface are driven by two processes: advection of water by animals and simple diffusion.

The overall redox state of the sediments has been shown by several investigators to play an important role in the mobilization of trace metals. Generally, as the redox-potential drops, the mobility of the sedimentary trace metals increases. Redox potential is particularly important in the mobilization of Fe, which is significant in the light of extensive adsorption to Fe compounds of other metals.

Diffusive fluxes across the sediment-water interface are usually calculated from Fick's first law.

$$F=-\theta Ds\frac{dc}{dx}$$

Where F is the diffusion flux θ is the sediment porosity, D_s is a diffusion coefficient, dC/dx is the concentration gradient (approximated as $\Delta C/\Delta X$, where X = 2.5 cm). Since porosity differs from station to station, an average porosity of 0.6 was suggested. It was assumed that the concentration gradients at the sediment water interface were linear and can be presented by the concentration difference between the overlying water concentrations and the 2.5 cm depth. It was also assumed that the transport within the pore water took place by diffusion.

Fluxes were calculated at 14°C in the summer and 8°C in the winter by fitting these values into the regression line of the diffusion coefficients at 0°C, 18°C, and at 25°C obtained by Li and Gregory (1974).

The coefficients of molecular diffusion (D_s) used here for Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+} were 5.49×10^{-6}, 5.19×10^{-6}, 5.49×10^{-6} and 7.26×10^{-6} $cm^2.s^{-1}$ in the summer and 4.57×10^{-6}, 4.3

x 10^{-6}, 4.59 x 10^{-6}, and 6.09 x 10^{-6} in the winter respectively.

The trace metals concentrations of the estuarine water used in these calculations were obtained from the Forth River Purification Board. The pore water metals concentrations were those of the surficial sediment at different stations and seasons (see Appendices).

Diffusive fluxes of trace metals at the water-sediment interface were as follows:

Summer 1991

Diffusive flux (10^{-6} $\mu g.cm^{-2}$ s^{-1})

	Stations	Copper	Nickel	Lead	Cadmium
Upper estuary	(A+B)	41.0	24.3	11.6	4.7
Middle estuary	(C+D)	128.0	76.6	4.1	0.96
Lower estuary	(E+F)	115.0	21.8	15.4	1.78

Winter 1991

Diffusive flux (10^{-6} $\mu g.cm^{-2}$ s^{-1})

	Stations	Copper	Nickel	Lead	Cadmium
Upper estuary	(A+B)	23.6	16.8	5.44	2.2
Middle estuary	(C+D)	16.6	14.9	3.67	0.9
Lower estuary	(E+F)	91.2	40.8	7.1	3.48

From the above calculated fluxes of trace metals, it is apparent that significant benthic fluxes of all trace metals occurred in the summer and winter seasons. However, fluxes of copper, nickel and lead seemed to increase in the summer in contrast to cadmium which remained constant in the middle of the estuary and then switched to an increase in the winter in the lower estuary. A significant benthic flux of copper to bottom water was predicted by Boyle et al. (1977) from advection diffusion modelling of Cu in the Pacific. Fluxes of copper, nickel and cadmium were measured using flux chambers by Westerlund, et al. (1986) in autumn and winter. The results showed lower values by factor of 5 and 10 for copper and nickel respectively in the winter with no significant difference for cadmium. Lu and Chen (1977) observed that under different sets of redox conditions, three general trends, first, the released amounts increased as the redox conditions became reducing (Fe, Mn), secondly, the released amount increased as the environment became more oxidizing (Cd, Cu, Ni, Pb and Zn), thirdly, there was no significant change of concentration in interfacial water (Hg and Cr).

Diffusive fluxes were also calculated for nitrate (No_3^-) and phosphate ions (HPO_4) following the argument of Kester and Pytkoowics (1967) that most of dissolved inorganic phosphate exist as HPO_4. The coefficients of molecular diffusion (D_s) were obtained following the same method discussed earlier.

The nutrients coefficients (D_s) calculated were: nitrate, 12.65×10^{-6} in the summer and 14.48×10^{-6} in the winter, and phosphate, 5.6×10^{-6} in the summer and 4.66×10^{-6} in the winter. The results are as follows:

Summer 1991

Diffusive Flux (10^{-6} µmol.cm^{-2} s^{-1})

	Stations	NO_3^-	HPO_4
Upper estuary	(A+B)	- 76.4	20.7
Middle estuary	(C+D)	- 11.2	4.53
Lower estuary	(E+F)	30.1	71.0

Winter 1991

Diffusive Flux (10^{-6} µmol.cm^{-2} s^{-1})

	Stations	NO_3^-	HPO_4
Upper estuary	(A+B)	37.2	2.11
Middle estuary	(C+D)	83.8	1.25
Lower estuary	(E+F)	34.8	2.78

Phosphorus liberation from sediments to overlying water was apparent from the flux measurements. It was clear that flux from sediments was enhanced in the summer season especially at more marine stations. This would exert oxygen demands in addition to that of direct discharges of effluents. It has been reported that phosphate is released to the overlying water as a result of the dissolution of precipitated metal phosphate at the sediment water interface (Aller, 1980; Krom, Berner, 1981; Klump, Martens, 1981; Callender, Hammond, 1982). High flux of phosphate in the summer could be due to temperature difference. Elderfield et al (1981) found similar results in Narragansett Bay. They concluded that the summer flux maximum follows the winter, spring phytoplankton bloom and may reflect the food supply to the benthos.

The absence of oxygen in the sediment plays an important role in the flux of phosphate. Blazer, (1982) ascribed the increasing fluxes to the redox boundary in the sediments, moving upwards in response to the decreasing oxygen concentrations. Migration out of sediment supplies 80 % of the nutrients entering Narragansett Bay during certain times of the year (Hale, 1974; Nixon et al 1976).

In contrast, the flux of nitrates was found to be abundant in the winter season. The observed flux reduced to a negative flux in the upper and middle reaches of the estuary in the summer suggesting higher concentrations of nitrates in the overlying water column. Negative fluxes were reported in summer and winter for the nitrate concentration in the coastal zone of the Southern Bight of the North Sea (Rutgers, M. 1980). The relatively rapid rates of temperature dependent microbial degradation of organic material support seasonally varying nutrient fluxes ranging from 20 to 1200 μmol. m^{-2}. hr^{-1} for dissolved ammonia and from -20 to 120 μmol. m^{-2}. hr^{-1} for total dissolved phosphate in organic rich anoxic sediments of Cape Lookout Bight (Klump and Martens, 1981).

The overall variations of benthic fluxes both spatially and temporally depends on a number of factors including climatic changes, and its effect on the supply and rates of degradation of organic matter in addition to its effects on the rate of advection and diffusion of pore water in the sediment-water interface. The spatial variability could reflect differences in interstitial water chemistry between the different stations.

CHAPTER 7 CONCLUSION

Spatial and temporal studies of an estuarine ecosystem are always difficult for a number of reasons, one of which, is the difficulty in the relocation of sampling sites. This will affect the reproducibility of the spatial and seasonal data. Weather conditions have also participated in postponement the scheduled time for sampling.

Sediments have long being considered as a sink of trace metals. However, changes in the overlying water conditions may result in mobilization of the trapped trace metals and hence their release. Therefore sediments could be regarded as a sink and a source of pollution at the same time.

In the present investigation, the particle size and organic matter content played a prominent role in determining the distribution of trace metals in the sediments. Generally, the distribution of trace metals in the sediments were similar to those of particle size and organic matter. This was attributed to the increase in surface area of fine grained-sediments mainly silt and clay and to the surface properties of clay minerals.

The trace metals, copper, lead and mercury in the less than 63 µm particles had higher concentrations than the bulk sediments. A clear picture of the distributions of trace metals in the Forth estuary was obtained when normalisation procedure against the less than 63 µm was performed. In station C (G'mouth) where industrial activities took place, low levels of trace metals were found. However, when normalised against particle size < 63 µm, high levels of trace metals were observed. In addition, the particle size and organic matter affected the concentrations of trace metals seasonally. This was clearly shown in the spring trace metals concentration results and those of particle size and organic matter when they were lower than other seasons. The low percentage of particle size (56.1 % < 63 µm) recorded in the spring season and its associated low concentrations of trace metals was attributed to the high river flow, high resuspension and immense mixing of surficial sediments especially in the top 10 cm of the sediments.

The variability in particle size exerting a substantial variation on trace element contents highlights the need for an international standard to limit the particle size to be employed to allow for comparison.

Iron and manganese in the sediments pore water showed an enrichment in the oxidized layers of the sediments and tended to decline when the sediments became reducing. This was interpreted as an indication of recycling between the solid and pore water solutions.

Variable depth profiles for the other trace metals were observed. This was attributed partly due to reducing conditions found in anoxic sediments which played a role in mobilizing trace metals especially in the winter season and partly due to bioturbation effects especially in the summer.

In this study, the trace metals investigated were all enriched in the interstitial water relative to their values in the overlying water. Enrichment factors in general were limited to 10-50 fold increases with the exception of iron and manganese that had higher enrichment factors. Lead and mercury were 10 fold higher while 50 fold higher values were obtained for nickel, copper and cadmium. This enrichment of trace metals in the pore water implies that there was a release of trace metals from sediment to pore water.

Dissolved sulphide was nearly absent from sediment's pore water even in the presence of active sulphide production by sulphate reduction. This phenomenon was attributed to the presence of high reactive iron which reacted with sulphide to form various iron sulphide minerals and eventually pyrite.

To understand the associations of trace metals with different phases of the sediments and the mechanisms of trace metals mobilization, sequential extractions have to be employed.

The current awareness of the importance of the effect of these trace metals on the aquatic system has led to the realisation of the importance of trace metals exchange between the sediment and water. More work has to be done to fully understand the water sediment interface in terms of flux of materials between these two phases in the Forth estuary. Till now, little has been done, as much of the work done is merely concerned with each layer as a separate entity i.e overlying water and surficial sediments.

Benthic flux calculations of trace metals to the overlying water indicated a significant flux of metals in the summer and winter. However, benthic fluxes of copper, nickel and lead seemed to increase in the summer.

Benthic fluxes of nutrients (phosphate and nitrates) were also calculated. The results emphasized the fact that the source of phosphate in the overlying water could be the sediments, where flux increased in the summer and tended to decrease in the winter. Nitrate fluxes were negative in the upper and middle reaches of the estuary in the summer. However, positive values were observed in the winter in the whole estuary especially in the middle reaches where high fluxes were calculated. In general, the benthic flux of nutrients and its eventual return to the overlying water are ultimately controlled by the rate at which sedimentary organic matter is degraded and its subsequent change into soluble inorganic species of nitrogen, phosphorus and may be carbon. Additional work is needed to cover a larger area and time to understand the temporal variation and their importance in governing the mass flux across the sediment-water interface better.

REFERENCES

Ackroyd, D.R., Millward, G.E and Morris, A.W.(1987). Periodicity in the trace metal content of estuarine sediments. *Oceanol. Acta,* v.10, no2. pp. 161-168.

Adams,D. D., Darby, D.A. and Young, R.J. (1980). Selected analytical techniques for characterizing the metal chemistry and the geology of fine-grained sediments and interstitial water. *Contaminants and sediments,* (2), 3-28, Ann Arbor science.

Aller, R.C., (1980). Diagenesis processes near the sediment water interface of Long Island Sound. 1. Decomposition and nutrient element geochemistry (S, N, P). *Adv. Geophys. 22: 237-350.*

Aller, R.C., Yingest, J.Y. (1980). Relationships between microbial distribution and the anaerobic decomposition of organic matter in surface sediments of Long Island Sound, USA. *Mar. Biol.* 56, 29-42.

Aller, R.C., Benninger, L.K. (1981). Spatial and temporal patterns of dissolved ammonia, manganese and silica fluxes from bottom sediments of Long Island Sound, U.S.A. *Journal of Marine Research,* 39, 295-314.

Anderson, J. (1974). A study of the digestion of sediment by HNO3-H2SO4 and the HNO3-HCL procedures. *Atomic Absorption Newsletter,* 13, (1), 31-32.

Aston, S.R.(1978). Estuarine chemistry. in: Riley, J.P. and Chester,R., Eds. *Chemical Oceanography.* 2nd Ed. Academic Press. 7: 362-440.

Aston, S.R.(1985). Trace element analysis. in: Head, P.C., ed. *Practical Estuarine Chemistry,* pp. 126-159. Cmbridge University Press, Cambridge.

Baker, W.E. (1973). The role of humic acids from Tasmanian podozolic soils in mineral degradation and metal mobilization. *Geochim. Cosmochim. Acta,* 37, 269-281.

Bakir, F.S.F., Damluji, L., Amin-Zaki, M., Murtadha, A. Khalidi, N.Y. Al-Rawi, S. Tikkriti, H.I. Dhahir, T.W. Clarkson, J.C. Smith and R.A. Doherty (1973). "Methylmercury poisoning in Iran," *Science* 18 (4096):230 241.

Bender, M.L., Fanning, K.A., Forehlich, P.N., Heath, G.R.& Maynard, V.(1977). Interstitial nitrate profiles and oxidation of organic matter in the eastern Equatorial Atlantic, *Science* 198, 605-608.

Bender, M.L., and Klinkhammer, G.P. (1978). Effect on the diagenetic status of sediments on the concentration of trace metals in pore-water. In: *First American-Soviet symposium on chemical pollution of the marine environment,* K.K. Turekian and A. I. Simonov (eds). Environmental Protection Agency, Gulf Breeze florida publication 600/9-78-038.

Berelson, W.M., D.E.Hammond & K.S. Johnson (1987). Benthic fluxes and the cycling of biogenic silica and carbon in two Southern California borderland basins. *Geochim. Cosmochim. Acta* 51: 1345-1363.

Bernard, P.B., and Westrich, J.T.(1984). The dependence of bacterial sulphate reduction on sulphate concentration in marine sediments. *Geochim.Cosmochim. Acta* 48, pp. 2503-2516.

Bernas, B. (1968). A new method for the decomposition and comprehensive analysis of silicates by atomic absorption spectroscopy. *Analytical chemistry,* 40,(11), 1682-1686.

Berner, R.A. (1964). An idealized model of dissolved sulphate distribution in recent sediments. *Geochim. Cosmochim. Acta* 28, 1497-1503.

Berner, R.A., Scott, M.R., and Tholinson, C. (1970). Carbonate alkalinity in the pore waters of anoxic sediments, *Limnol. Oceanogr.,* 15, 544-549.

Berner, R.A.(1971). *Principles of chemical sedimentology.* 240 p. Mc Graw Hill, New York.

Berner, R.A.(1980). *Early diagenesis.* A theoretical approach. Princeton Univ. press, NJ, 241PP.

Berner, R.A. (1980). A new geochemical classification of sedimentary environment. *J. Sed. Pet.* 51: 359-365.

Bertine, K.K and Goldberg, E.D. (1977). History of heavy metal pollution in Southern California coastal Zone reprise, *Environ. Sci. Technol.*, 11, 297.

Billen, G. (1975). Nitrification in the Scheldet estuary. *Estuarine and coastal marine science* 3, 79- 89.

Billen, G. (1978). A budget of Nitrogen recycling in North sea sediment off the Belgian coast. *Est. Coast. Mar. Sci.* 7: 127-146.

Blazer, W. (1982). On the distribution of iron and manganese at the sediment water interface: thermodynamic vs. kinetic control. *Geochim. Cosmochim. Acta* 46, 1153-1161.

Blazer, W., (1984). Organic matter degradation and Biogenic elements cycling in a near-shore sediment (Kiel Bight). *Limnol. Oceanogr.* 29: 1231-1246.

Bonin, P., Gilewicz, M., Bertrand, C. (1989). Effects of oxygen concentration on each step of denitrification. *Can. J. Microbiol.* 35: 1061-1064.

Bonin, P., and Raymond, N. (1990). Effects of oxygen on denitrification in marine sediments. *Hydrobilogia*, 207: 115-122.

Bothner, M.H.,Jahnke, R.A., Peterson, M.L., Carpenter, R. (1980). Rate of Mercury Loss from contaminated estuarine sediments. *Geochim. Cosmochim. Acta*, 44:273-285.

Boudreau, B.P., Westrich, J.T.(1984). The dependence of bacterial sulphate reduction on sulphate concentration in marine sediments. *Geochimica et Cosmochimica Acta* Vol, 48, pp. 2503-2516.

Boyle., E.A., Sclater., F.R., and Edmond, J.M.(1977). The distribution of dissolved Copper in the Pacific, *Earth Planet Sci. Lett.* 37, 38-54.

Bray, J.T.(1973). The behaviour of phosphate in the interstitial waters of Chesapeake Bay sediments. *Ph.D. dissertation*, 149 pp., The Johns Hopkins University, Baltimore.

Brooks, R.R., Presley, B.J., and Kaplan, I.R. (1967). APDC-MIBK Extraction system for the determination of trace elements in saline waters by Atomic Absorption Spectrophotometry. *Talanta*, 1967, vol. 14, pp. 809-816.

Brooks, R.R., Presley, B.J., and Kaplan, I.R. (1968). Trace elements in the interstitial water of marine sediments. *Geochim. et.Cosmochim. Acta*, 32, 397-414

Browne, M.A.E. (1987). The physical geography and geology of the estuary and Firth of Forth, Scotland. *Proceeding of the Royal Society of Edinburgh*. V.93B, 235-244.

Bruland, K.W., Franks, R.P., Knauer, G.A., and Martens, J.H. (1979). Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in sea water. *Analytica. Chimica Acta*, 103, 233-245.

Buchanan, J.B., and M.R. Longbottom (1970). The determination of organic matter in marine muds: the effect of the presence of coal and the routine determination of protein. *J. Expl. Mar. Biol. Ecol.*, 5, 158-169.

Buller, A.T., McManus, J.(1978). Sediment sampling and analysis. in: *Estuarine Hydrography and sedimentation.* ed. Dyer, K.R. pp 88-92. Cambridge University Press, Cambridge.

Burns, P.A. & Salomon, M. (1969). Phosphate adsorption by Kaolin in saline environments. *proceedings of the National Shellfish Association*. 59, 121-125.

Burton, J.D., and Leatherland, T.M. (1972). Mercury in a Coastal Marine environment. *Nature*, 231, 440-441.

Byers, S.C., Mills, E.L. and Stewart, P.L., (1978). A comparison of methods for determining organic carbon in marine sediments, with suggestion for a standard method. *Hydrobiologia*, 58 (1), 43-47.

Cambray, R.S., Jefferies, D.E. & Topping, G. (1975). An estimate of the input of atmospheric trace elements into the North sea and the Clyde Sea (1972-73). Wantage; *Atomic Energy Research Establishment, R7733.*

Callender E., Hammond D.E., (1982). Nutrient exchange across the sediment water interface in the Potomac River Estuary, *Estuarine Coastal Shelf Sci.*, 15, 395-413.

Calvert, S.E., and Price, N.B. (1972). Diffusion and reaction profiles of dissolved manganese in the pore-water of marine sediments. *Earth Planet. Sci. Letters*, 16, 245-249.

Calvert, S.E and Karlin, R.E. (1991). Relationships between sulphur, organic carbon, and iron in the modern sediments of the Black Sea. *Geochimica et Cosmochimica Acta* Vol. 55, pp. 2483-2490.

Canfield, D.E., and Berner, R.A.(1987). Dissolution and Pyritization of Magnetite in anoxic marine sediments. *Geochim. Cosmochim. Acta* 51, 645--659.

Carignan, R., Rapin, F., and Tesssier, A. (1985). Sediment pore water sampling for metal analysis: A comparison of techniques. *Geochimica et Cosmochimica Acta* Vol. 49, pp. 2493-2497.

Cauwet, G. (1987). Influence of sedimentological features on the distribution of trace metals in marine sediments. *Marine Chemistry*, 22, 221-234.

Chapman, P.M., Brinkhurst, R.O. (1981). Seasonal changes in interstitial salinities and seasonal movements of subtidal benthic invertebrates in the Fraser River estuary. *Estuarine, Coastal and Shelve Science*, 12, 49-66.

Chanton, J.B., Martens, C.S. and Goldhaber, M.B. (1987). Biogeochemical cycling in an organic-rich coastal marine basin. 7. Sulphur mass balance, oxygen uptake and sulphide retention. *Geochim. Cosmochim. Acta* 51, 1187-1200.

Chen, Y.S.R., Buller, J.N. & Stumm ,W. (1973). Kinetic study of phosphate reaction with Aluminium oxide and Kaolinite. *Environmental science and Technology* 7, 327-323.

Collett, W.F. (1961). A preliminary investigation of the pollution of the upper Forth estuary. *Journal of the proceedings of institute for sewage purification* 1961, 418-434.

Collett, W.F. (1972). The quality of the Forth estuary. *Proceeding of the Royal Society of Edinburgh* 71B, 137-141.

Curray, J.R. (1969). History of continental shelves. In the new concepts of continental margin sedimentation. *Am. Geol. Inst., Wash., JC6,* 1-18.

Danielsson, L.G., Magnusson, B. Westerlund, S. and Zhang, K. (1982). Trace metal determinations in Estuarine waters by Electrothermal Atomic Absorption Spectrometry after extraction of Dithiocarbamate complexes into FREON. *Analytica Chemica Acta,* 144,183-188.

Danielsson, L.G., Magnusson, B. and Westerlund, S. (1978). An improved metal extraction procedure for the determination of trace metals in sea water by atomic absorption spectrometry with electrothermal atomisation. *Anal. Chim. Acta.* 98, 47-57.

Davies, I. M. (1976). The atmospheric deposition of some heavy metals around the Firth of Forth. Copenhagen; *International Council for Exploration of the Sea,* C.M. 1976/E;35.

Davies, I. M. (1977). Further observations of the atmospheric deposition of some heavy metals around the Firth of Forth. Copenhagen; *International Council for Exploration of Sea,* C.M. 1977/E;35.

Davies, I.M., Griffith, A.H., Leatherland, T.M. & Metcalfe, A.P. (1986). Particulate mercury fluxes in the Forth estuary, Scotland. *International Council for Exploration of Sea.* 186, 301-305.

Davies, I.M. (1987). Trace metals and organohalogen compounds in the Forth, Scotland. *Proceedings of the Royal Society of Edinburgh* 93B, 315-326.

Davis, G.K., R. Jordan, J.J. Kubota, H.A. Laitinen, G. Matrone, P.M. Newberne,B.L. O'Dell and J.S. Webb (1974). "Copper and Molybdenum," in: *Geochemistry and the environment,* Volume 1. The relation of selected Trace Elements to Health and Disease, National Academy of Sciences, Washington, D.C. , p. 70.

Degens, E.T., Kenneth, M., (1976). Factors controlling the distribution and early diagenesis of marine organic material in marine sediments. ch 31, In: *Chemical Oceanography*, Riley, J.P and Chester R, eds. pp 75.

De Groot, A., Zchuppe, K., and Solomons, W., (1982). Standardization of methods of analysis for heavy metals in sediments: *Hydrobiologia*, v. 92, p. 689-695.

Duchart, P., Calvert, S.E. and Price, N.B. (1973). Distribution of trace metals in the pore-waters of shallow marine sediments. *Limnol. and Oceanogr.*, 18, 605-610.

Duinker, J.C. (1980). Suspended matter in estuaries: adsorption and desorption processes. in: Olausson, E. and Cato, I., Eds. *Chemistry and Biogeochemistry of estuaries*: Wiley; 71-119.

Duinker, J.C.(1986). Formation and transformation of element species in estuaries. In: Bernhard, M., Brinckam, F.E and Sadler, P. T., Eds. *Speciation in Environmental processes*, Dahlem Konferenzen: Springer Verlag; 365-384.

Dyer, K.R. (1973) *Estuaries: A physical introduction*. John Wiley, London, 140 pp.

Dyer, K.R. (1979). *Estuarine hydrography and sedimentation EBSA handbook*, Cambridge university press, Cambridge, 230 pp.

Elderfield, H., and Hepworth, A. (1975). Diagenesis, metals and pollution in estuaries. *Mar. Pollu. Bull.*, 6, 85-87.

Elderfield, H.(1981). Metal organic associations in interstitial waters of Narraganset Bay sediments. *Am.J.Sci.*, 281:1184-1196.

Emerson, S.(1976). Early diagenesis in anaerobic lake sediments: Chemical eqilibria in interstitial waters. *Geochim cosmochim Acta*, 40: 925-934.

Emerson S., Jahnke R., and Heggie D. (1984). Sediment water exchange in shallow estuarine sediments. *J. Mar. Res.* 42, 709-730.

Emmery, K.O. (1968). Relict sediments on contaminated shales of the world. *Bull. Am. Assoc. Pet. Geol.*, 52, 445-464.

Fanning, K.A. and Pilson, M.E. (1971). Interstitial Silica and pH in marine sediments; Some effects of sampling procedures. *Science* , 173, 1228-1231

Fenchel, T.M., and Riedl, R.J. (1970). The sulphide system : a new biotic community underneath the oxidized layer of marine sand bottoms. *Mar. Biol.*, 7, 255-268.

Fernandez, F. J. and Manning, D. (1971). Atomic absorption analyses of metals pollutants in water using a heated graphite atomizer. *Atomic Absorption Newsletter*, 10,65-90.

Filipek, L.,and Owen, R., (1979). Geochemical associations and grain size partitioning of heavy metals in lacustrine sediments: *Chemical Geology*, v. 26, p.105-117.

Flannagan, J.F. (1970). Efficiencies of various grabs and corers in sampling fresh water benthos. *J. Fish, Res. Board*, Canada, 27, 1961.

Forstner, U. (1981b). In : *Handbook of Strata-Bound and Stratiform Ore Deposits*, Vol. 9(Wolf, K.H., ed.), p. 179, Elsevier, Amesterdam.

Forstner, U., and Muller, G. (1973). Heavy metal accumulation in river sediments, a response to environmental pollution. *Geoforum*, 14, 53-62.

Forstner, U. & Wittmann, (1979). *Metal pollution in the aquatic environment*. Chapter D. Metal pollution assessment from sediment analysis, pp. 110-118.

Forstner , U., and Wittmann, G., (1981). *Metal pollution in the aquatic environment*, 2nd revised edition, New York, Springer-Verlag, 486 p.

Forstner, U., Calmàno, W. and Schoer, J., (1982). Metals in sediments from the Elbe, Weser and Ems estuaries and from the German Bight; grain size effects and chemical forms. *Int. symbosium on the chemistry of the Mediterranean*, Primoston, Yugosalvia. Thalassia Jugosol., 12:

30-36.

Forstner, U., (1982a). Chemical forms of metal enrichment in recent sediments, in Amstutz, G., and others, eds., *Ore genesis*, New York, Springer Verlag, p 191-199.

Forstner, U., (1982b). Accumulative phases for heavy metals in limnic sediments: *Hydrobiologia*, v. 91, p. 269-284.

Froleich, P.N., Bender, M.L. Luedtzke, N.A., Heath, G.R., and De Vries, T. (1982). The marine phosphorous cycle. *Amer. J. Sci.*, 282, 474-511.

FRPB, (1981). Hydrographic survey of the Forth estuary from Kincardine to south Queensferry, Edinburgh. *Forth River Purification Board.*

FRPB, (1986). A second survey of resuspension of solids in the upper Forth estuary. Report number ES1/86. Edinburgh: *Forth River Purification Board.*

FRPB, (1988). Marine Biological and sedimentological methods. *Report TW2/88 Forth River Purification Board.*

FRPB, (1989). Results of analysis of sediments from the lower forth estuary, 1979-87. An appraisal. Report TW 04/89. *Forth River Purification Board.*

Geochemistry and the Environment.(1974). The Relation of Selected Trace elements to Health and Disease, *National Academy of Sciences*, Washington, D.C. V.I, p.113.

Geochemistry and the Environment.(1977). The Relation of Other Selected Trace elements to Health and Disease, *National Academy of Sciences*, Washington, D.C. V.II, p.163.

Geochemistry and the Environment.(1974). Distribution of Selected Trace elements Related to the Occurrence of Certain Cancers, Cardiovascular Diseases and Urolithiasis, *National Academy of Sciences*, Washington, D.C. V. III p.113.

Gibbs, R. (1973). Mechanisms of trace metals transport in rivers: *Science*, v. 180, p. 71-73.

Gibbs, R. (1977). Transport phases of transition metals in the Amazon and Yukon Rivers: *Geological Society of America Bulletin*, v.88, p.829-843.

Gieskes, J.M. (1973). Initial reports of the Deep Sea Drilling Project, ed. B.C. Heezen, et al, 20, 813-29. Washington DC. GPO. 958 pp.

Gieskes, J.M. (1974). Initial reports of the Deep Sea Drilling Project, ed. E.S.W. Simpson et al, 25, 361-94. Washington DC. GPO. 884 pp.

Goldberg, E.D. (1972). Man's role in the major sedimentary cycle. In Dyrssen, D. and Jagner, D. (eds.) *The changing chemistry of the Oceans*. Nobel Symposium, pp. 267-288.

Goldhaber, M.B., and Kaplan, I.R. (1974). The Sulphur cycle. In: *The Sea*, Vol.5, E. D. Goldberg (ed.) John Wiley and Sons, New York, 566-655.

Goldhaber, M.B., and Kaplan, I.R. (1975). Control and consequences of sulphate reduction rates in recent marine sediments. *Soil Sci.* 119, 42-55.

Goldhaber, M.B., Aller, R.C., Cochran, J. K., Rosenfield, L.K., Martens, C.S., and Berner, R.A. (1977). Sulphate reduction, diffusion and bioturbation in Long Island Sound Sediments. *Am. Jour. of Sci.*, 277, 655-673.

Grant, J. and B.T. Hargrave (1987). Benthic metabolism and the quality of sediment organic carbon. *Biol. Oceanogr.*, 4, 243-264.

Griffith, A. H. (1987). Water quality of the estuary and Firth of Forth, Scotland. *Proceeding of the Royal Society of Edinburgh* 93B. 303-314.

Grim, R., (1968). *Clay mineralogy*, 2nd edition, New York, McGraw-Hill, 596p.

Gunnarsson, L.A.H., and Ronnow, P.H.(1982). Inter-relationships between sulphate reducing and methane producing bacteria in coastal sediments with intense sulphide production. *Mar. Biol.* 69, 121-128.

Hahne, H.C., and Kroontje, W. (1973). Significance of pH and chloride concentration on behaviour of heavy metal pollutant: Mercury (II), Cadmium (II), Zinc (II) and Lead (II). *J. Environ. Quality,* Vol.2, no,4. pp 444-450.

Hale, S.S. (1974). The role of benthic communities in the nutrient cycles of Narragansett Bay. *MSc Thesis,* Univ. of Rhode Island, Kingston. 123 pp.

Hallberg, R.O. (1973). Sedimentary sulphide mineral formation - an energy circuit system approach. *Mineral Deposita,* 7:189-201.

Hammond, P.B. (1978)."Human Health Implications," in: *Lead in the environment,* W.R. Boggess and B.G. Wixson, Eds., pp. 195-198.

Harper, D.J., Fileman, C.F., May, P.V and Portmann, J.E. (1989). *Aquatic environment protection: Analytical methods,* no.3. Methods of analysis for trace metals in marine and other samples.

Harrison, S.J. (1981). Rainfall in the Stirling area. *Forth Naturalist and Historian* 5, 23-24.

Harrison, S.J. (1987). Climatic conditions over the Forth estuary and the Firth of Forth, Scotland. *Proceedings of the Royal Society of Edinburgh.* 93B. 303-314.

Hartmann, M., Koegler, F.C., Mueller, P., Suess, E. (1973b). Preliminary results of Geochemical and Soil Mechanical Investigations on Pacific Ocean Sediments. Presented at Symp. Origin and Distribution of Manganese Nodules, Hawaii.

Hartwig, E.O. (1976). The impact of nitrogen and phosphorus release from a silicious sediment on the overlying water. In: *Estuarine processes,* vol. 1, edited by M. Wiley, Academic Press, New York, pp. 103-117.

Heggie, D.T., Burell, D.C.(1982). Depth distribution of copper in the water column and interstitial waters of an Alaskan fjords. In: *The dynamic environment of the ocean floor* (eds. K.A.Fanning and F.T.Manheim), pp. 317-335. Lexington Books.

Hines, M. E., Orem, W.H., Lyons, W.B. Jones, G.E. (1982). Microbial activity and bioturbation induced oscillations in pore-water chemistry of estuarine sediments in spring. *Nature*, 299, 433-435.

Hirner, A., Kritsotakis, K., and Tobschall, H.(1990). Metal-organic associations in sediments - I, comparison of unpolluted recent and ancient sediments and sediments affected by anthropogenic pollution: *Applied Geochemistry*, v.5, p. 491-506.

Holdren, Jr., G. R., Bricker, O.P., and Matisoff, G. (1975). A model for the control of dissolved manganese in the interstitial waters of Chesapeake Bay. In: *Marine chemistry in the coastal environment*, T.M. Church (ed.), Am. Chem. Soc., Washington, p. 364-381.

Holeman, J.N. (1968). The sediment yield of major rivers of the world. *Water Resource. Res.*, 4, 737-747.

Holmes, C. W., Slae, E. A., McLerran, C. J.(1974). Migration and redistribution of Zinc and Cadmium in Marine estuarine systems. *Enviro. Sci. Technol.* 8: 255-259.

Hopkinson JR, C.S., (1987). Nutrient regeneration. in: shallow water sediments of the estuarine plume region of Nearshore Georgia Bight. USA. *Mar. Biol.* 94: 127-142.

Horowitz, A., and Elrick, K., (1987). The relation of stream sediment surface area, grain size and composition to trace element chemistry: *Applied chemistry*, v.2, p.437-451.

Horowitz, A., and Elrick, K., (1988). Interpretation of bed sediment trace metal data: methods for dealing with the grain size effect, In: Lichtenberg, J., and others, eds., *chemical and biological characterization of sludges, sediment, dredge spoils, and drilling muds*, ASTM STP 976, Philadelphia, Penn., p. 114-128.

Horowitz, A.,(1991). *A Primer on sediments-trace element chemistry*. Corrections for grain size differences. p. 84., 2nd edition. Lewis Publisher.

Jenne, E., (1968). Controls of Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significance of

Hydrous Mn and Fe oxides: *Advances in Chemistry Series*, v. 73, p. 337-387.

Jenne, E., (1976). Trace element sorption by sediments and soils- sites and processes, in: Chappel, W., and Peterson, K., eds., *Symposium on Molybdenum*, v. 2, New York, Marcel Decker, p. 425-553.

Jenne, E., Kennedy, V., Burchard, J., and Ball, J.(1980). Sediment collection and processing for selective extraction and for total metal analysis, In: Baker, R., ed., *Contaminants and sediment*, v. 2, Ann Arbor, Mich., Ann Arbor Science Publishers, Inc., P. 169-189.

Jones, B., and Bowser, C., (1978). The mineralogy and related chemistry of lake sediments, in :Lerman, A., ed. *Lakes: chemistry, geology, physics*, New York, Springer Verlag, p. 179-235.

Jorgensen, B.B. (1978a). A comparison of methods for the quantification of bacterial sulphate reduction in coastal marine sediments. 1. Measurements with radio-tracer techniques. *J. Geomicrobiol.* 1, 11-27.

Jorgensen, B.B. (1978a). A comparison of methods for the quantification of bacterial sulphate reduction in coastal marine sediments. II. Calculations from mathematical model. *J. Geomicrbiol* 1, 29-51.

Kaplan, I.R., and Ritenberg, S.C. (1964). Microbiological fractionation of sulphur isotopes. *J. Gen. Microbil.* 34, 195-212.

Kapralek, F., Jechova, E., Otavova, M. (1982). Two sites of oxygen control in induced synthesis of respiratory nitrate reductae in Escherichia coli. *J. Bact.* 149: 1142-1145.

Kauadio, I., and Trefry, J.H. (1987). Sediment trace metal contamination in the Ivory Coast, West Africa. *Water, Air, and Soil pollution*. 32: 145-154.

Keith, L.H., Crummett, W., Deegan, J., Libby, R.A., Taylor, J.K and Wentler, G. (1983). Principles of environmental analysis, *Analytical Chemistry*, 55, 2211-2218.

Kershaw, P.J.(1980). An investigation of factors Influencing the concentration of trace metals in the bottom sediments of the forth estuary. *Ph.D. thesis* university of Dundee.

Kester, D. R., Pytkowics R.M., (1967). Determination of the apparent dissolution constants of Phosphoric acid in sea water, *Limnol. Oceanogr.,* 12, 243-252.

Klinkhammer, G.P. (1980). Early diagenesis in sediments from the Eastern Equatorial Pacific, 2. Pore water metal analysis. *Earth and Planet. Sci. Lett.* 49, 81-101.

Klinkhammer, G.P., and Bender, L.M. (1981). Trace metals distribution in the Hudson River estuary. *Estuarine Coastal and Shelf Science.* 12: 629-643.

Klump, J.V., Martens, C.S., (1981). Biogeochemical cycling in an organic rich coastal marine basin. 2: Nutrient sediment-water exchange processes, *Geochim Cosmochim. Acta,* 45, 101-121.

Klump, J.V.(1987). Biochemical cycling in an organic rich coastal marine basin. 5. sedimentary nitrogen and phosphorus budgets based upon kinetic models, mass balances, and the stoichiometry of Nutrient regeneration. *Geochim. Cosmochim. Acta* 51: 1161-1173.

Krauskopf, K., (1956). Factors controlling the concentration of thirteen rare metals in sea water: *Geochimica et Cosmochimica Acta,* v. 9, p. 1-32.

Krom, M.D., Sholkovitz, E.R.(1978). On the association of Iron and Manganese with organic matter in anoxic marine pore-water. *Geochim Cosmochim. Acta* 42: 606-611.

Krom, M.D., Berner, R.A. (1981). The diagenesis of phosphorus in a nearshore marine sediment. *Geochim Cosmochim. Acta* 45: 207-216.

Kuenen, Ph. M. (1950). *Marine Geology,* John Wiley and Sons, 551 pp.

Kurland, L.T., Faro, S.N and Siedler, H.S.(1960). "Minamata disease," *World Neurol.* 1:320-325.

Langmyhr, F.G., Paus, P.E. (1968). The analysis of inorganic siliceous materials by atomic absorption spectroscopy spectrophotometry and the hydrofluoric acid decomposition technique. *Analytica Chimica Acta,* 43, 397-408.

Leatherland, T.M. (1987). The estuary and Firth of Forth, Scotland; uses and aims. *Proceeding of the Royal Society of Edinburgh.* 93B, 285-297.

Li, Y., Bischoff, J., and Mathieu, G. (1969). The migration of manganese in the Arctic Basin sediments. *Earth planet. Sci. Letters,* 7, 265-270.

Li, Y.H., Gregory S., (1974). Diffusion of ion in sea water and deep sea sediments. *Geochim. Cosmochim. Acta,* 38, 703-714.

Liu, U. (1976). Carbohydrates in Lake Ontario sediments, in: *Environmental Biogeochemistry,* Nriagu, J.E., editor, Ann Arbor Science, Ann Arbor, 185-190

Lu, C.S.J., Chen, K.Y. (1977). Migration of trace metals in interfaces of seawater and polluted surficial sediments. *Envi. Sci. and Technol.* 11:174-182.

Lyons, W. B., Wilson K. M., Armstrong, P. B., Smith, G. M., Gaudette, H.E.(1980). Trace metal pore-water geochemistry of near-shore Bermuda carbonate sediment. *Oceanol Acta.* 3:263-366.

Lyons, W. B., Fitzgerald, W.F. (1978). Nutrients production in nearshore tidal flat pore-waters: a kinetic study. *Environmental Biogeochemistry and Geomicrobiology,* 1, 237-244.

MacDonald, R.W., and O'Brien, M.C. (1985). Extending the use of certified reference sediments for the assessment of accuracy in determinations of trace metals. *Analytica Chimica Acta,* 177, 81-91.

Marshall, N. (1972). Interstitial community and sediments of shoal benthic environments. *Geol. Soc. Am. Mem.,* 133, 409-415.

Mayer. L.M., and Fink, K.J.R. (1980). Granulometric dependence of Chromium accumulation in estuarine sediments in

Maine. *Estuarine Coastal Marine Science.*, 11: 491-503

McCave, I.N. (1972). Transport and escape of fine grained sediment from shelf areas. In : *Shelf Sediment Transport*: Swift, Duane, and Pilkey ed., 225-247.

Mclusky, D.S., (1989). *The Estuarine Ecosystem.* 2nd edition. Blakie and Son Ltd.

Mackay, D.W. & Leatherland, T.M. (1976). Chemical processes in an estuary receiving major inputs of industrial and domestic wastes. In : *Estuarine Chemistry*, ed. Burton, J.D. & Liss, P.J., Chap.7, 185-218. London; Academic press.

Martens, C.S., Goldhaber, M.B. (1978). Early diagenesis in transitional sedimentary environments of the White Oak River estuary, North Carolina. *Limnology and Oceanography*, 23,428-441.

Martens, C. S., and Berner, R.A. (1977). Interstitial water chemistry of anoxic Long Island Sound sediments. 1. Dissolved gasses. *Limnol. and Oceanogr.*, 22, 10-25.

Matissof, G., Bricker, O. B., Holdren, Jr., G. R., and Kaerk, P. (1975). Spatial and temporal variations in the interstitial water chemistry of Chesapeake Bay sediments. In: *Marine Chemistry in the Coastal Environment*, T.M. Church (ed.), Am. Chem. Soc., Washington, D. C., 343-363.

Mertz, W., Angino, E.E,. Cannon, H.L., Hambidge, M., and Vours, A.W. (1974). "Chromium" in: *Geochemistry and the Environment*, Vol. 1, *The Relation of Selected Trace Elements to Health and Disease*, National Academy of Sciences, Washington, D.C. p.70.

Montgomery, J.R., Zimmerman, C.F., Price, M.T. (1979). The collection, analysis and variation of nutrients in estuarine pore-water, *Estuarine and Coastal Marine Science*, 14,203-214.

Morris, A., Bale, A. J. & Howlland, R. J.M. (1981). Nutrient distribution in an estuary: evidence of chemical precipitation of dissolved silicate and phosphate. *Estuarine and Coastal Shelf Science* 12, 205-216.

Muller, G. and Forstner, U. (1975). Heavy metals in sediments of the Rhine estuaries: mobilization or mixing effect. *Environ. Geol.;* 1: 33-39.

Murray, J., and Irvine, R. (1895). On the chemical changes which take place in the composition of sea water associated with blue muds on the floor of the ocean. *Trans. Roy. Soc. Edinburgh*, 37, 481-508.

Nakkai, N. and Jensen, M.L. (1964). The kinetic isotope effect in the bacterial reduction and oxidation of sulphur. *Geochim. Cosmochim. Acta*, 28, 1892-1912.

National Research Council of Canada. (1990). Marine Sediment Reference Materials for Trace Elements and other Constituents BCSS-1, MESS-1, PACS-1, BEST-1.

Nedwell, D.B. and Abram, J.W. (1978). Bacterial sulphate reduction in relation to sulphur geochemistry in two contrasting salt-marsh sediments. *Est. Coast. Mar. Sci.* 6, 341-351

Nicholson, R.A.& Moore, P.J. (1978). IGS studies of the geology of the Firth of Forth and its approaches. *Institute of Geological Sciences Report* 77/17, 30-40.

Nissenbaum, A., Baedecker, M.j., and Kaplan,I.R. (1971). Studies on dissolved organic matter from interstitial water of reducing marine fjord. *Adv. in Org. Geochem.* Gaerther, L., and Wehner, H. (eds.), Pergamon Press, P. 427-440).

Nissenbaum, A., Presley, B.J., and Kaplan, I.R. (1972). Early diagenesis in a reducing fjord; Saanich Inlet, British Columbia 1. chemical and isotopic changes in major components of interstitial water. *Geochem. et Cosmochim Acta, 36, 1007-1027.*

Nissenbaum, A., Swaine, D. J. (1976). Organic matter - metal reactions in recent sediments:The role of humic substances. *Geochim Cosmochim. Acta*, 40:809-816.

Nixon, W.S., C.A. Oviatt & S.S. Hale, (1976). Nitrogen regeneration and the metabolism of coastal marine bottom communities. In: J.M., Anderson & A. MacFadyen. *The role of terrestrial and aquatic organisms in decomposition processes*. Blackwelll, Oxford: 269-283.

Nriago, J., and Coker, R., (1980). Trace metals in humic and fulvic acids from Lake Ontario sediments, *Environmental Science and Technology*, v. 14, p. 443-446.

Panturakul. S., and Baeyens, W. (1991). Behaviour of heavy metals in a mud flat of the Scheldt Estuary, Belgium. *Mar. Poll. Bull.*, V. 22, 3, pp. 128-134.

Parker, J.G., (1983). A comparison of methods used for the measurements of organic matter in marine sediment. *Chemistry in Ecology*, 1, 201-210.

Pearson, T.H. and Stanley, S.O., (1979). Comparative measurement of the redox potential of marine sediments as a rapid means of assessing the effect of organic pollution. *Mar. Biol.*, 53, 371-379

Ponnamperund, F.N. (1972). The chemistry of submerged soils. In: *Advances in agronomy*, vol. 24, N.C. Brady (ed.). Academic press, New York.

Postma, H. (1980). Sediment transport and transportation. In: *Chemistry and biogeochemistry of estuaries*. Ed. Olausson, E and Cato, I. John Wiley & Sons Ltd.

Presley, B. J.,Kolodny, Y., Nissenbaum, A., Kaplan,I.R. (1972). Early diagenesis in reducing Fjord, Saanich Inlet British Columbia. 2. Trace element distribution in interstitial waters and sediment. *Geochim Cosmochim Acta*, 36: 1073-1090.

Presley B. J.,Trefry, J. H. (1980). Sediment water interactions and the geochemistry of interstitial waters. In: Ollausson E. Cato, I. (eds) *Chemistry and Biogeochemistry of estuaries*. Wiley, New York: 187- 222. Academic Press.

Price, N.B., (1976). Chemical diagenesis in sediments. Ch.30. in: Riley and Chester,(eds) *Chemical Oceanography*. Vol. 6 2nd edition.

Price, N.B., and Calvert, S.E. (1973a). *ICSU/SCOR Symp., Cambridge 1970. Inst. Geol.Sci.* Rep. 70/16, 185.

Pritchard, D.W. (1967). What is an estuary; physical viewpoint. In *Estuaries*, ed Lauff, G.H., pp.3-5. Washington; American Association for the Advancement of Science, publication number 83.

Raaphorst, W.Van, P.Ruardij & A.G.Brinkman, (1988). The assessment of benthic phosphorus regeneration in an estuarine ecosystem model. *Neth. J. Sea Res.* 22: 23-36.

Raaphorst, W.Van,. Kloosterhuis, H.T., Cramer, A. and Bakker, K.J., (1990). Nutrient early diagenesis in the sandy sediments of the Dogger bank area, north sea: Pore water results. *Neth. J. Sea Res.* 26 (1): 25-52.

Raisewell, R., Berner, R.A. (1985). Pyrite formation in euxinic and semi-euxinic sediments. *Amer. J. Sc.* 285, 710-724.

Robbins, L.A., and Callender E. (1975). Diagenesis of manganese in Lake Michigan sediments. *Am. J. Science,* 275, 512-533.

Robertson, L.A. and Kuenen, J.G. (1984b). Aerobic denitrification. a controversy revived. *Arch. Microbiol.* 139: 351-354.

Rutgers Van Der Leoff, M.M. (1980). Nutrients in the Interstitial waters of the Southern Bight of the North Sea. *Netherlands Journal of Sea Research,* 14 (2): 144-171.

Salomons, W., Mook, W.G.(1977). Trace metals concentrations in estuarine sediments: mobilization, mixing or precipitation. *Neth. J. Sea Res.* 11: 199-209.

Salomons, W. Forstner, U. (1984). In: *Metals in the Hydrocycle.* chap.3 sediments and the transport of metals. p.63

Sayles, F. L., Wilson, T.R., Hume, D.N. and Mangelsdorf, P.C. (1973b). In situ sampler for marine sedimentary pore waters: evidence for potassium depletion and calcium enrichment. *Science,* 181, 154-156.

Segar, D. and Gonzales, J. (1972). Evaluation of atomic absorption with a heated graphite atomizer for the direct determination of trace transition metals in sea water. *Analytica Chimica Acta,* 58, 7-14.

Socha, S.B., Carpenter, R. (1987). Factors affecting pore water hydrocarbon concentrations in Puget Sounds sediments *Geochimica et Cosmochimica Acta* Vol. 51, pp. 1273-1284.

Subosu, P. F. and others, (1989). Ion chromatography of inorganic anions in brine samples. *J. Chromatogr. Sci.* 27: 680-784.

Suess, E. (1976a). Nutrients near the depositional interface. In: I.N. McCave. *The benthic boundary layer.* Plenum press, New York: 57-79.

Sweeney, R.E. (1972). Pyratization during diagenesis of marine sediments. *Ph.D. thesis,* Dept. of Geology, University of california, Los Angeles, 184pp.

Swift, D.J.P. (1976). Continental shelf sedimentation. In *Marine sediment Transport and Environmental Management* 4, Stanley and Swift ed., John Wiley, 311-351.

Takai, Y., and **Kamura, T.** (1966). The mechanism of reduction in waterlogged paddy soil. *Folia Microbiol.* (Prague), 11, 314-313.

Thomas, R.L., (1972). The distribution of Mercury in the sediments of Lake Ontario. *Can. J. Earth Sci.,* 9: 636-651.

Thomas, A.J.. and **Marten, J.M.,** (1982). Chemical composition of river suspended sediment. *Mitt. Geol. Palaentol. Inst.* Univ. Hamburg, 52: 555-564.

Thorne, L., and **Nickless, G.** (1981). The relation between heavy metals and particle size fraction within the Severn estuary (U.K.) inter-tidal sediments: *The Science of the Total Environment,* v. 19 p. 207-213.

Thornton, I., Walting, H. and **Darracott, A.** (1975). Geochemical studies in several rivers and estuaries used for oyster rearing. *Sci. Total Environ.,* 4: 325-345.

Trefry, J.H., Metz, S., and **Trocine, R.P.** (1985). The decline in lead transport by the Mississippi River. *Science,* 230: 439-441.

Troup, B.N. (1974). The interaction of iron with phosphate, Carbonate, and sulphide in Chesapeake Bay interstitial water: a thermodynamic interpretation. *Ph.D. Dissertation,* 114 pp., The Johns Hopkins University, Baltimore.

Turner, T.T., and Patrick, Jr., W.H. (1968). Chemical changes in waterlogged soils as a result of oxygen depletion. *Trans. 9th Int. Congr. Soil Sci.* (Adelaide, Aust.), 53-65.

Underwood, E.J. (1971). *Trace elements in Humans and Animal Nutrition,* 3rd ed. New York: Academic Press. Inc.

Vanderborght, J., Wollast,. R. and Billen, G. (1977). Kinetic models of diagenesis in disturbed sediments. Part 2. Nitrogen diagenesis. *Limnol, Oceanogr.* 22, 794-803.

Vosjan, J.H. (1974). Sulphate in water and sediments of the Dutch Wadden Sea, *Netherlands J. Sea Res.* v.8, p.208-213.

Watson, P.G., Frickers, P.E., Goodchild, C.M. (1985). A comparison of Nutrients in the Interstitial water of reducing (Tamar Estuary) and oxic (Carmarthen Bay) coastal sediments. *Netherlands Journal of Sea Research,* 19 (3/4): 231-239.

Watson, P.G., Frickers, P.E., Goodchild, C.M. (1985). Spatial and seasonal variations in the chemistry of sediment interstitial waters in the Tamar Estuary. *Estu. Coast. and Shelf Science* 21, 105-119.

Weaver, C.E, and Wampler, J.M. (1972). *Geochim. Cosmochim. Acta,* 36, 1.

Webb, A.J. & Metcalfe, A.P. (1987). Physical aspects, water movements and modelling studies of the Forth estuary, Scotland. *Proceeding of the Royal Society of Edinburgh* 93B, 259-272.

Welz, B. (1985). *Atomic Absorption Spectrometry,* (2nd edition). VCH Publishers.

Westerlund, S.F.G., and others (1986). Benthic fluxes of cadmium, copper, nickel, zinc and lead in the coastal environment, *Geochimica et Cosmochimica Acta* 50 pp, 1289-1296.

Westrich, J.T. (1983). The consequence and controls of bacterial sulphate reduction in marine sediments. *Ph.D.*

dissertation. Yale university.

Westrich, J.T. and Berner, R.A. (1984). The role of sedimentary organic matter in bacterial sulphate reduction: the G model tested. *Limnol. Oceanogr.* 29, 236-249.

Whitefield, M. (1979). Eh as an operational parameter in estuarine studies. *Limnol. and Oceanogr.*, 14, 547-558.

Windom, H.L. (1976). Lithogenous material in marine sediments.In *Chemical Oceanography*, Riley and Chester, ed., Acad.Press, 103-135.

Wood, J.M. (1974). Biological cycles for toxic elements in the environment. *Science*, 183, 1049-1052.

Williams, S.C., Simpson, H.J., Olsen, C.R. and Bopp, R.F., (1978). Sources of Heavy metals in sediments of the Hudson River Estuary. *Mar. Chem.*, 6: 195-213.

Wilson, J.O., Valiela, I., and T. Swan, (1985). Sources and concentrations of vascular plant material in sediments of Buzzards Bay, Massachusetts, USA. *Mar. Biol.*, 129-138.

Windom, H.L., Slippipat, S., and Hungspreugs, M. (1984). Trace metals composition and accumulation rates of sediments in the upper Gulf of Thailand. *Estuarine, Coastal and Shelf Science* 19: 133-142.

Wittmann, G.T.W., and Forstner, U. (1975). Metal enrichment of sediments in inland waters *The Hatbeespoort Dam. Water SA*, 1, 76-82.

Zeitschell, B., (1980). Sediment water interactions in nutrient dynamics. In: K.R. Tenore & B.C. Coull. *Marine benthic dynamics*. University of South Carolina Press: 195-218.

ZoBell, C.E. (1946). Studies on redox potential of marine sediments. *Bull. Am. Assoc. Petrol. Geologists*, 30, 447-513.

Appendix A1

Percentage of Particle size < 63 um in the Sediment

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	64.50	97.00	64.50	48.00	75.50	20.00
	2.5-5	89.00	98.00	70.50	54.50	80.50	28.00
	5-7.5	86.00	98.00	80.50	61.50	86.00	29.00
	7.5-10	95.00	95.50	90.00	61.50	77.50	28.00
Autumn 91	0-2.5	83.50	90.50	55.00	39.50	86.50	80.50
	2.5-5	80.00	85.00	73.00	55.50	84.00	87.50
	5-7.5	69.50	91.00	94.50	54.50	85.50	83.50
	7.5-10	63.50	85.50	90.00	56.00	88.00	83.00
Winter 92	0-2.5	74.50	95.50	87.50	70.50	74.00	85.50
	2.5-5	79.50	97.50	92.00	55.00	67.00	79.50
	5-7.5	74.50	94.50	93.50	73.00	67.50	68.50
	7.5-10	76.50	85.00	95.50	77.50	76.50	76.50
Spring 92	0-2.5	78.00	96.00	24.00	45.50	70.00	57.00
	2.5-5	70.50	91.50	34.50	27.00	60.50	49.00
	5-7.5	66.00	89.00	24.00	48.50	55.50	52.50
	7.5-10	76.50	91.00	26.00	48.50	35.00	30.50
Summer 92	0-2.5	84.50	94.50	76.50	63.50	83.00	69.00
	2.5-5	79.50	88.00	64.00	67.00	80.50	64.50
	5-7.5	71.50	77.50	54.00	63.00	78.50	49.50
	7.5-10	68.00	91.00	50.00	70.50	80.00	62.50
Autumn 92	0-2.5	64.00	90.50	24.50	61.50	85.50	33.00
	2.5-5	73.50	87.00	19.00	64.50	89.00	60.00
	5-7.5	74.50	91.50	22.00	64.00	90.50	50.50
	7.5-10	78.00	89.50	15.50	70.00	92.50	62.50

Appendix A2

Percentage of Organic Matter Loss On Ignition in the sediment

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	14.00	15.00	10.00	8.00	10.00	6.00
	2.5-5	13.00	14.00	11.00	7.00	10.00	5.00
	5-7.5	13.00	15.00	10.00	9.00	14.00	8.00
	7.5-10	14.00	15.00	9.00	6.00	11.00	7.00
Autumn 91	0-2.5	12.00	12.00	8.00	6.00	13.00	10.00
	2.5-5	13.00	12.00	7.00	5.00	11.00	11.00
	5-7.5	13.00	9.00	7.00	6.00	14.00	12.00
	7.5-10	11.00	7.00	7.00	3.00	13.00	10.00
Winter 92	0-2.5	10.00	14.00	10.00	9.00	10.00	12.00
	2.5-5	9.00	12.00	14.00	8.00	9.00	10.00
	5-7.5	11.00	14.00	13.00	10.00	12.00	8.00
	7.5-10	12.00	7.00	12.00	7.00	11.00	9.00
Spring 92	0-2.5	11.00	11.00	4.00	7.00	10.00	8.00
	2.5-5	14.00	7.00	5.00	5.00	9.00	7.00
	5-7.5	14.00	6.00	4.00	5.00	10.00	9.00
	7.5-10	11.00	7.00	3.00	4.00	6.00	7.00
Summer 92	0-2.5	12.00	13.00	11.00	8.00	12.00	8.00
	2.5-5	12.00	8.00	7.00	10.00	12.00	9.00
	5-7.5	13.00	5.00	9.00	9.00	9.00	8.00
	7.5-10	9.00	6.00	8.00	8.00	10.00	9.00
Autumn 92	0-2.5	9.00	11.00	5.00	8.00	11.00	4.00
	2.5-5	7.00	5.00	6.00	8.00	11.00	6.00
	5-7.5	8.00	6.00	4.00	10.00	12.00	7.00
	7.5-10	7.00	6.00	4.00	9.00	12.00	8.00

Appendix A3

Percentage of Total Organic Carbon in the sediment

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	9.27	5.06	5.32	2.84	3.95	3.93
	2.5-5	5.28	5.06	4.37	2.73	4.66	2.48
	5-7.5	5.31	5.17	3.80	3.27	4.43	2.59
	7.5-10	5.66	4.38	3.18	2.86	4.20	2.61
Autumn 91	0-2.5	4.46	4.75	2.11	3.51	5.83	3.76
	2.5-5	4.69	4.49	1.78	1.87	5.04	3.71
	5-7.5	5.04	6.48	2.44	1.49	5.25	4.92
	7.5-10	5.42	1.46	2.07	1.04	5.45	4.13
Winter 92	0-2.5	5.18	4.78	4.37	3.38	3.72	3.97
	2.5-5	4.28	5.10	4.53	3.14	3.34	4.08
	5-7.5	4.14	4.43	4.15	3.63	3.50	2.86
	7.5-10	5.16	1.67	4.40	3.46	4.33	2.95
Spring 92	0-2.5	5.76	4.40	2.61	4.06	3.36	2.57
	2.5-5	5.35	2.98	3.50	2.98	2.79	2.49
	5-7.5	5.77	1.85	1.83	0.68	3.76	2.98
	7.5-10	5.64	1.72	2.09	1.42	2.87	4.18
Summer 92	0-2.5	5.10	4.42	3.97	3.25	4.24	3.14
	2.5-5	5.69	2.97	4.44	3.31	4.09	3.11
	5-7.5	3.41	1.62	3.47	3.32	3.86	2.16
	7.5-10	3.03	1.68	3.09	3.01	3.91	2.29
Autumn 92	0-2.5	3.59	4.28	4.31	3.58	3.74	1.66
	2.5-5	3.71	2.35	2.71	4.22	4.64	2.04
	5-7.5	3.91	1.65	3.81	4.35	4.32	3.13
	7.5-10	3.60	1.65	2.62	3.22	4.51	4.47

Appendix A4

Percentage Values of Total organic Nitrogen in the sediment

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	0.27	0.19	0.15	0.23	0.34	0.36
	2.5-5	0.22	0.13	0.18	0.28	0.44	0.38
	5-7.5	0.14	0.16	0.10	0.14	0.46	0.35
	7.5-10	0.20	0.07	0.10	0.12	0.29	0.41
Autumn 91	0-2.5	0.39	0.47	0.31	0.25	0.54	0.34
	2.5-5	0.46	0.44	0.36	0.31	0.33	0.37
	5-7.5	0.74	0.48	0.29	0.32	0.42	0.39
	7.5-10	0.35	0.22	0.32	0.25	0.42	0.43
Winter 92	0-2.5	0.63	0.49	0.68	0.27	0.39	0.41
	2.5-5	0.26	0.44	0.47	0.09	0.44	0.19
	5-7.5	0.41	0.57	0.35	0.35	0.41	0.39
	7.5-10	0.36	0.28	0.22	0.32	0.19	0.37
Spring 92	0-2.5	0.22	0.25	0.10	0.10	0.22	0.15
	2.5-5	0.28	0.16	0.10	0.10	0.09	0.11
	5-7.5	0.21	0.10	0.07	0.09	0.15	0.14
	7.5-10	0.28	0.08	0.31	0.07	0.09	0.13
Summer 92	0-2.5	0.27	0.35	0.24	0.14	0.25	0.23
	2.5-5	0.28	0.17	0.24	0.18	0.25	0.16
	5-7.5	0.27	0.23	0.16	0.17	0.19	0.10
	7.5-10	0.18	0.16	0.17	0.17	0.18	0.16
Autumn 92	0-2.5	0.29	0.34	0.30	0.33	0.32	0.21
	2.5-5	0.28	0.32	0.29	0.27	0.39	0.23
	5-7.5	0.32	0.21	0.34	0.29	0.36	0.31
	7.5-10	0.26	0.25	0.26	0.31	0.37	0.39

Appendix A5

Values of Carbon : Nitrogen ratio in the sediment

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	34.32	26.66	35.45	12.34	11.63	10.93
	2.5-5	24.02	38.92	24.27	9.76	10.58	6.52
	5-7.5	37.95	32.29	37.95	23.38	9.63	7.40
	7.5-10	28.28	62.57	31.76	23.82	14.49	6.37
Autumn 91	0-2.5	11.43	10.11	6.82	14.03	10.80	11.04
	2.5-5	10.20	10.21	4.95	6.03	15.29	10.03
	5-7.5	6.81	13.50	8.43	4.67	12.51	12.61
	7.5-10	15.50	6.66	6.47	4.16	12.98	9.61
Winter 92	0-2.5	8.22	9.75	6.42	12.52	9.53	9.69
	2.5-5	14.25	11.60	9.71	34.89	7.60	12.47
	5-7.5	10.09	7.78	14.07	10.37	8.52	7.34
	7.5-10	14.33	6.51	20.43	10.80	22.85	7.98
Spring 92	0-2.5	26.18	17.60	26.10	44.60	15.27	17.13
	2.5-5	19.11	18.63	35.00	29.80	31.00	22.64
	5-7.5	22.48	18.50	26.14	7.60	25.06	21.29
	7.5-10	20.14	21.50	6.74	20.29	31.89	32.15
Summer 92	0-2.5	18.88	12.64	16.54	23.22	16.95	13.67
	2.5-5	20.31	17.48	18.50	18.39	16.36	19.45
	5-7.5	12.64	7.06	21.66	19.53	20.31	21.62
	7.5-10	16.82	10.51	18.15	17.71	21.73	14.31
Autumn 92	0-2.5	12.37	12.58	14.35	10.84	11.70	7.91
	2.5-5	13.24	7.35	9.34	15.64	11.91	8.89
	5-7.5	12.23	7.85	11.20	15.01	12.01	10.09
	7.5-10	13.83	6.58	10.06	10.38	12.20	11.46

Appendix A6

Concentrations of Aluminium in the sediment %

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	6.40	8.70	6.60	5.60	7.70	4.30
	2.5-5	7.60	8.60	6.80	5.70	8.10	4.60
	5-7.5	8.10	8.50	7.10	6.40	8.10	4.80
	7.5-10	8.40	8.10	8.30	6.60	7.70	5.20
Autumn 91	0-2.5	7.60	8.30	6.50	5.20	6.60	7.60
	2.5-5	7.80	8.50	7.20	5.80	7.80	7.80
	5-7.5	7.90	7.70	7.60	6.10	8.00	7.90
	7.5-10	6.90	7.00	8.10	6.50	7.90	7.70
Winter 92	0-2.5	7.20	8.70	8.10	6.40	6.60	7.00
	2.5-5	7.90	8.90	7.90	7.40	7.40	6.20
	5-7.5	7.00	8.20	8.90	6.70	8.40	5.50
	7.5-10	6.80	7.20	8.20	7.10	7.00	7.60
Spring 92	0-2.5	6.80	7.70	4.60	6.20	6.50	7.20
	2.5-5	6.90	8.70	6.70	5.00	6.80	5.80
	5-7.5	6.80	6.50	5.40	6.10	7.30	7.30
	7.5-10	6.90	6.40	5.70	6.10	8.10	6.00

Appendix A7

Concentrations of Iron in the sediment g\kg

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	33.00	37.00	31.00	25.00	30.00	16.00
	2.5-5	35.00	36.00	30.00	24.00	31.00	19.00
	5-7.5	40.00	38.00	30.00	27.00	33.00	19.00
	7.5-10	44.00	36.00	36.00	27.00	36.00	19.00
Autumn 91	0-2.5	33.00	35.00	27.00	22.00	32.00	30.00
	2.5-5	31.00	33.00	31.00	25.00	30.00	32.00
	5-7.5	27.00	30.00	35.00	26.00	32.00	32.00
	7.5-10	28.00	29.00	36.00	27.00	29.00	33.00
Winter 92	0-2.5	27.00	37.00	35.00	27.00	34.00	33.00
	2.5-5	29.00	36.00	32.00	25.00	35.00	32.00
	5-7.5	33.00	38.00	36.00	30.00	32.00	31.00
	7.5-10	33.00	29.00	42.00	30.00	33.00	34.00
Spring 92	0-2.5	30.00	31.00	28.00	21.00	29.00	24.00
	2.5-5	30.00	31.00	26.00	16.00	29.00	22.00
	5-7.5	29.00	29.00	22.00	18.00	31.00	25.00
	7.5-10	32.00	30.00	21.00	19.00	26.00	22.00
Summer 92	0-2.5	30.82	37.08	32.26	23.83	31.11	27.10
	2.5-5	31.06	31.26	33.00	26.46	32.20	25.30
	5-7.5	28.97	29.38	28.63	24.89	29.70	23.00
	7.5-10	29.16	29.96	27.30	25.52	29.13	25.16
Autumn 92	0-2.5	25.55	34.27	32.57	22.10	33.07	23.30
	2.5-5	24.33	27.30	37.00	22.47	39.30	24.77
	5-7.5	26.37	27.70	30.50	23.97	39.17	24.77
	7.5-10	26.62	26.70	28.70	25.90	35.60	32.50

Appendix A8

Concentrations of Manganese in the sediment g\kg

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	0.55	0.70	0.73	0.44	0.83	0.57
	2.5-5	0.70	0.23	0.87	0.44	0.88	0.57
	5-7.5	0.80	0.40	1.20	0.55	0.95	0.58
	7.5-10	1.00	0.38	0.90	0.64	1.13	0.56
Autumn 91	0-2.5	0.76	0.73	0.68	0.42	0.85	0.66
	2.5-5	0.57	0.65	0.74	0.49	0.88	0.69
	5-7.5	0.62	0.78	0.57	0.46	0.76	0.75
	7.5-10	0.63	0.79	0.56	0.43	0.79	0.70
Winter 92	0-2.5	0.44	0.76	0.56	0.42	0.75	0.61
	2.5-5	0.68	0.76	0.59	0.51	0.80	0.64
	5-7.5	0.63	0.71	0.68	0.53	0.80	0.57
	7.5-10	0.76	0.67	1.16	0.56	0.85	0.61
Spring 92	0-2.5	0.48	0.34	0.50	0.41	0.54	0.50
	2.5-5	0.48	0.35	0.72	0.36	0.62	0.39
	5-7.5	0.47	0.42	0.46	0.31	0.67	0.54
	7.5-10	0.54	0.48	0.59	0.27	0.57	0.34
Summer 92	0-2.5	0.48	0.76	0.48	0.82	0.78	0.62
	2.5-5	0.82	0.60	0.91	0.72	0.81	0.89
	5-7.5	0.78	0.79	0.78	0.64	0.67	0.71
	7.5-10	0.82	0.78	0.75	0.76	0.77	0.81
Autumn 92	0-2.5	0.36	0.40	0.97	0.31	0.66	0.47
	2.5-5	0.36	0.39	0.93	0.34	0.77	0.47
	5-7.5	0.35	0.43	0.81	0.36	0.75	0.41
	7.5-10	0.39	0.40	0.92	0.36	0.73	0.41

Appendix A9

Concentrations of Lead in the Sediment mg\kg

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	63.00	71.00	57.00	35.00	58.00	41.00
	2.5-5	73.00	71.00	58.00	31.00	61.00	174.00
	5-7.5	70.00	73.00	40.00	43.00	70.00	67.00
	7.5-10	78.00	65.00	35.00	37.00	63.00	66.00
Autumn 91	0-2.5	65.10	70.80	47.20	39.10	74.60	62.10
	2.5-5	63.30	60.60	40.30	23.70	74.80	64.10
	5-7.5	60.30	42.70	39.00	20.30	80.90	82.30
	7.5-10	58.20	16.60	28.30	14.70	76.70	82.20
Winter 92	0-2.5	57.60	71.40	55.40	42.20	52.30	65.70
	2.5-5	57.40	71.00	58.00	40.50	48.20	64.00
	5-7.5	58.10	66.90	65.80	43.40	58.10	56.40
	7.5-10	65.50	17.40	52.70	36.70	64.90	61.70
Spring 92	0-2.5	69.50	82.80	42.00	58.80	71.50	62.60
	2.5-5	73.00	66.80	52.20	48.10	61.80	61.10
	5-7.5	71.70	43.70	39.40	27.00	74.40	88.50
	7.5-10	80.00	18.90	48.80	31.80	50.60	97.90
Summer 92	0-2.5	68.10	54.30	68.00	43.30	64.60	48.00
	2.5-5	66.70	24.40	68.90	53.50	68.50	48.70
	5-7.5	59.10	9.50	60.20	55.10	61.30	38.90
	7.5-10	62.70	8.00	56.50	57.20	64.50	47.20
Autumn 92	0-2.5	53.80	61.50	44.30	59.90	62.40	56.60
	2.5-5	60.20	31.50	42.60	68.90	71.60	49.80
	5-7.5	69.60	29.20	48.60	75.50	71.20	47.60
	7.5-10	75.50	33.00	49.70	78.10	72.50	80.90

Appendix A10

Concentrations of Cadmium in the sediment mg\kg

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	0.31	0.26	0.22	0.21	0.30	0.33
	2.5-5	0.28	0.24	0.35	0.19	0.30	0.26
	5-7.5	0.29	0.20	0.18	0.29	0.37	0.28
	7.5-10	0.32	0.18	0.10	0.22	0.29	0.30
Autumn 91	0-2.5	0.41	0.36	0.22	0.16	0.27	0.16
	2.5-5	0.31	0.38	0.21	0.32	0.25	0.17
	5-7.5	0.38	0.28	0.20	0.12	0.36	0.38
	7.5-10	0.37	0.14	0.13	0.10	0.23	0.20
Winter 92	0-2.5	0.57	0.33	0.08	0.17	0.13	0.10
	2.5-5	0.45	0.29	0.08	0.14	0.14	0.11
	5-7.5	0.39	0.28	0.18	0.18	0.13	0.08
	7.5-10	0.58	0.22	0.13	0.10	0.16	0.12
Spring 92	0-2.5	0.33	0.29	0.09	0.15	0.12	0.16
	2.5-5	0.42	0.25	0.13	0.13	0.12	0.11
	5-7.5	0.31	0.17	0.10	0.08	0.13	0.15
	7.5-10	0.34	0.14	0.10	0.07	0.09	0.13
Summer 92	0-2.5	0.34	0.18	0.16	0.31	0.22	0.16
	2.5-5	0.30	0.14	0.15	0.31	0.29	0.14
	5-7.5	0.33	0.08	0.64	0.31	0.23	0.14
	7.5-10	0.29	0.07	0.14	0.30	0.23	0.14
Autumn 92	0-2.5	0.29	0.24	0.15	0.15	0.18	0.12
	2.5-5	0.25	0.14	0.10	0.17	0.20	0.08
	5-7.5	0.29	0.09	0.11	0.20	0.19	0.10
	7.5-10	0.31	0.13	0.13	0.17	0.17	0.13

Appendix A11

Concentrations of Copper in the sediment mg\kg

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	52.10	65.20	44.70	16.20	47.00	17.30
	2.5-5	67.00	63.50	46.50	14.80	48.20	267.0
	5-7.5	68.60	64.20	24.70	28.30	60.80	26.10
	7.5-10	72.80	51.40	22.60	22.20	51.20	27.00
Autumn 91	0-2.5	47.00	52.80	41.10	21.70	67.00	36.50
	2.5-5	48.40	49.50	37.50	12.80	60.80	40.00
	5-7.5	39.80	33.30	26.70	9.70	63.40	42.30
	7.5-10	38.80	8.70	16.90	6.60	58.60	33.70
Winter 92	0-2.5	42.30	55.80	38.00	34.00	39.00	36.40
	2.5-5	41.80	59.10	38.90	29.00	33.40	35.70
	5-7.5	45.70	57.30	43.80	34.70	44.50	29.60
	7.5-10	46.90	15.70	34.50	22.90	50.30	36.80
Spring 92	0-2.5	48.20	56.60	18.30	26.90	33.40	25.50
	2.5-5	48.80	30.90	21.60	21.30	34.60	39.90
	5-7.5	47.30	13.00	22.10	11.20	42.20	49.70
	7.5-10	46.00	9.20	16.33	11.10	30.90	119.00
Summer 92	0-2.5	51.60	52.40	43.50	32.60	52.40	32.20
	2.5-5	49.00	26.10	42.80	38.70	57.00	31.60
	5-7.5	42.00	11.50	34.80	41.50	52.80	20.90
	7.5-10	45.20	11.60	33.20	43.00	56.30	36.90
Autumn 92	0-2.5	50.00	43.00	16.00	27.70	47.30	28.50
	2.5-5	44.50	14.00	16.50	27.30	54.00	21.50
	5-7.5	48.00	13.00	13.00	31.00	53.00	25.30
	7.5-10	40.30	11.50	3.30	22.00	44.30	33.30

Appendix A12

Concentrations of Nickel in the sediment mg\kg

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	37.70	41.40	29.00	19.60	30.70	16.70
	2.5-5	43.90	43.60	29.00	24.80	34.70	16.90
	5-7.5	44.70	43.00	35.10	27.50	40.70	16.20
	7.5-10	46.70	39.00	38.60	26.20	41.40	15.50
Autumn 91	0-2.5	38.10	42.70	28.50	21.70	36.30	34.20
	2.5-5	35.80	40.10	31.40	23.10	35.40	36.90
	5-7.5	31.00	36.70	38.60	22.80	38.10	37.30
	7.5-10	30.60	29.90	37.50	21.90	36.30	38.60
Winter 92	0-2.5	29.40	40.10	29.40	27.90	32.80	35.60
	2.5-5	33.20	39.20	41.30	26.20	28.10	34.10
	5-7.5	32.00	38.60	42.50	29.20	31.10	30.90
	7.5-10	34.50	24.40	42.60	32.60	33.90	34.90
Spring 92	0-2.5	37.10	43.90	22.90	23.60	31.90	24.70
	2.5-5	37.60	41.30	23.40	21.20	28.90	23.60
	5-7.5	37.50	35.80	21.80	19.30	29.60	31.30
	7.5-10	37.30	32.80	17.40	19.30	23.70	24.10
Summer 92	0-2.5	45.70	40.10	38.40	26.30	33.10	36.30
	2.5-5	46.80	30.90	40.90	20.70	36.70	36.10
	5-7.5	46.00	37.90	39.50	18.30	34.30	34.40
	7.5-10	51.20	38.20	33.00	25.50	33.20	33.50
Autumn 92	0-2.5	33.70	38.30	30.30	45.70	39.30	27.70
	2.5-5	33.30	32.00	30.70	48.70	42.30	33.30
	5-7.5	33.70	32.20	33.70	52.30	42.70	36.00
	7.5-10	36.70	35.00	35.00	52.30	43.30	40.30

Appendix A13

Concentrations of Mercury in the sediment mg\kg

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	2.70	2.90	4.10	0.70	2.20	0.50
	2.5-5	3.20	2.70	3.70	0.80	2.80	1.20
	5-7.5	3.20	3.10	1.30	1.30	3.00	1.70
	7.5-10	3.20	2.80	0.50	1.10	2.60	2.00
Autumn 91	0-2.5	1.80	2.40	2.90	2.10	4.30	2.60
	2.5-5	2.20	3.20	1.40	1.00	4.30	2.80
	5-7.5	2.10	2.00	1.70	0.50	4.20	4.00
	7.5-10	1.20	0.20	1.70	0.50	4.20	2.90
Winter 92	0-2.5	1.70	3.10	2.00	2.10	1.80	2.90
	2.5-5	2.40	3.00	2.10	2.10	2.10	2.10
	5-7.5	1.80	3.20	3.10	1.90	2.70	1.70
	7.5-10	2.70	0.30	1.50	1.30	4.30	1.80
Spring 92	0-2.5	2.20	2.60	0.89	1.40	1.20	2.30
	2.5-5	2.30	1.20	1.20	1.50	1.60	1.20
	5-7.5	2.10	0.31	1.40	0.63	1.50	2.40
	7.5-10	2.20	0.28	4.90	0.67	1.30	1.50
Summer 92	0-2.5	2.06	2.22	1.68	1.09	2.09	1.09
	2.5-5	2.07	0.87	1.37	1.59	2.10	1.08
	5-7.5	1.63	0.41	1.23	1.65	2.15	0.87
	7.5-10	2.09	0.25	1.11	1.66	2.55	1.34
Autumn 92	0-2.5	1.70	1.89	0.67	1.16	2.13	0.57
	2.5-5	1.22	0.58	0.58	1.44	2.35	0.63
	5-7.5	1.32	0.29	0.64	1.49	2.34	1.23
	7.5-10	1.33	0.23	0.47	1.64	2.19	1.83

Appendix A14

Values of Hydrogen Ion concentration in the Porewater

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	7.40	6.90	7.60	7.70	7.50	7.70
	2.5-5	7.50	7.40	7.90	7.50	7.70	7.80
	5-7.5	7.50	7.70	8.00	7.80	7.80	8.00
	7.5-10	7.70	7.70	7.80	7.80	7.90	8.00
Autumn 91	0-2.5	7.50	6.90	8.10	7.60	8.20	7.60
	2.5-5	7.70	7.10	8.10	7.80	8.30	7.60
	5-7.5	7.90	8.00	8.30	8.00	8.20	7.60
	7.5-10	8.30	8.10	8.30	8.10	8.10	7.70
Winter 92	0-2.5	7.20	6.70	6.90	7.00	7.80	7.60
	2.5-5	7.30	6.80	7.60	7.20	7.50	7.60
	5-7.5	7.40	7.50	8.00	7.50	7.70	7.90
	7.5-10	7.80	8.00	7.90	8.00	8.00	7.90
Spring 92	0-2.5	7.50	7.30	7.70	7.80	7.80	7.30
	2.5-5	7.90	7.60	7.80	8.00	7.60	7.50
	5-7.5	8.10	7.80	8.00	8.10	8.00	8.00
	7.5-10	7.80	8.00	8.20	8.10	8.00	7.90
Summer 92	0-2.5	7.70	7.70	7.87	7.38	7.70	7.36
	2.5-5	7.90	7.73	7.96	7.86	7.97	7.70
	5-7.5	8.30	7.91	8.05	7.84	7.86	7.84
	7.5-10	8.20	8.02	8.07	7.79	7.94	7.91
Autumn 92	0-2.5	7.78	7.59	8.18	7.56	7.78	7.93
	2.5-5	7.95	8.00	8.18	7.95	7.87	7.98
	5-7.5	7.92	7.84	8.20	7.82	7.95	8.06
	7.5-10	7.78	7.96	8.20	7.88	8.00	8.06

Appendix A15

Values of Total Alkalinity in the Porewater meq\l

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	4.00	5.00	3.00	2.00	7.00	2.00
	2.5-5	9.00	6.00	4.00	3.00	12.00	3.00
	5-7.5	12.00	7.00	5.00	3.00	16.00	3.00
	7.5-10	15.00	8.00	7.00	3.00	18.00	3.00
Autumn 91	0-2.5	4.00	4.00	5.00	3.00	6.00	5.00
	2.5-5	4.00	5.00	10.00	4.00	8.00	7.00
	5-7.5	5.00	6.00	10.00	6.00	11.00	8.00
	7.5-10	7.00	6.00	10.00	5.00	14.00	9.00
Winter 92	0-2.5	4.00	3.00	3.00	5.00	4.00	5.00
	2.5-5	5.00	4.00	5.00	5.00	5.00	5.00
	5-7.5	6.00	5.00	7.00	7.00	7.00	6.00
	7.5-10	6.00	5.00	10.00	8.00	10.00	7.00
Spring 92	0-2.5	3.00	2.00	4.00	2.00	4.00	4.00
	2.5-5	6.00	3.00	4.00	3.00	7.00	5.00
	5-7.5	8.00	3.00	5.00	3.00	8.00	7.00
	7.5-10	7.00	3.00	6.00	4.00	9.00	5.00
Summer 92	0-2.5	3.00	4.00	11.00	4.00	6.00	5.00
	2.5-5	5.00	5.00	12.00	6.00	9.00	7.00
	5-7.5	7.00	6.00	13.00	7.00	10.00	8.00
	7.5-10	6.00	7.00	14.00	8.00	11.00	9.00
Autumn 92	0-2.5	2.00	2.00	3.00	3.00	6.00	3.00
	2.5-5	3.00	3.00	4.00	5.00	8.00	3.00
	5-7.5	5.00	4.00	5.00	7.00	9.00	3.00
	7.5-10	7.00	4.00	3.00	8.00	11.00	4.00

Appendix A16

Concentrations of Chloride in the Porewater meq\l

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	519.0	800.0	817.0	768.0	825.0	844.0
	2.5-5	465.0	783.0	754.0	756.0	848.0	811.0
	5-7.5	414.0	775.0	727.0	769.0	820.0	781.0
	7.5-10	369.0	757.0	723.0	752.0	765.0	791.0
Autumn 91	0-2.5	342.0	699.0	956.0	971.0	983.0	1017.0
	2.5-5	283.0	876.0	936.0	939.0	989.0	1204.0
	5-7.5	146.0	857.0	900.0	952.0	990.0	1221.0
	7.5-10	118.0	843.0	914.0	957.0	993.0	1246.0
Winter 92	0-2.5	124.0	429.0	750.0	743.0	769.0	935.0
	2.5-5	124.0	451.0	727.0	747.0	880.0	903.0
	5-7.5	123.0	460.0	722.0	750.0	886.0	792.0
	7.5-10	59.0	447.0	720.0	777.0	844.0	783.0
Spring 92	0-2.5	131.0	503.0	598.0	606.0	705.0	756.0
	2.5-5	110.0	465.0	592.0	549.0	698.0	779.0
	5-7.5	104.0	448.0	564.0	504.0	770.0	758.0
	7.5-10	70.0	475.0	578.0	518.0	737.0	770.0
Summer 92	0-2.5	111.0	468.0	516.0	705.0	554.0	599.0
	2.5-5	108.0	436.0	586.0	597.0	529.0	648.0
	5-7.5	113.0	479.0	569.0	587.0	520.0	652.0
	7.5-10	113.0	481.0	607.0	434.0	565.0	724.0
Autumn 92	0-2.5	57.0	478.0	390.0	529.0	542.0	517.0
	2.5-5	75.0	423.0	485.0	532.0	550.0	523.0
	5-7.5	83.0	442.0	470.0	529.0	523.0	466.0
	7.5-10	86.0	434.0	474.0	523.0	529.0	477.0

Appendix A17

Values of conductivity in the pore water mS/cm

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	28.00	58.00	62.00	56.00	61.00	64.00
	2.5-5	24.00	49.00	54.00	57.00	62.00	58.00
	5-7.5	18.00	48.00	50.00	59.00	55.00	52.00
	7.5-10	17.00	49.00	48.00	56.00	55.00	55.00
Autumn 91	0-2.5	13.00	39.00	44.00	45.00	49.00	51.00
	2.5-5	12.00	42.00	43.00	46.00	47.00	54.00
	5-7.5	7.00	38.00	40.00	43.00	51.00	51.00
	7.5-10	6.00	35.00	38.00	48.00	50.00	52.00
Winter 92	0-2.5	8.40	34.00	50.00	52.00	52.00	56.00
	2.5-5	8.60	37.00	47.00	49.00	51.00	54.00
	5-7.5	8.90	38.00	48.00	46.00	52.00	53.00
	7.5-10	4.60	34.00	46.00	49.00	51.00	53.00
Spring 92	0-2.5	14.00	34.00	41.00	40.00	43.00	46.00
	2.5-5	10.00	31.00	40.00	38.00	44.00	46.00
	5-7.5	9.10	31.00	37.00	38.00	43.00	44.00
	7.5-10	7.30	31.00	38.00	38.00	41.00	42.00
Summer 92	0-2.5	8.70	33.80	37.70	45.80	46.30	49.70
	2.5-5	9.10	39.00	41.00	44.80	47.90	48.30
	5-7.5	10.30	37.00	40.00	43.80	48.20	49.40
	7.5-10	11.80	36.00	39.00	47.20	45.80	50.40
Autumn 92	0-2.5	5.50	28.70	40.20	42.30	42.10	41.30
	2.5-5	5.80	29.30	37.10	40.90	43.50	42.60
	5-7.5	6.40	29.60	33.90	41.00	41.10	41.80
	7.5-10	7.20	29.40	35.30	40.00	41.90	43.00

Appendix A18

Concentrations of Sulphate in the Porewater meq\l

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	23.00	44.00	51.00	48.00	42.00	58.00
	2.5-5	15.00	35.00	39.00	47.00	27.00	52.00
	5-7.5	7.00	29.00	32.00	47.00	17.00	46.00
	7.5-10	2.00	28.00	26.00	45.00	10.00	47.00
Autumn 91	0-2.5	11.00	27.00	34.00	41.00	39.00	45.00
	2.5-5	9.00	25.00	23.00	40.00	31.00	44.00
	5-7.5	3.00	27.00	18.00	41.00	27.00	39.00
	7.5-10	0.30	25.00	14.00	42.00	22.00	37.00
Winter 92	0-2.5	2.40	27.00	38.00	38.00	47.00	65.00
	2.5-5	2.10	27.00	34.00	37.00	53.00	59.00
	5-7.5	0.40	28.00	27.00	29.00	47.00	45.00
	7.5-10	0.10	24.00	20.00	30.00	35.00	41.00
Spring 92	0-2.5	8.10	29.00	34.00	45.00	42.20	43.70
	2.5-5	1.30	25.00	27.00	19.00	37.10	35.70
	5-7.5	0.10	25.00	24.00	31.50	34.50	23.20
	7.5-10	0.00	25.00	25.00	32.50	26.70	20.00
Summer 92	0-2.5	9.00	35.60	27.10	28.40	29.90	40.40
	2.5-5	6.90	35.60	27.40	27.30	25.00	40.80
	5-7.5	5.70	32.00	24.90	26.50	22.30	37.50
	7.5-10	5.10	29.00	26.80	17.80	22.30	34.70
Autumn 92	0-2.5	3.50	32.70	31.60	40.00	37.60	44.00
	2.5-5	1.90	30.00	37.80	33.40	33.20	38.80
	5-7.5	0.90	29.70	34.80	29.20	24.90	37.70
	7.5-10	0.22	23.00	35.00	25.60	21.00	37.90

Appendix A19

Concentrations of nitrate in the pore water umol / l

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	8.10	1.60	13.00	1.60	29.00	4.80
	2.5-5	3.20	1.60	21.00	23.00	45.00	21.00
	5-7.5	1.60	1.60	18.00	13.00	4.80	4.80
	7.5-10	4.80	1.60	6.50	71.00	1.60	8.10
Autumn 91	0-2.5	4.80	4.80	21.00	1.60	1.60	6.50
	2.5-5	1.60	1.60	6.50	1.60	1.60	1.60
	5-7.5	35.00	4.80	1.60	1.60	1.60	1.60
	7.5-10	4.80	29.00	1.60	1.60	1.60	1.60
Winter 92	0-2.5	68.00	29.00	15.00	71.00	8.10	35.00
	2.5-5	39.00	35.00	35.00	19.00	26.00	11.00
	5-7.5	58.00	26.00	15.00	39.00	18.00	4.80
	7.5-10	24.00	53.00	26.00	26.00	11.00	42.00
Spring 92	0-2.5	20.00	31.00	156.00	113.00	100.00	15.00
	2.5-5	160.00	11.00	298.00	1000.00	269.00	35.00
	5-7.5	32.00	4.80	198.00	526.00	77.00	35.00
	7.5-10	48.00	19.00	497.00	994.00	198.00	8.40
Summer 92	0-2.5	23.00	37.00	52.00	1065.00	710.00	305.00
	2.5-5	23.00	29.00	127.00	219.00	56.00	85.00
	5-7.5	15.00	213.00	48.00	171.00	376.00	45.00
	7.5-10	135.00	71.00	26.00	426.00	269.00	31.00
Autumn 92	0-2.5	34.00	1.40	9.00	17.00	17.00	4.00
	2.5-5	9.00	1.40	3.00	34.00	4.00	4.00
	5-7.5	4.00	9.00	4.00	4.00	3.00	3.00
	7.5-10	9.00	4.00	9.00	34.00	4.00	1.00

Appendix A20

Concentrations of phosphate in the pore water umol / l

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	8.40	25.00	8.40	1.10	68.00	40.00
	2.5-5	4.20	53.00	27.00	1.10	88.00	16.00
	5-7.5	6.30	49.00	8.40	1.10	60.00	8.40
	7.5-10	5.30	45.00	24.00	1.10	73.00	4.20
Autumn 91	0-2.5	4.20	3.20	13.00	6.30	38.00	12.00
	2.5-5	3.20	8.40	32.00	6.30	71.00	34.00
	5-7.5	3.20	8.40	21.00	27.00	92.00	61.00
	7.5-10	4.20	3.20	32.00	5.30	102.00	49.00
Winter 92	0-2.5	5.30	1.10	0.00	4.20	0.20	6.30
	2.5-5	2.10	6.30	4.20	3.20	3.20	8.40
	5-7.5	6.30	9.50	43.00	1.10	16.00	15.00
	7.5-10	20.00	0.00	78.00	1.10	66.00	0.00
Spring 92	0-2.5	8.40	24.00	4.20	8.40	6.30	25.00
	2.5-5	4.20	19.00	9.50	7.40	9.50	71.00
	5-7.5	3.20	6.30	5.30	8.40	6.30	100.00
	7.5-10	2.10	8.40	4.20	9.50	2.10	20.00
Summer 92	0-2.5	6.00	6.00	3.50	6.00	0.40	10.00
	2.5-5	16.00	21.00	0.00	3.00	4.00	15.00
	5-7.5	9.00	13.00	0.00	13.00	28.00	23.00
	7.5-10	6.00	8.00	0.00	8.00	27.00	12.00
Autumn 92	0-2.5	1.20	0.50	1.20	3.00	1.10	1.20
	2.5-5	5.50	0.50	1.40	3.60	1.10	1.20
	5-7.5	0.40	0.60	0.10	2.40	6.70	1.40
	7.5-10	1.70	0.60	1.20	4.20	6.10	1.20

Appendix A21

Concentrations of Dissolved Organic Carbon in the Porewater mg\l

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	21.00	80.00	19.00	19.00	19.00	19.00
	2.5-5	32.00	66.00	18.00	27.00	29.00	22.00
	5-7.5	37.00	24.00	20.00	11.00	34.00	10.00
	7.5-10	47.00	23.00	26.00	12.00	37.00	12.00
Autumn 91	0-2.5	12.00	35.00	22.00	27.00	24.00	23.00
	2.5-5	14.00	25.00	30.00	13.00	26.00	23.00
	5-7.5	21.00	14.00	28.00	47.00	31.00	28.00
	7.5-10	23.00	12.00	31.00	26.00	36.00	22.00
Winter 92	0-2.5	23.00	64.00	73.00	53.00	60.00	67.00
	2.5-5	30.00	53.00	51.00	47.00	54.00	45.00
	5-7.5	29.00	55.00	49.00	97.00	45.00	57.00
	7.5-10	28.00	27.00	56.00	48.00	44.00	32.00
Spring 92	0-2.5	33.00	20.00	64.00	77.00	78.00	68.00
	2.5-5	39.00	15.00	31.00	36.00	74.00	54.00
	5-7.5	39.00	11.00	35.00	28.00	74.00	46.00
	7.5-10	34.00	10.00	36.00	18.00	52.00	49.00
Summer 92	0-2.5	40.00	82.00	58.00	37.00	35.00	42.00
	2.5-5	85.00	44.00	59.00	32.00	35.00	26.00
	5-7.5	55.00	19.00	60.00	33.00	32.00	26.00
	7.5-10	37.00	15.00	62.00	30.00	32.00	23.00
Autumn 92	0-2.5	35.00	27.00	53.00	56.00	61.00	94.00
	2.5-5	47.00	31.00	53.00	50.00	63.00	60.00
	5-7.5	44.00	31.00	54.00	52.00	68.00	63.00
	7.5-10	46.00	35.00	52.00	57.00	69.00	71.00

Appendix A22

Concentrations of Iron in the Porewater mg\l

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	17.00	24.00	6.00	1.30	14.00	0.10
	2.5-5	20.00	36.00	7.00	7.00	2.00	0.10
	5-7.5	18.00	11.00	0.60	0.40	0.30	0.50
	7.5-10	32.00	5.00	0.80	0.30	0.40	0.30
Autumn 91	0-2.5	0.80	28.00	16.00	5.10	0.70	8.10
	2.5-5	3.50	31.00	9.00	4.20	0.60	10.00
	5-7.5	17.00	5.00	7.80	6.70	0.30	12.00
	7.5-10	16.00	1.30	5.40	0.90	0.50	5.30
Winter 92	0-2.5	4.20	29.00	11.00	12.00	1.60	4.80
	2.5-5	14.00	33.00	3.40	15.00	5.30	4.40
	5-7.5	16.00	19.00	0.90	9.00	4.00	3.30
	7.5-10	15.00	2.60	0.80	3.00	1.50	3.30
Spring 92	0-2.5	13.00	12.00	3.20	2.90	9.10	6.20
	2.5-5	15.00	8.20	5.80	1.70	16.00	3.70
	5-7.5	20.00	3.70	5.10	1.50	11.00	1.00
	7.5-10	22.00	2.60	1.10	0.90	0.80	2.30
Summer 92	0-2.5	0.30	3.30	5.10	5.40	0.70	6.70
	2.5-5	3.10	5.50	3.20	3.70	0.40	5.40
	5-7.5	3.80	4.70	3.20	3.30	1.00	3.20
	7.5-10	4.00	2.70	3.20	2.50	0.50	1.30
Autumn 92	0-2.5	2.10	5.80	1.00	3.60	4.00	1.80
	2.5-5	16.70	4.80	0.70	7.70	3.20	1.50
	5-7.5	18.70	4.20	4.20	5.20	2.00	1.10
	7.5-10	27.80	1.50	2.50	3.30	1.30	1.70

Appendix A23

Concentrations of Manganese in the Porewater mg\l

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	11.00	20.00	2.60	5.00	8.30	3.20
	2.5-5	12.00	8.30	3.60	4.20	11.00	2.00
	5-7.5	8.00	5.40	3.10	3.40	10.00	1.50
	7.5-10	8.00	4.50	1.80	2.60	9.40	1.30
Autumn 91	0-2.5	2.70	18.00	10.00	2.50	6.10	14.00
	2.5-5	4.20	6.80	8.60	2.60	8.60	10.00
	5-7.5	5.20	3.10	3.00	2.40	8.10	12.00
	7.5-10	4.20	2.00	4.00	1.40	8.40	7.60
Winter 91	0-2.5	2.20	11.00	7.00	5.00	13.00	8.60
	2.5-5	5.10	8.70	7.70	5.30	11.00	7.60
	5-7.5	4.80	7.60	8.50	4.70	8.00	5.30
	7.5-10	4.40	3.20	6.10	4.10	8.20	5.00
Spring 92	0-2.5	6.30	3.20	5.50	3.70	10.00	9.40
	2.5-5	6.00	3.10	4.70	1.40	14.00	7.00
	5-7.5	6.50	2.00	3.60	1.30	11.00	3.70
	7.5-10	6.60	1.80	2.30	1.30	7.00	3.20
Summer 92	0-2.5	2.51	2.60	14.78	3.27	6.16	5.88
	2.5-5	2.92	3.21	11.18	3.41	6.32	3.99
	5-7.5	3.44	3.43	9.74	3.41	5.54	2.91
	7.5-10	3.27	2.24	11.38	3.15	5.20	2.77
Autumn 92	0-2.5	1.10	1.93	0.82	2.14	8.92	2.11
	2.5-5	3.53	2.31	0.48	3.02	8.98	0.91
	5-7.5	4.15	2.67	0.98	3.13	9.23	1.20
	7.5-10	4.57	2.39	0.69	3.18	8.01	1.19

Appendix A24

Concentrations of Lead in the Porewater ug\l

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	6.29	1.22	2.58	2.17	9.09	2.99
	2.5-5	2.38	5.56	2.58	3.26	2.72	2.45
	5-7.5	6.60	4.89	4.48	3.80	2.31	3.39
	7.5-10	3.94	3.26	4.07	2.45	1.90	2.58
Autumn 91	0-2.5	4.23	1.52	3.67	3.23	1.21	1.21
	2.5-5	3.37	2.36	1.85	5.00	1.04	4.42
	5-7.5	3.86	0.89	2.12	7.90	2.00	2.57
	7.5-10	2.26	4.52	2.97	1.94	1.40	1.44
Winter 92	0-2.5	3.96	1.65	2.75	2.83	5.10	1.91
	2.5-5	2.08	0.84	2.78	2.39	2.19	1.27
	5-7.5	1.76	2.51	2.08	2.19	3.51	1.49
	7.5-10	2.13	4.53	1.06	2.19	1.60	1.76
Spring 92	0-2.5	2.80	2.80	4.30	5.35	3.30	3.10
	2.5-5	2.50	5.40	4.25	8.00	2.60	2.10
	5-7.5	1.50	6.30	6.15	4.80	3.50	3.15
	7.5-10	5.20	7.50	2.65	3.20	3.90	3.20
Summer 92	0-2.5	5.50	5.10	4.66	2.44	3.60	3.30
	2.5-5	4.03	3.51	4.55	2.53	3.36	3.95
	5-7.5	2.55	4.66	3.66	2.90	5.95	4.02
	7.5-10	2.73	1.31	1.31	1.32	6.80	6.08
Autumn 92	0-2.5	3.54	3.08	1.97	2.11	2.66	1.97
	2.5-5	1.90	1.97	1.96	1.44	3.02	3.03
	5-7.5	3.47	1.85	0.80	2.32	3.20	2.96
	7.5-10	2.67	1.26	0.10	2.84	1.96	2.32

Appendix A25

Concentrations of Cadmium in the Porewater ug\l

Seasons\	Stations	S.Alloa A	Kennet B	G'mouth C	Culross D	Bo'ness E	P.Edgar F
	Depth (cm)						
Summer 91	0-2.5	3.58	0.73	0.77	2.26	1.39	0.65
	2.5-5	2.65	3.04	3.60	0.34	1.57	0.96
	5-7.5	2.65	3.56	2.00	1.86	2.29	0.27
	7.5-10	0.83	1.65	1.56	1.68	2.14	0.20
Autumn 91	0-2.5	2.12	1.60	1.22	2.64	1.72	1.17
	2.5-5	1.70	1.78	1.61	1.68	1.63	1.46
	5-7.5	1.97	2.79	1.74	4.49	1.29	0.76
	7.5-10	1.30	3.40	2.45	4.13	1.55	1.11
Winter 91	0-2.5	2.04	0.00	0.86	0.63	3.20	4.70
	2.5-5	0.64	0.42	1.03	0.00	1.25	4.41
	5-7.5	1.34	0.91	0.76	0.01	2.11	4.70
	7.5-10	1.18	2.39	1.99	0.84	2.56	4.99
Spring 92	0-2.5	3.45	3.89	1.12	2.82	1.62	0.43
	2.5-5	2.14	3.32	2.52	5.91	1.48	4.15
	5-7.5	2.95	5.40	1.72	2.72	0.74	1.50
	7.5-10	1.85	1.60	1.30	0.90	1.89	3.30
Summer 92	0-2.5	2.58	1.79	3.28	2.98	1.31	1.61
	2.5-5	2.50	1.61	2.81	2.90	1.61	2.32
	5-7.5	1.73	2.29	1.34	3.69	1.05	1.34
	7.5-10	2.42	2.88	1.61	3.72	2.73	1.14
Autumn 92	0-2.5	1.00	1.00	0.49	1.25	0.70	0.40
	2.5-5	0.45	1.58	1.32	1.28	0.50	0.77
	5-7.5	1.97	1.29	1.73	1.56	0.67	0.72
	7.5-10	2.73	0.60	0.20	0.50	0.60	0.37

Concentrations of copper in the pore water ug\l

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	32.00	16.00	98.00	70.00	88.00	38.00
	2.5-5	16.00	54.00	52.00	52.00	36.00	22.00
	5-7.5	34.00	68.00	56.00	96.00	52.00	49.00
	7.5-10	50.00	76.00	62.00	66.00	79.00	44.00
Autumn 91	0-2.5	25.00	50.00	32.00	58.00	28.00	18.00
	2.5-5	60.00	28.00	22.00	42.00	56.00	24.00
	5-7.5	24.00	18.00	18.00	50.00	22.00	22.00
	7.5-10	49.00	36.00	34.00	32.00	26.00	17.00
Winter 92	0-2.5	22.40	15.00	16.00	19.00	84.00	25.10
	2.5-5	37.00	13.00	19.00	12.00	75.00	16.90
	5-7.5	34.00	26.00	24.00	14.20	33.00	13.50
	7.5-10	16.30	19.10	20.00	19.00	58.00	16.90
Spring 92	0-2.5	28.50	29.00	20.00	23.00	12.00	21.80
	2.5-5	22.00	32.00	22.00	32.00	18.00	21.30
	5-7.5	32.00	37.00	30.00	26.00	23.00	16.90
	7.5-10	35.00	46.00	15.00	18.00	39.00	33.40
Summer 92	0-2.5	24.25	25.80	25.10	22.20	31.40	9.93
	2.5-5	24.20	31.70	25.00	24.20	16.60	29.60
	5-7.5	24.20	28.90	31.50	27.60	24.40	22.50
	7.5-10	36.10	31.20	29.50	31.20	7.70	24.40
Autumn 92	0-2.5	20.80	24.60	28.80	30.20	25.10	20.40
	2.5-5	22.90	25.10	36.90	22.10	16.70	28.70
	5-7.5	23.90	26.70	33.80	25.70	25.30	24.40
	7.5-10	27.30	28.50	11.40	29.10	18.90	26.00

Appendix A27

Concentrations of Nickel in the Porewater ug\l

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	20.00	65.00	62.00	22.00	18.00	25.00
	2.5-5	16.00	59.00	70.00	12.00	25.00	19.00
	5-7.5	43.00	52.00	41.00	52.00	14.00	31.00
	7.5-10	10.00	72.00	30.00	25.00	10.00	16.00
Autumn 91	0-2.5	13.00	22.00	18.00	47.00	9.00	36.00
	2.5-5	22.00	25.00	16.00	32.00	16.00	55.00
	5-7.5	48.00	56.00	20.00	39.00	22.00	22.00
	7.5-10	41.00	67.00	17.00	34.00	40.00	29.00
Winter 92	0-2.5	16.80	22.00	14.90	19.60	40.00	23.00
	2.5-5	12.30	13.60	41.50	15.00	67.00	29.00
	5-7.5	24.00	22.20	47.00	21.20	44.00	38.00
	7.5-10	31.00	28.00	59.80	31.50	55.00	48.00
Spring 92	0-2.5	16.00	13.40	19.40	15.30	13.60	8.00
	2.5-5	18.80	51.10	35.80	33.20	10.60	13.70
	5-7.5	45.80	44.00	32.80	25.80	10.70	13.40
	7.5-10	14.50	28.20	15.90	40.00	2.20	17.50
Summer 92	0-2.5	17.00	7.00	15.90	14.00	11.30	16.20
	2.5-5	17.30	19.00	14.10	16.10	30.70	31.60
	5-7.5	9.70	11.40	14.50	9.30	17.90	27.10
	7.5-10	12.90	9.10	24.20	21.60	11.80	37.90
Autumn 92	0-2.5	13.00	7.10	10.90	10.00	18.80	11.40
	2.5-5	8.40	11.70	16.60	6.50	9.20	11.20
	5-7.5	17.20	10.50	10.60	6.90	10.40	7.60
	7.5-10	7.50	9.70	14.00	8.10	23.40	12.60

Appendix A28

Concentrations of Mercury in the Porewater ng\l

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	181.00	30.00	55.00	53.00	55.00	35.00
	2.5-5	180.00	35.00	54.00	54.00	35.00	37.00
	5-7.5	162.00	81.00	45.00	46.00	108.00	40.00
	7.5-10	106.00	57.00	35.00	34.00	106.00	45.00
Autumn 91	0-2.5	58.00	14.00	150.00	46.00	61.00	460.00
	2.5-5	106.00	74.00	96.00	38.00	60.00	111.00
	5-7.5	312.00	68.00	815.00	74.00	49.00	94.00
	7.5-10	1108.00	40.00	100.00	56.00	78.00	45.00
Winter 92	0-2.5	87.00	30.00	0.00	12.00	35.00	55.00
	2.5-5	14.00	13.00	1.00	18.00	38.00	49.00
	5-7.5	3.00	23.00	7.00	130.00	60.00	56.00
	7.5-10	159.00	9.00	21.00	55.00	0.00	75.00
Spring 92	0-2.5	290.00	3.00	40.00	260.00	119.00	7.00
	2.5-5	210.00	5.00	37.00	83.00	121.00	5.00
	5-7.5	432.00	8.00	63.00	205.00	79.00	4.00
	7.5-10	76.00	8.00	33.00	19.00	182.00	4.00
Summer 92	0-2.5	39.90	2.70	162.30	37.96	n.s	6.63
	2.5-5	1.94	9.06	6.80	80.96	53.96	18.48
	5-7.5	45.20	62.50	26.40	59.60	14.00	21.58
	7.5-10	68.10	26.70	134.70	128.70	18.68	60.46
Autumn 92	0-2.5	60.22	3.44	14.55	11.27	20.82	5.66
	2.5-5	25.26	5.66	32.91	13.13	22.18	16.27
	5-7.5	32.20	16.60	9.45	25.22	31.20	9.11
	7.5-10	95.30	37.84	117.20	21.04	15.99	6.92

Appendix A29

Trace metals concentration in the less than 63 um fraction mg\kg

Elements	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Lead	0-2.5	58.30	66.60	69.10	70.20	80.90	76.40
	2.5-5	62.10	42.10	72.80	73.00	82.00	79.80
	5-7.5	54.90	27.80	71.50	74.50	82.90	70.30
	7.5-10	57.20	28.90	65.40	76.60	82.30	83.60
Cadmium	0-2.5	0.24	0.18	0.21	0.25	0.23	0.19
	2.5-5	0.38	0.05	0.29	0.27	0.22	0.19
	5-7.5	0.24	0.08	0.24	0.25	0.20	0.17
	7.5-10	0.24	0.09	0.23	0.26	0.21	0.14
Copper	0-2.5	44.90	50.70	55.60	37.50	52.70	42.80
	2.5-5	52.60	28.50	55.20	45.10	50.90	46.00
	5-7.5	38.30	17.50	45.70	44.20	47.60	34.10
	7.5-10	48.60	11.90	47.50	44.70	44.50	44.80
Nickel	0-2.5	43.50	44.30	41.20	31.50	34.60	44.50
	2.5-5	40.50	46.30	51.60	38.50	33.70	44.00
	5-7.5	44.50	42.90	52.30	45.70	48.60	42.90
	7.5-10	48.10	41.40	30.60	43.50	32.30	51.90
Mercury	0-2.5	1.73	1.73	1.60	1.75	2.12	1.17
	2.5-5	1.66	0.80	1.59	1.90	2.06	1.42
	5-7.5	1.67	0.31	1.56	2.08	2.13	1.17
	7.5-10	1.95	0.22	1.46	1.76	2.53	1.85

Appendix A 30

Values of Redox Potential in the sediment mV

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	60.0	20.0	90.0	290.0	40.0	20.0
	2.5-5	17.0	10.0	-110.0	45.0	-120.0	-37.0
	5-7.5	-5.0	-25.0	-150.0	-120.0	-115.0	-55.0
	7.5-10	-10.0	-30.0	-160.0	-115.0	-150.0	-75.0
Autumn 91	0-2.5	70.0	91.0	37.0	59.0	25.0	75.0
	2.5-5	57.0	40.0	-9.0	37.0	-115.0	-10.0
	5-7.5	33.0	22.0	-20.0	29.0	-190.0	-35.0
	7.5-10	-3.0	-7.0	-35.0	25.0	-215.0	-73.0
Winter 92	0-2.5	65.0	20.0	235.0	215.0	260.0	120.0
	2.5-5	15.0	10.0	123.0	20.0	230.0	-10.0
	5-7.5	-5.0	-20.0	40.0	-20.0	35.0	-15.0
	7.5-10	-15.0	-30.0	-30.0	-55.0	-33.0	-25.0
Spring 92	0-2.5	-18.0	5.0	360.0	190.0	250.0	325.0
	2.5-5	-50.0	-30.0	12.0	15.0	-5.0	130.0
	5-7.5	-50.0	-50.0	42.0	-10.0	-30.0	10.0
	7.5-10	-65.0	-65.0	-40.0	-15.0	-50.0	-22.0
Summer 92	0-2.5	35.0	50.0	-12.0	20.0	45.0	55.0
	2.5-5	-10.0	-15.0	-42.0	-60.0	-5.0	30.0
	5-7.5	-195.0	-30.0	-50.0	-65.0	-55.0	5.0
	7.5-10	-260.0	-85.0	-15.0	-110.0	-80.0	-15.0
Autumn 92	0-2.5	100.0	10.0	45.0	145.0	-15.0	-150.0
	2.5-5	-10.0	-45.0	-10.0	30.0	-25.0	-180.0
	5-7.5	-45.0	-95.0	-5.0	-30.0	-35.0	-195.0
	7.5-10	-185.0	-135.0	-10.0	-70.0	-125.0	-200.0

Appendix A 31

Summary of the analyses of variance

variables	Stations	Seasons	Depths
pore water variables			
Nitrate	0.00	0.00	0.64
Phosphate	0.00	0.00	0.01
DOC	0.04	0.00	0.00
pH	0.00	0.00	0.00
Alkalinity	0.00	0.00	0.00
Conductivity	0.00	0.00	0.00
Chloride	0.00	0.00	0.25
Sulphate	0.00	0.00	0.00
cadmium	0.09	0.00	0.69
Copper	0.11	0.00	0.44
Nickel	0.01	0.00	0.02
Lead	0.62	0.00	0.34
Mercury	0.02	0.02	0.53
Iron	0.00	0.38	0.00
Manganese	0.00	0.06	0.00
Sediment variables			
Particle size	0.00	0.00	0.87
Organic matter (LOI)	0.00	0.00	0.00
Total organic carbon	0.00	0.00	0.01
Total organic nitrogen	0.00	0.00	0.19
Carbon:Nitrogen	0.01	0.00	0.09
Redox potential	0.12	0.00	0.00
Cadmium	0.00	0.00	0.78
Copper	0.00	0.03	0.23
Nickel	0.00	0.00	0.41
Lead	0.00	0.23	0.17
Mercury	0.00	0.03	0.61
Aluminium	0.00	0.00	0.12
Iron	0.00	0.00	0.26
Manganese	0.00	0.00	0.16

Appendix A32

Values of dilution factors

Seasons	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	1.55	1.03	1.55	2.08	1.32	5.00
	2.5-5	1.12	1.02	1.42	1.83	1.24	3.57
	5-7.5	1.16	1.02	1.24	1.63	1.16	3.45
	7.5-10	1.05	1.05	1.11	1.63	1.29	3.57
Autumn 91	0-2.5	1.20	1.10	1.82	2.53	1.16	1.24
	2.5-5	1.25	1.18	1.37	1.80	1.19	1.14
	5-7.5	1.44	1.10	1.06	1.83	1.17	1.20
	7.5-10	1.57	1.17	1.11	1.79	1.14	1.20
Winter 92	0-2.5	1.34	1.05	1.14	1.42	1.35	1.17
	2.5-5	1.26	1.03	1.09	1.82	1.49	1.26
	5-7.5	1.34	1.06	1.07	1.37	1.48	1.46
	7.5-10	1.31	1.18	1.05	1.29	1.31	1.31
Spring 92	0-2.5	1.28	1.04	4.17	2.20	1.43	1.75
	2.5-5	1.42	1.09	2.90	3.70	1.65	2.04
	5-7.5	1.52	1.12	4.20	2.10	1.80	1.90
	7.5-10	1.31	1.10	3.85	2.10	2.86	3.28
Summer 92	0-2.5	1.18	1.06	1.31	1.57	1.20	1.45
	2.5-5	1.26	1.14	1.56	1.49	1.24	1.55
	5-7.5	1.40	1.14	1.85	1.59	1.27	2.02
	7.5-10	1.47	1.10	2.00	1.42	1.25	1.60
Autumn 92	0-2.5	1.56	1.10	4.08	1.63	1.17	3.03
	2.5-5	1.36	1.15	5.26	1.55	1.12	1.67
	5-7.5	1.34	1.09	4.55	1.56	1.10	1.98
	7.5-10	1.28	1.12	6.45	1.43	1.08	1.60

Mean values of dilution factors

Season\St.	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
Summer 91	1.22	1.03	1.33	1.79	1.25	3.90
Autumn 91	1.37	1.14	1.34	1.99	1.17	1.20
Winter 92	1.31	1.08	1.09	1.48	1.41	1.30
Spring 92	1.38	1.09	3.78	2.53	1.94	2.24
Summer 92	1.33	1.11	1.68	1.52	1.24	1.66
Autumn 92	1.39	1.12	5.09	1.54	1.12	2.07
Overall mean	1.33	1.09	2.38	1.81	1.35	2.06

Appendix A 33

Ratio of Iron : Aluminium in the sediments

Seasons\	Stations	S.Alloa	Kennet	G'mouth	Culross	Bo'ness	P.Edgar
		A	B	C	D	E	F
	Depth (cm)						
Summer 91	0-2.5	0.52	0.43	0.47	0.45	0.39	0.37
	2.5-5	0.46	0.42	0.44	0.42	0.38	0.41
	5-7.5	0.49	0.45	0.42	0.42	0.41	0.40
	7.5-10	0.52	0.44	0.43	0.41	0.47	0.37
Autumn 91	0-2.5	0.43	0.42	0.42	0.42	0.48	0.39
	2.5-5	0.40	0.39	0.43	0.43	0.38	0.41
	5-7.5	0.34	0.39	0.46	0.43	0.40	0.41
	7.5-10	0.41	0.41	0.44	0.42	0.37	0.43
Winter 92	0-2.5	0.38	0.43	0.43	0.42	0.52	0.47
	2.5-5	0.37	0.40	0.41	0.34	0.47	0.52
	5-7.5	0.47	0.46	0.40	0.45	0.38	0.56
	7.5-10	0.49	0.40	0.51	0.42	0.47	0.45
Spring 92	0-2.5	0.44	0.40	0.61	0.34	0.45	0.33
	2.5-5	0.43	0.36	0.39	0.32	0.43	0.38
	5-7.5	0.43	0.45	0.41	0.30	0.42	0.34
	7.5-10	0.46	0.47	0.37	0.31	0.32	0.37