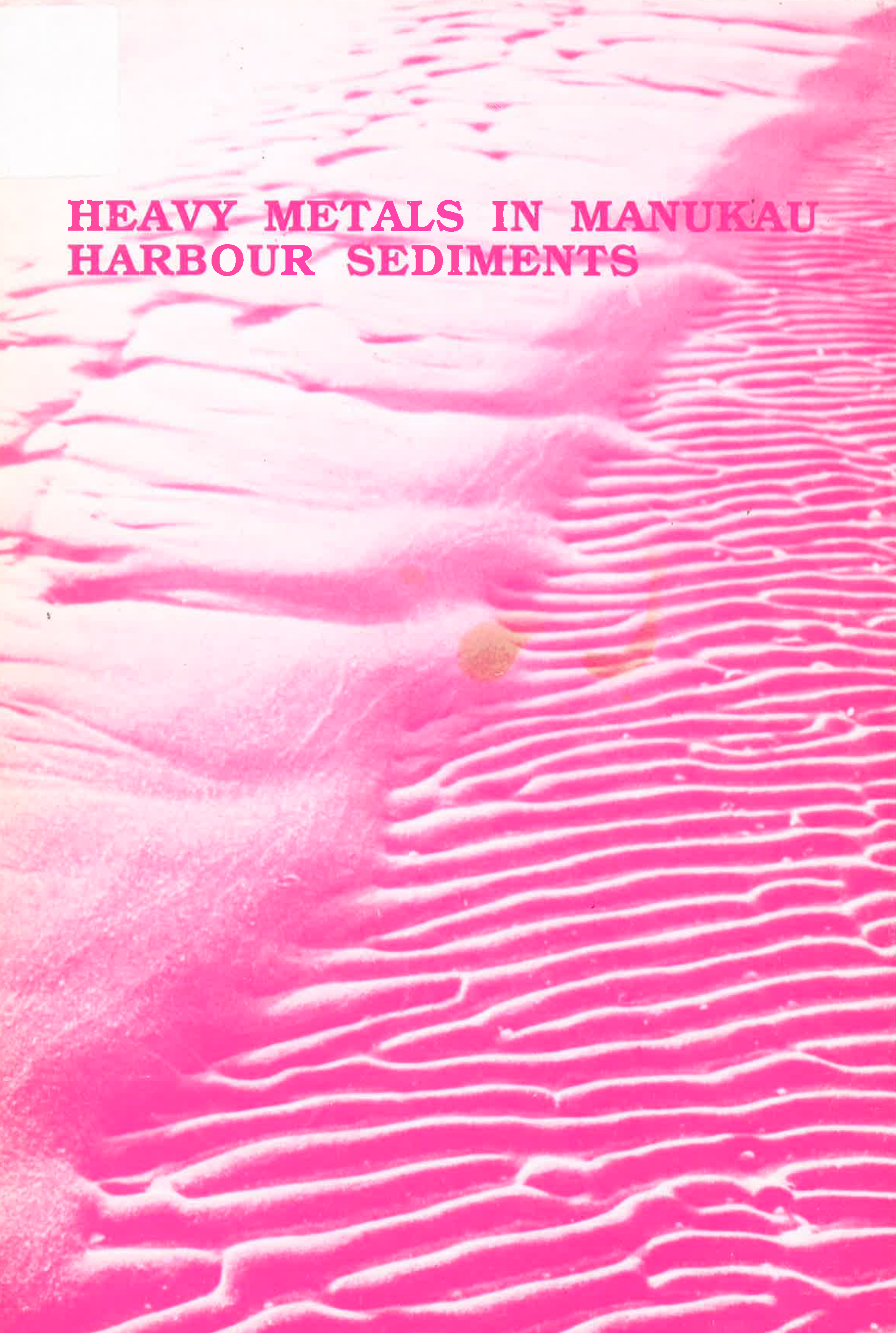
HEAVY METALS IN MANUKAU HARBOUR SEDIMENTS



HEAVY METALS IN MANUKAU HARBOUR SEDIMENTS

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CONTENTS

SUMMARY

This study is a re-examination of some published information on the textural and pollution characteristics of sediments in Manukau Harbour, and an appraisal of the factors affecting the distribution of heavy metals in sediments throughout the harbour. Data on heavy metal levels from three studies is examined in this report. Glasby et al. (1988) analysed 135 sediment samples in Manukau Harbour for 9 elements as part of a general survey of heavy-metal pollution in Auckland harbours. Analyses were carried out on the < 20 µm size fraction of the sediment. Bioresearches (1985-1990) collected samples from up to 10 sites in the Waiuku Estuary in the southwest part of the harbour, from 1985 to 1990, as part of a monitoring programme of the N.Z. Steel Mill effluent discharge. The Auckland Regional Water Board (1987a, 1987b, 1988) also monitored metals from 1985 until 1988 downstream from the steel mill. These latter two studies were based on the analysis of bulk (total) samples.

This report re-evaluates this information to gain a better understanding on the fate of heavy metal pollutants in sediments of Manukau Harbour. We examined depth trends, longitudinal trends and time trends in sediment composition as well as sample variance as a function of site location, proximity to pollution source, and sediment texture and mineralogy in order to test various ideas on factors controlling pollutant distribution. The survey of the heavy metal content of the <20 µm fraction from sediments throughout the harbour (Glasby et al. 1988) allowed reappraisal of harbour-wide contamination. The receiving water sediment monitoring programmes for the Glenbrook Steel Mill discharge (Bioresearches 1985-1990, ARWB 1987a, 1987b, 1988) allowed the study of localised heavy metal inputs.

Proximity to source

The longitudinal concentration profiles based on the data of Glasby et al. (1988) show a decline in heavy-metal content with distance from Mangere Inlet, a severely polluted area. These plots indicate relatively little influence of the discharge from the Manukau Sewage Purification Works. Longitudinal profiles in the Waiuku Estuary show that high Zn concentrations near the Steel Mill outfall declined rapidly (within a few hundred metres) and, thereafter, concentrations were indistinguishable from those found elsewhere in the Waiuku Estuary or indeed elsewhere in the harbour.

Concentrations of metals in total sediment samples (Bioresearches 1985-1990) decrease rapidly (particularly Zn, Cr, V, and possibly Pb) near the Steel Mill outfalls. This decrease occurred over very short distances (< 300 m), and further away, the longitudinal surveys down the estuary (ARWB 1987a, 1987b, 1988) did not show any indication of decreasing concentrations with distance or increasing concentrations with time. The surveys of total and the <20 µm fraction of the surface sediments were therefore in good agreement.

Depth profiles

Metals associated with pollution (Pb, Zn, Cr and Cu) decreased in concentration with depth in the sediment while concentrations of non-pollutant metals (Fe, Ni and Co) were relatively constant. A few sites had higher concentrations at depth, probably due to localised, high sedimentation rates. Baseline concentrations were calculated from the depth profiles.

Comparison of surface sediment and baseline concentrations demonstrated widespread, low-level contamination by Zn, Pb, Cu and possibly Cr throughout the harbour.

Other factors controlling heavy metal distributions

The composition of the <20 µm sediment fraction was largely independent of the sediment type sampled (e.g., it is similar for high energy sandy sites and for sheltered muddy sub-estuaries).

In the Waiuku Estuary (Bioresearches 1985-1990), the compositions of total sediment samples varied considerably between sites and between years at any given site, as assessed by the Al_2O_3, SiO_2 and Fe concentrations. In contrast, each monitoring site (a plot 50 x 2.5 m) had little variation in Al_2O_3 and SiO_2 concentrations each year which suggests that the sediments were reasonably homogeneous within the plot. The Al_2O_3 content was highly correlated to mud, SiO_2 and Fe contents, and seemed the best parameter to describe the sediment characteristics. The larger variation of sediment composition from site to site and from year to year suggests that the data should be normalised (to constant Al_2O_3 concentration) before comparing concentrations of heavy metals between years and between sites. The effects of normalising was examined at three sites which had increasing Zn and Cr concentrations with time. At two of the sites remote from the current discharge point, the change in heavy metal concentration was correlated with a change in major sediment characteristics. Normalising with Al_2O_3 removed these trends.

Comparison of results from <20 µm and total sediment fractions was able to be carried out for the 3 studies in the Waiuku Estuary, because sampling dates nearly coincided. The <20 µm fraction showed much higher concentrations in sandy sediments than found in total sediment samples, as expected. However, there were remakably similar concentrations in the <20 µm and total sediment fractions when the original sediment sample contained >40% mud, so it appears that metal concentrations are largely independent of particle size in muddy sediments.

Sample variance

The replicated sampling of sediments in the Waiuku estuary allowed us to examine sample variance for major sediment components (Al_2O_3, SiO_2, Fe) and for the heavy metals (Zn, Pb, Cd, V, Co, Mn, Cr, Ni). Sediments in the monitoring plots (50 x 2.5 m) showed little variation in Al_2O_3 and SiO_2 concentrations on any sampling occasion (Coefficient of variance (CoV) ranged from 0 to 6%). This indicates that these plots were reasonably homogeneous in respect to sand and mud content. Fe and Mn content varied more widely (CoV range from 0-25%), which probably produced a corresponding variation in their associated trace metal concentrations.

For the heavy-metals, the most abundant metal Zn had CoV ranging from 0-40%. The other elements (Pb, Cd, Ni, Cr, Cu, V) had a wide range of CoV from 0-35% for Pb to 0-50% for Cu. CoV for major and minor contaminants were therefore similar. The CoV for the trace elements did not vary systematically with location, proximity to mill, magnitude of concentration, nor could be explained by changes in major sediment components such as Al_2O_3 and SiO_2. It is possible that analytical error is a major source of variation, but we were unable to confirm this, so we could not confidently suggest a way of reducing this variance e.g., by normalisation or alternative sampling techniques. Therefore it appears that the monitoring programmes had a high variability in trace heavy-metal concentrations. If future work demonstrates this to be an intrinsic property of surface sediments over distances of 50m, then this will limit ability to detect trends in heavy metal pollution studies.

1 INTRODUCTION

Estuaries act as sediment traps for pollutants and they are the most stressed of the marine systems (GESAMP 1990). The extent of estuarine pollution in New Zealand was appraised in 1976, and 6 of the 301 estuaries in New Zealand were considered grossly polluted and 26 moderately polluted (McLay 1976). Inputs of pollutants to estuaries are thought to have decreased in recent times and further management practices have been proposed to decrease them further, but there is no way to predict how rapidly and well the remedial measures will clean up the pollution. Because cleaning up an estuary is an expensive task, scientific studies to establish the degree of pollution and the ability of the sediments to recover from pollution are imperative. In 1989 a programme of studies were initiated to consider the question of sediment and ecosystem recovery. Initially, this programme is addressing the fate of pollutants trapped in sediments. In particular, it examines the processes leading to their burial, translocation or flushing from the estuary and is pursuing these studies in the Manukau Harbour (Williamson and Hume 1990).

Manukau Harbour is the second largest estuary in New Zealand, and probably the most contaminated. It has multiple sources of contamination and the most industrialized area in New Zealand lies at the head of Mangere Inlet, in the north-east corner of the harbour. In parts of the harbour, sediments contain high concentrations of Pb, Cu, Cd, Cr and Zn. This report evaluates information that may lead to a better understanding on the fate of these and other heavy metal pollutants in sediments.

Information on the processes and subsequent fate of pollutants is expensive to obtain. A number of comprehensive studies have already collected a large amount of data on heavy metal concentration in Manukau Harbour sediments and described the distributions of heavy metals through space and time. These distributions are the result of the contaminant dispersion processes, and the first aim of this report is to re-examine some of this data to see if it will throw light on these processes. The second aim is to provide a more comprehensive view on the distribution of heavy metals throughout the harbour than is available at present, so as to provide a background against which future work can examine the fate and cycling of pollutants in the harbour. Another aim is to describe the sampling variation, so as to obtain guidance for future field work. These aims have been addressed through the following questions:

1 Over what distance do metal sources affect the harbour sediment quality?
2 What are the background concentrations of the metals in the sediment, and what is the depth of pollution in the sediment?
3 What insights can be gained on other factors controlling heavy metal concentrations such as sediment texture or mineralogy and hydraulic environment?
4 What are the variations in metal concentrations at a given site in both the polluted and unpolluted areas?

Data on heavy metal levels from three studies were examined in this report. We have not attempted to combine data which has been collected or analysed differently. Glasby et al. (1988) analysed 135 sediment samples in Manukau Harbour for 9 elements as part of a general survey of heavy metal pollution in the two Auckland harbours. The samples were collected in 1985 and the analysis were carried out on the <20 µm size fraction of the sediment. Bioresearches (1985-1990) collected samples from up to 10 sites in the Waiuku Estuary in the southwest part of the harbour, from 1985 to 1990, as part of a monitoring programme of the N.Z. Steel Mill effluent discharge. The Auckland Regional Water Board (1987a, 1987b, 1988) also monitored metals in sediments from 1985 to 1988 downstream from the steel mill discharge in this estuary. In the latter two programmes, bulk samples (minus the coarse shell fraction) were analysed.

In addition to the above, this report examines and collates historical information on catchment development to establish when pollution began.

2 MANUKAU HARBOUR AND ITS DEVELOPMENT

2.1 Physical setting

Manukau Harbour (37°02'S, 174°41'E) is a large, shallow estuarine lagoon located on the west coast of the North Island of New Zealand, covering an area of 344 km^2 (Fig. 2.1). Of that area, a large proportion (145 km^2) is exposed at spring tide as low-gradient, intertidal flats. The intertidal sediments are consolidated sands in the main body of the harbour, and soft muds in the tidal creeks. Four main channels drain the harbour. The water circulation is mainly tidal with a mean residence time for water of 22 days (Heath et al. 1977). Tidal range in the harbour lies between 1.9m (neap tides) and 3.8m (spring tides). The volume of water that flows out of the harbour between high and low tides is 450 million m^3 (neap) and 690 m^3 (spring). Tidal flows dominate over freshwater inflows. Sediment disturbance is mainly caused by wave action. The total catchment area of the harbour is 1100 km^2 and only small streams flow into the harbour.

Mangere Inlet lies at the northeastern end of Manukau Harbour. It has an area of 6.6 km^2 and a catchment of 34.5 km^2 (Hume 1979). The inlet is relatively shallow with a maximum depth of 8.3 m below mean sea level. It is a site of sediment deposition because it is sheltered from the effects of strong tidal currents and high-energy wave action (Tonkin and Taylor 1986).

2.2 Inputs of pollutants

Manukau Harbour receives waste, including heavy metals, organochlorines and PAHs, from Auckland city via sewage, urban and industrial stormwater and farm runoff. The most important in the past were inputs from industrial point sources to Mangere Inlet (Glasby et al. 1988). Since 1962, these would have been treated at the Manukau Sewage Purification Works (MSPW). The MSPW now treats much of the waters from domestic, commercial, and industrial sources together with some storm water from the Auckland region and discharges about 250 000 m^3 of treated water per day into the harbour. MSPW effluent is known to contain PAH, chlordane, Pb, Zn, Cu, Ni and Cr. Nonetheless, Mangere Inlet probably remains the most polluted estuary in New Zealand. A number of other minor treatment plants also discharge treated sewage effluent to the Manukau Harbour and dredge spoil is dumped in Purakau Channel. In addition, Glenbrook Steel Mill discharges Fe, Zn, minor quantities of Pb and Cr, and possibly PAH to the Waiuku Estuary. The current level of pollution in the sediments has been described in various reports (e.g. Bioresearches 1985-90, Fox et al.1988; Glasby et al. 1988; Roper et al. 1988; Auckland Regional Water Board 1990) which have identified a number of zones where toxic substances are concentrated. A summary of some of the principal sources of pollutants in the harbour have been described by Glasby et al. (1988).

In addition to discharges from point sources, there is a runoff from urban and rural areas. The urban runoff

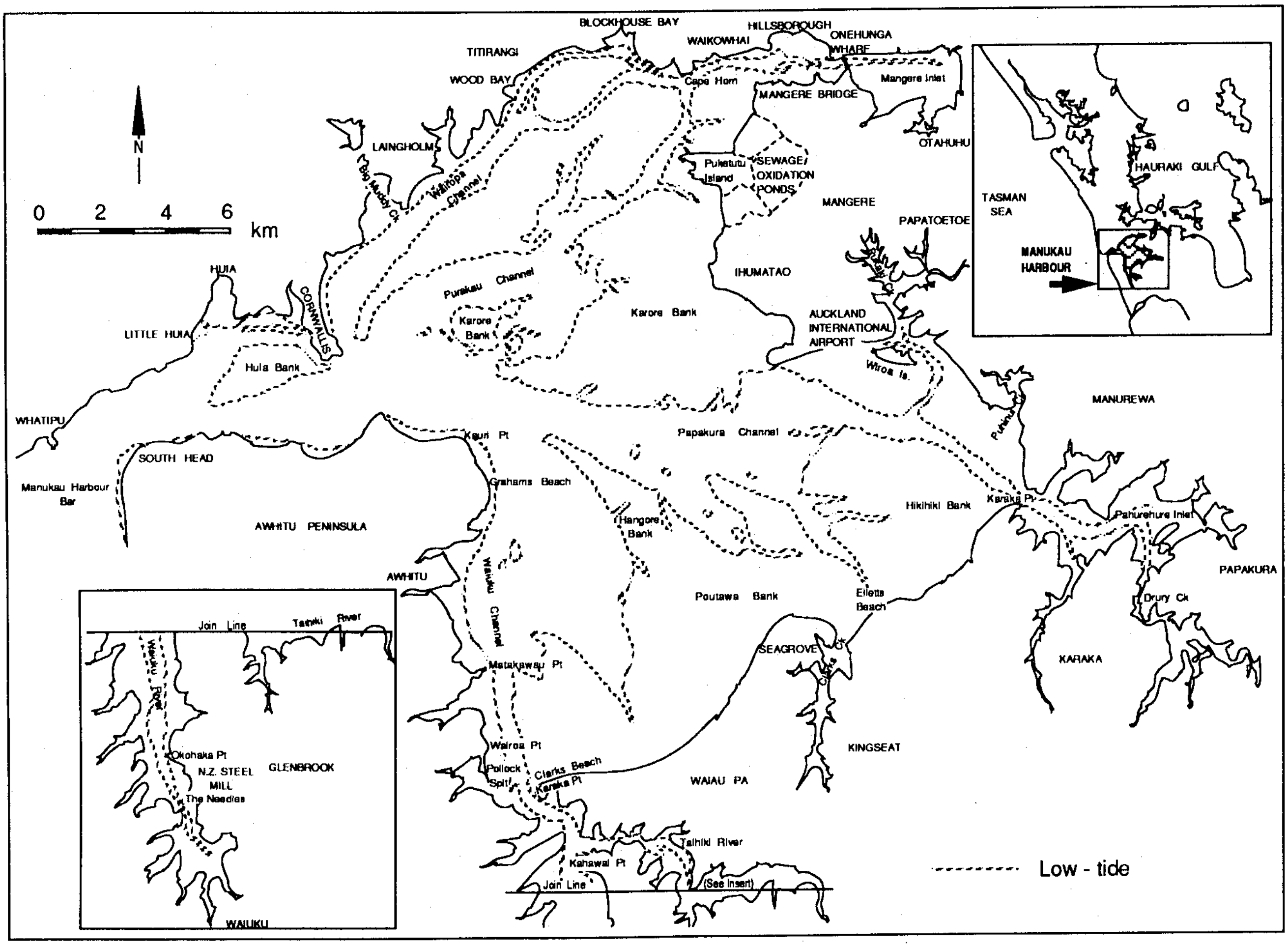


Fig. 2.1 Principal features of Manukau Harbour.

carries PAH, Pb, Cu and Zn to the harbour. Rural runoff includes diffuse source pollutants from pasture and a large number of treated effluents from piggeries and cowsheds. There is a significant amount of horticulture in the catchment and this, together with the pasture, carries an unknown quantity of pesticides.

At present, the Auckland urban area has a population of 865 000 with a density of 760 people per km^2. This is the ultimate source of much of present inputs to the harbour.

2.3 Catchment development

Prior to the arrival of Europeans in the 1850s, Manukau Harbour was rich in fish, bird and forest food and had been occupied by the Maori for a thousand years. Since that time, the Auckland region has experienced a steadily increasing population, and the area around Mangere Inlet has become one of the most industrialized areas in New Zealand (Linge 1959, Fig. 39). This development has obvious implications for the level of pollution in Mangere Inlet and the rest of Manukau Harbour. Developments in the region through time are given in Table 2.1. These may serve as time markers for pollution events in the harbour. The table is based on information given in Anon (1927, 1946, 1948, 1953), Hargreaves (1943), Linge (1959), Onehunga Borough Council (1963), Mogford (1977), Craig (1982), Laing (1985) and Glasby et al. (1988). While this table may not be comprehensive, it does give an idea of the time frame of development. The most detailed account of industrial development in the Auckland region is that of Linge (1959). The history and nature of the sewerage systems in the region is summarised in Table 2.2.

Table 2.1. Development of the area around Mangere Inlet (including Huia, Papakura, Onehunga, Otahuhu and Penrose) by decade since European settlement.

1850s	First arrival of settlers; burning of bush; flour mill at Onehunga; Manukau Harbour becomes important for shipping.
1860s	Shipbuilding and sawmill plus substantial wharf built at Onehunga; gum digging at Papakura; flax mill at Waiuku.
1870s	Manukau becomes a rich dairying area; general engineering works at Onehunga.
1880s	Pit sawing in Huia; tannery, woollen mills and cardboard box factory in Onehunga; N.Z. Iron and Steel Company set up and closed down in Onehunga (1883-1886).
1890s	Fellmongery in Onehunga
1900s	First trials with artificial fertilizer at Papakura.
1910s	N.Z. Fertilizer Co. in Onehunga (1916); first Mangere Bridge; soap production at Penrose; damming of streams in Huia.
1920s	Introduction of chrome tanning of leather at Otahuhu; damming of streams at Huia; bay at Huia left littered with debris from bush clearance with great many scars on the landscape; railway workshops opened in Otahuhu; by the 1920s, the following factories were operating in the upper part of the Manukau (woollen mills, three gigantic fertilizer works, freezing works, abattoirs, tanneries and fellmongeries, glue works, glass works, timber mills, ironworks, soap and candle works, reinforced concrete pipe works and wool scouring establishments); over 300 vessels with a gross tonnage of 180,000 tonnes operating in Manukau Harbour.
1930s	Development of Penrose industrial area including Reidrubber, asbestos-cement factory, furniture manufacturing, die casting, steel industry and dairy equipment; manufacture of truck, tractor and marine engines at Papakura; quarrying begins for millions of m^3 of aggregate on Huia hills.
1940s	Further development of Penrose industrial area including paint, plastics, furniture, dairy equipment, electrical and tobacco factories and timber processing; expansion of Papakura military camp; perpetual drainage problems in Papakura especially from additional sewage outfalls.
1950s	Engineering and sheetmetal works and Colonial Oil and Chemical Co. in Penrose; boom in shipping at Onehunga Wharf.
1960s	Manukau Sewage Purification Works commissioned (1962); New Zealand Steel Ltd begins galvanising (1968) and manufacturing (1970) steel at Glenbrook.

Table 2.2. Summary of sewerage systems in areas adjacent to Manukau Harbour. Information supplied by K.R. Davis (pers. comm.).

Mount Roskill Borough Drainage System	First portion of borough sewered in 1925. Discharged to harbour after passing through a "septic tank" beyond end of Queenstown Road. Sewered area confined to eastern side of borough. Other areas (from northern side of Mt Albert Rd to north (Auckland City) and southern side to Queenstown Rd and Manukau Harbour) sewered from about 1940.
New Lynn Borough Council	"Treatment tanks" and sewers constructed 1929. Discharge to harbour at Green Bay. The tanks had no means for providing sludge removal other than by discharge to the harbour. Tanks designed for 3,600 persons. In 1954, 7850 persons were connected.
One Tree Hill Borough Council	Sewerage from area No.3 is discharged into the Onehunga Borough Council System. The other sections are pumped to the Auckland system (Waitemata Harbour). Sewered in 1940 or thereabouts.
Otahuhu Borough Council	First sewers built in 1910 or thereabouts. These were gradually extended until, by 1954, about 80% of the borough had been sewered. Only a portion of borough sewage went to Manukau Harbour. Three of four septic tanks discharged into Tamaki Estuary. Sewage from psychiatric hospital treated by Imhoff tank and discharged into Manukau Harbour. Sludge sluiced into harbour from all tanks.
Onehunga Borough Council	First sewers constructed in 1910. By 1954, borough completely sewered. Storage tanks with outfall were located at the end of Whurangi Street. Volcanic rocks provided good soakage for stormwater.
Overall	In 1954, about 45,000 persons were connected to sewers which ultimately discharged into Manukau Harbour. From Otahuhu to Onehunga, there were 18 trade waste outfalls (described in Glasby et al 1988). In 1955, it was estimated that 20 x 10^6 m^3 of untreated trade waste plus 0.7 x 10^6 m^3 of domestic sewage (from industrial premises) were being discharged into Manukau Harbour. The 5 day BOD was estimated to be 27000 kg (equivalent to a population of 400000 people).

3 FACTORS CONTROLLING THE DISTRIBUTION OF TRACE ELEMENTS IN SEDIMENT

3.1 Proximity to source

Metal enrichment in the sediments is generally located close to past and present sources of pollution and in more sheltered areas of the harbour where flushing is restricted (see Fig. 2.1). Various reports have identified a number of distinct zones where toxic substances are concentrated. The major polluted areas are Mangere inlet, off the MSPW and Glenbrook Steel Mill, and in Drury Creek. In fact, the most industrialized area in New Zealand lies at the head of Mangere Inlet and for many years effluents were discharged directly into the inlet. Moderately polluted areas are located immediately away from Mangere inlet, in bays and sub-estuaries adjacent to urbanised catchment, at the dredge spoil disposal site in the Purakau Channel and away from agricultural land having a history of application of chemicals. Most of these sites are in sheltered muddy sub-estuaries or bays.

3.2 Sediment texture

Metal concentrations in marine and estuarine sediments are determined not only by metal inputs but also by sediment characteristics. One of the most important sediment characteristics is the reactive surface or binding-site density, which is largely controlled by grain size. Contaminants concentrate in finer sediments due to the larger surface area/volume ratio, the high cation exchange capacity and overall surface charge that provides numerous sites for adsorption of metals and other contaminants.

Sediments vary considerably in appearance and composition from place to place throughout the Manukau Harbour. Sediments are dominantly fine sands, with muds in sheltered inlets, and calcareous sands and gravel in the channels (Fig. 3.1). Sedimentation rates appear to be highest in the muddy sediments which are found in the sheltered tidal creeks (Fig. 3.2). Most pollution is associated with the finer sediments near the sources of pollution.

3.3 Establishing and improving comparability of sediment analysis

A recent review by Luoma (1990) describes a number of ways to improve the sensitivity on comparing metal concentrations. We describe some of these approaches here which are relevent to the the following discussions.

Contamination of sediments depends in part on the ability of the sediment to bind or adsorb the contaminant. Normalising metal concentrations in the sediment to a textural or compositional characteristic may therefore improve the sensitivity of comparisons of metal concentration in the sediment. Among several different ways to normalise, the use of a "conservative" (or reference) element is the most common (Salomons and Forstner 1984). The most usual approach here is to use an element that reflects the texture of the sediment. Such elements increase in concentration as the particle size decreases (in response to an increase in clay minerals) or

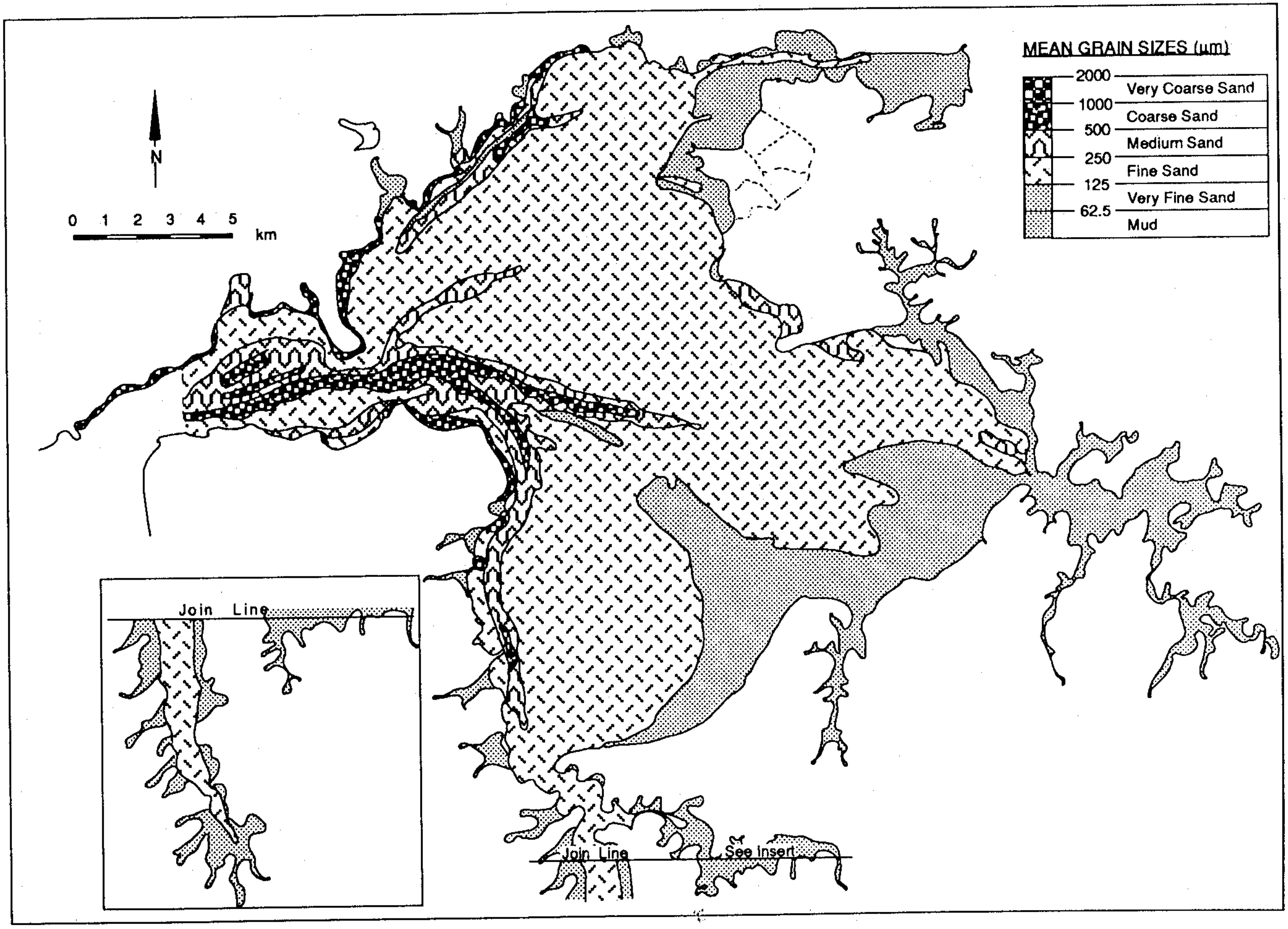


Fig. 3.1. Principal sediment types in Manukau Harbour.

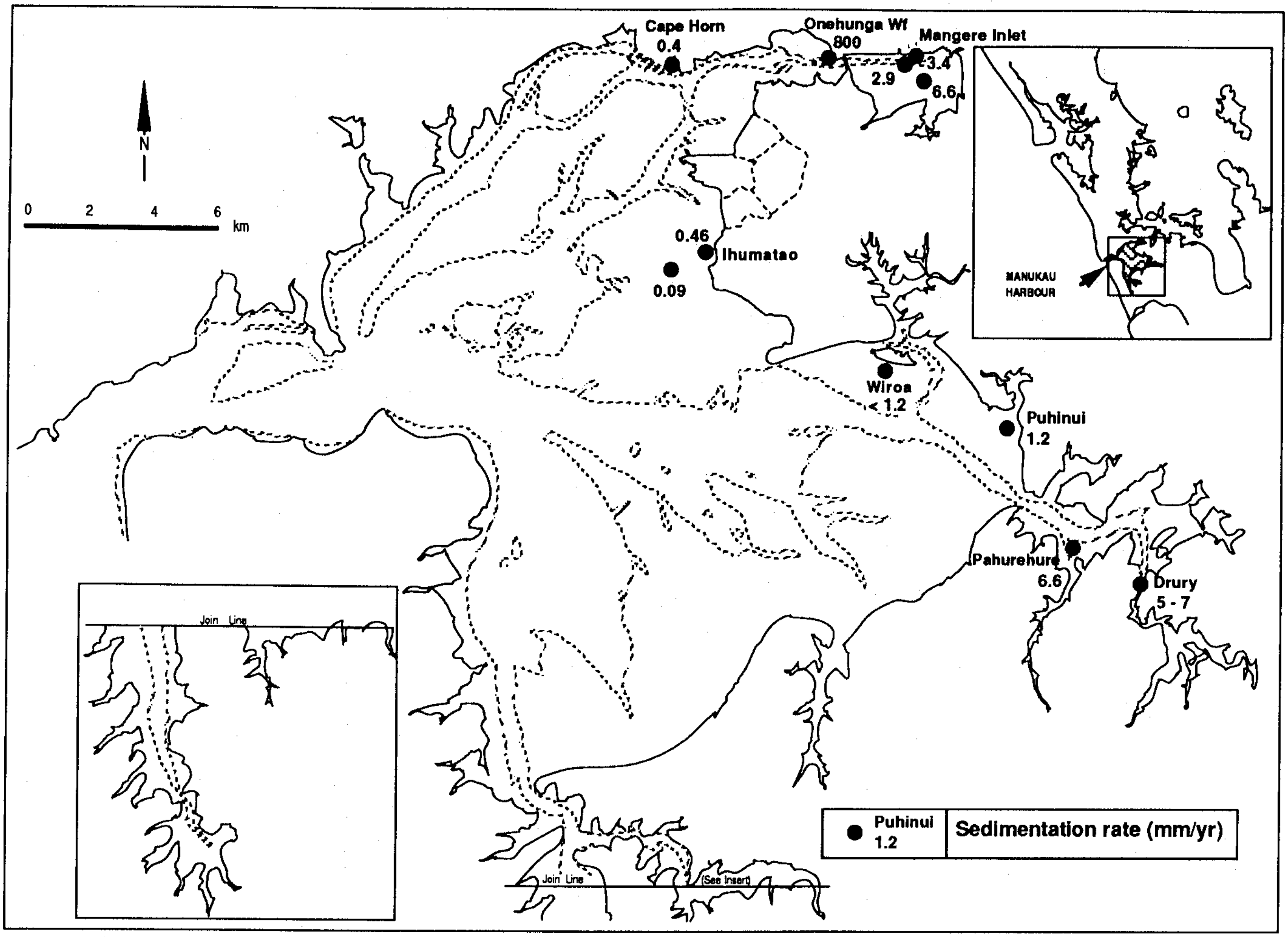


Fig. 3.2. Sedimentation rates in Manukau Harbour.

as the amount of silica sand decreases. Elements that are generally recognised as "conservative" in this category are Al, Rb, Sc and Cs. Alternatively, Si can be used. One way of normalising is to carry out a regression analysis between the examined and the reference element. The confidence limits for the regression are found and metal anomalies are identified as values that lie outside the confidence limits. Another way to normalise is by simply dividing the pollutant concentration by the reference element concentration. In an unpolluted environment, this should give a constant ratio.

Instead of using conservative elements, the particle size or specific surface area can be used directly. For example, normalisation was achieved by regression analysis between the mud content of a sample and the element concentration in the carbonate-free fraction of the sediment (Khalaf et al. 1982). This method was employed by Ports of Auckland (1990) for Manukau Harbour sediments.

Other potentially useful normalisation techniques are based on sediment composition, such as the amount of organic matter (Siedemann 1992) or the amount of amorphous iron oxyhydroxides. Both of these components are important sites for pollutant adsorption.

Instead of carrying out the normalisation procedure for grain size effects after analysis, it is also possible to separate specific grain size fractions and analyse them. ARWB (1989) proposed analysis of the <63 µm (mud) fraction since the mud fraction is the most important fraction in transporting trace elements. Others favour the <20 µm fraction (e.g., Glasby et al 1988) or even the <2 µm fraction (Forstner & Whitman 1983).

4 HARBOUR-WIDE SURVEY OF THE <20 µm SEDIMENT FRACTION

Introduction

In 1988, Glasby et al. published their study on heavy metal pollution in Manukau and Waitemata Harbours in which 135 samples from Manukau Harbour were analysed for 9 elements. Of these samples, 93 were surface sediments and the rest were taken from depth by coring. The analyses were carried out on the <20 µm size fraction of the sediment. Metals were extracted by HNO_3/H_2SO_4 digestion and their concentrations determined by atomic absorption spectrometry. The raw data are presented in Appendix 1. The locations of the sampling sites are shown in Fig. 4.1.

To evaluate the level of man-made pollution, an index of geoaccumulation (Igeo) was calculated: Igeo = log (C) - log (1.5 B), where C is the measured concentration of the element and B is the background concentration (in this case taken to be the concentrations found in world average shale). The degree of contamination can be designated on a scale from 0 to 6, where 0 means uncontaminated and 6 extremely contaminated. This index makes it possible to estimate the level of contamination relative to background.

Glasby et al. (1988) divided the harbour into four areas (Fig. 4.1 - Area A Mangere Inlet, Area B Puketutu Is, Area C the middle harbour and Area D Waiuku Estuary) and prepared maps of the Igeo indices. These demonstrate that surface sediments from the whole harbour are uncontaminated to moderately contaminated with Pb, Zn and Cu. Surface sediments from Mangere Inlet display strong to moderate contamination of these elements and from the Waiuku estuary uncontaminated to moderately to strongly contamination of Zn. Surface sediments adjacent to the MSPW are somewhat enriched in these elements compared with the central harbour. To supplement information in the Igeo Index maps, we present maps of sediment concentrations for Zn, Pb, Cu and Cr in Fig. 4.2A and B.

Distributions

Histograms of each of the analysed elements in the harbour sediments show that Pb, Zn and Cu are the most contaminated elements (Fig. 4.3). 60% of the Pb analyses, 37% of the Zn analyses and 23% of the Cu analyses lie above the uncontaminated category (Igeo class 0). 5% of Mn analyses also lie above the Igeo class 0 category but this is probably due to the influence of redox characteristics in the sediment on the Mn concentration rather than the effects of contamination.

Variation of depth

Glasby et al. (1988) compared element concentrations in surface sediments with those found at depth. Only in two areas of the harbour (A and C - Fig. 4.1) were sufficient samples studied to carry out statistical analysis on the data in the form of matched pairs of surface and subsurface sediments. With some exceptions, they found that Pb, Zn and Cu concentrations were significantly higher in surface

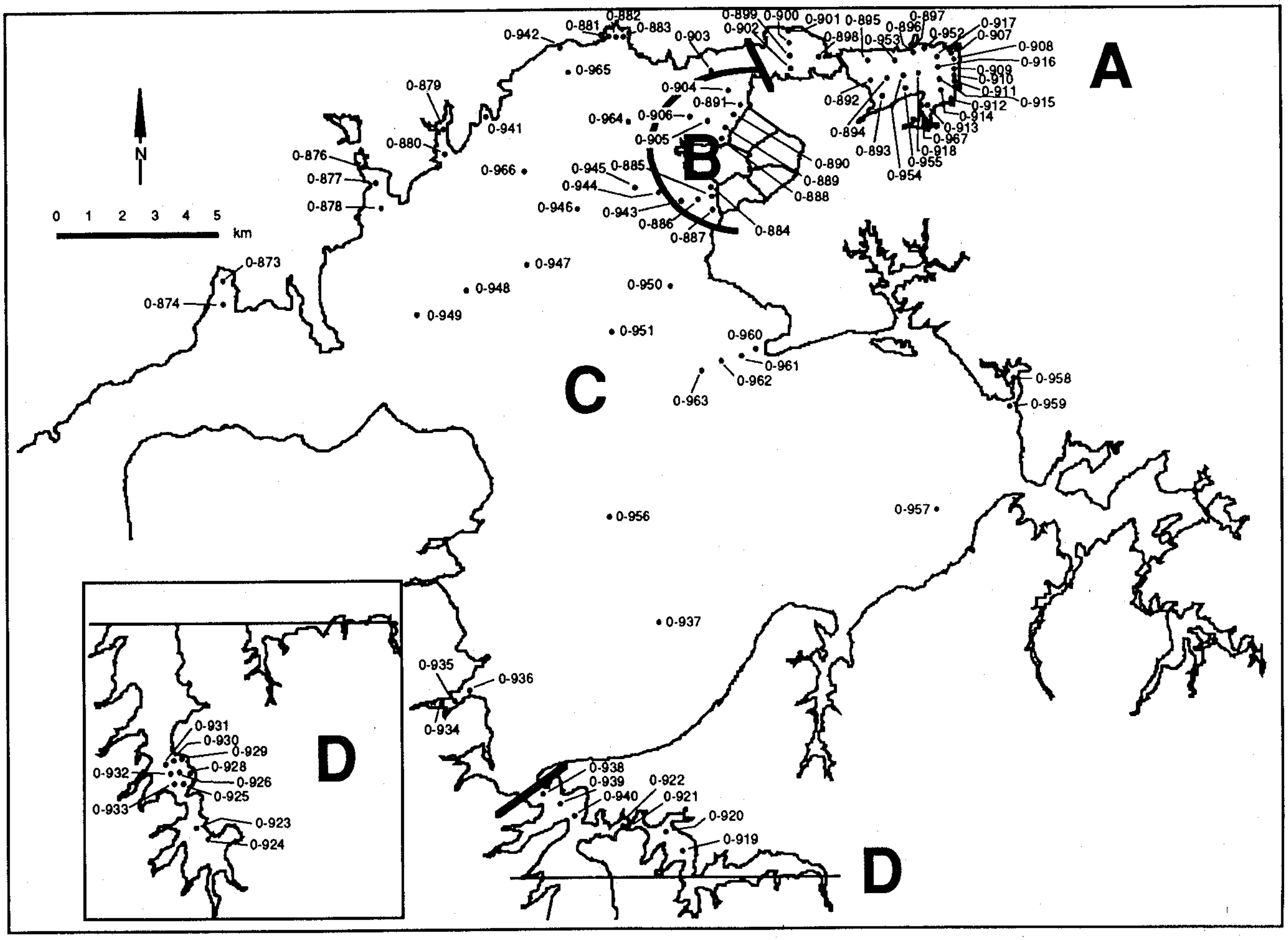
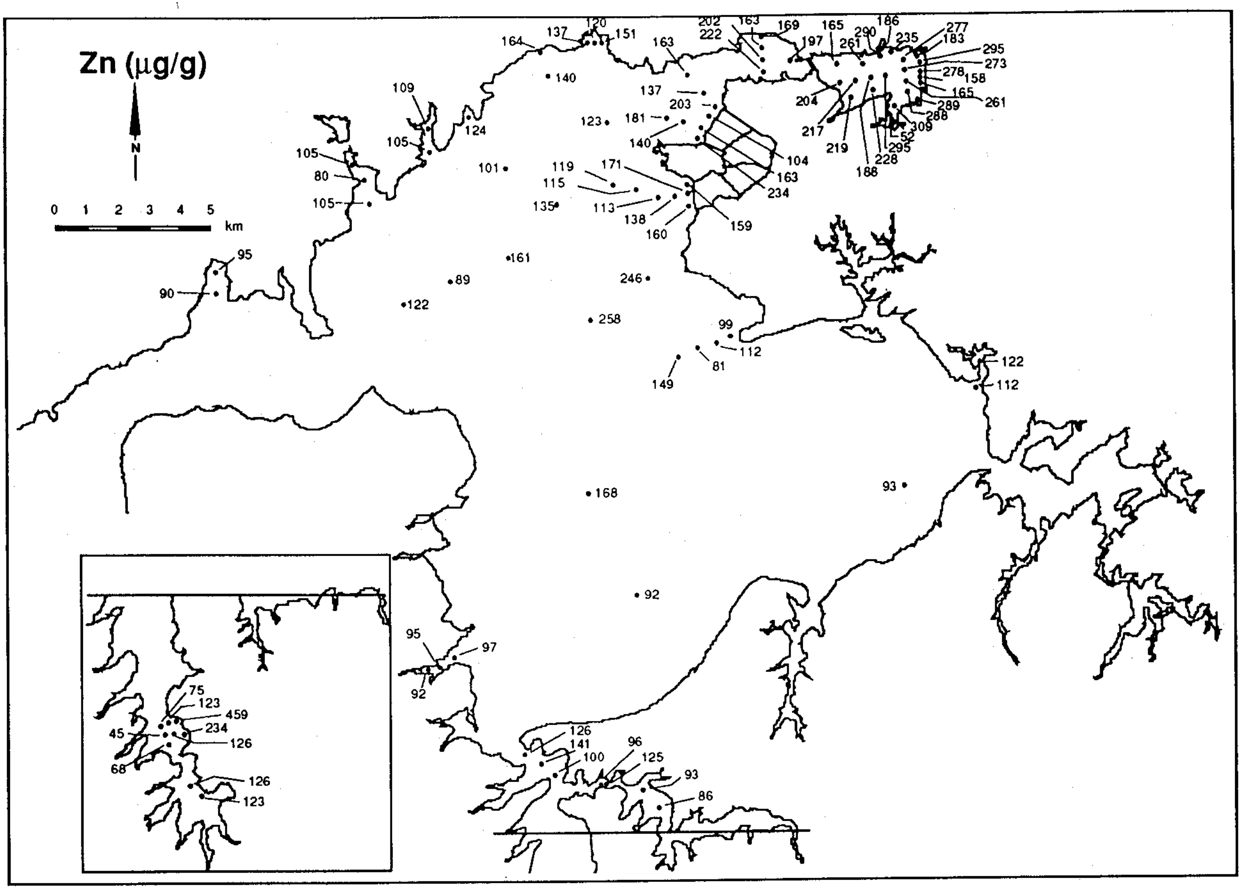


Fig. 4.1 Glasby et al. 1988 sample site locations.

Fig. 4.2A Concentrations of Zn and Pb throughout the harbour in the <20 µm sediment fraction. Data from Glasby et al. 1988.



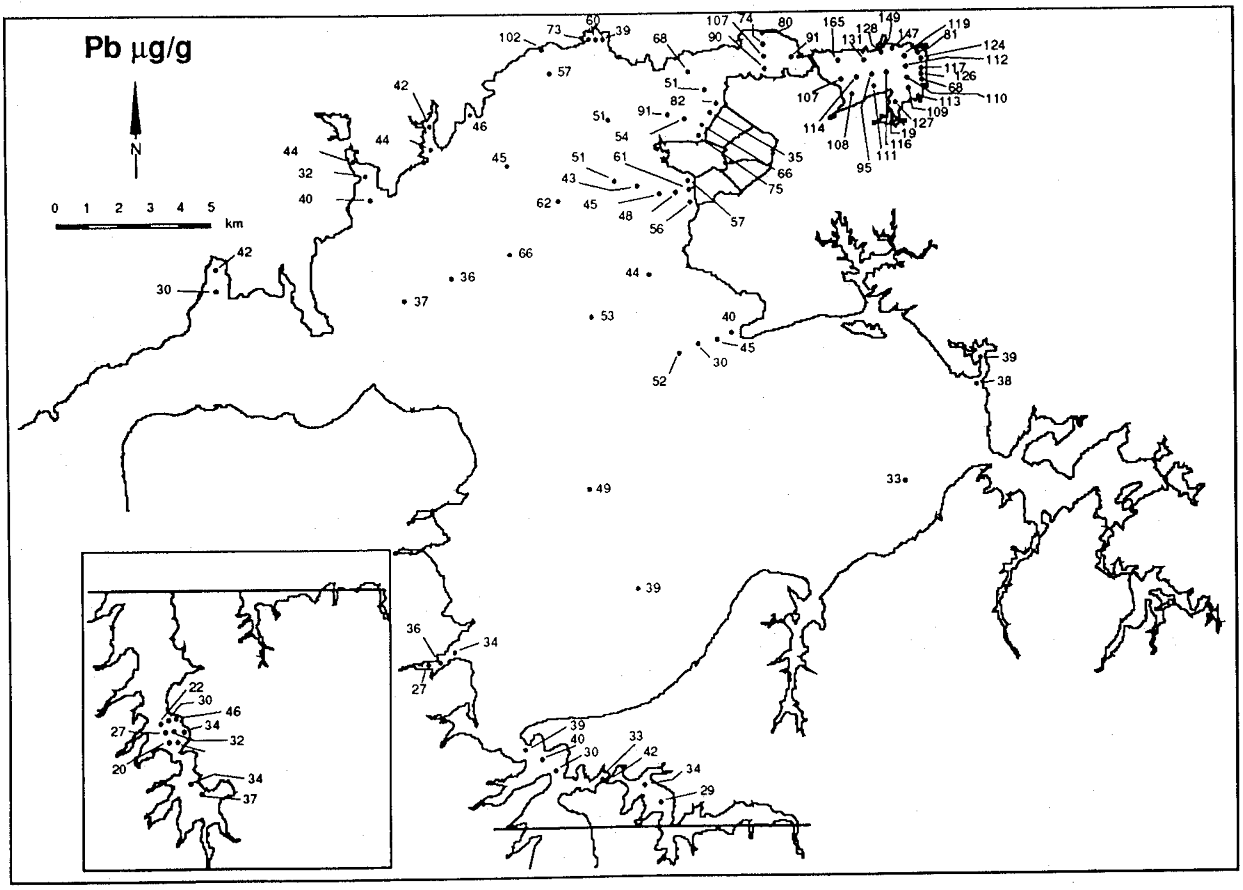


Fig. 4.2B Concentrations of Cu and Cr throughout the harbour in the <20 µm sediment fraction. Data from Glasby et al. 1988.

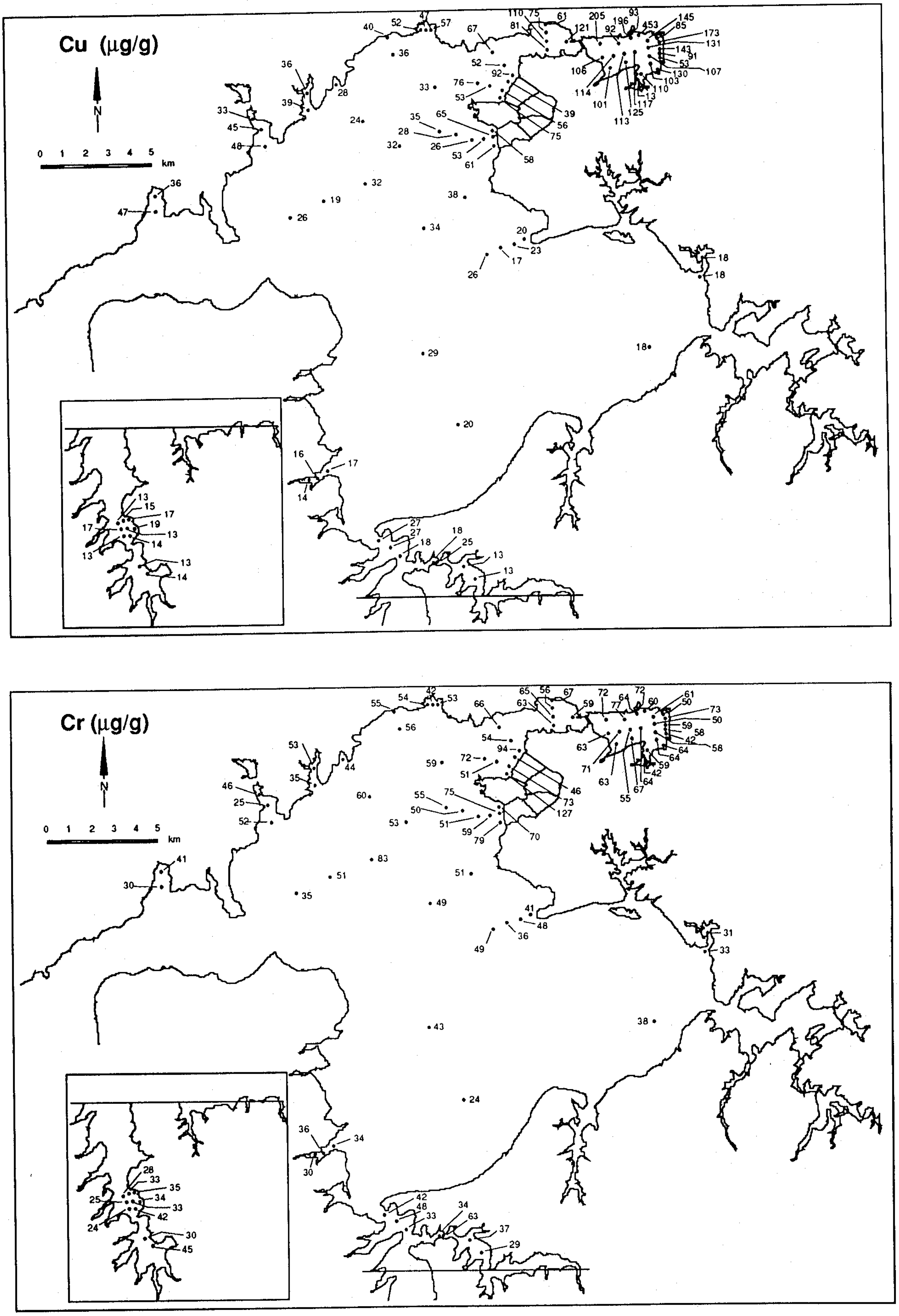
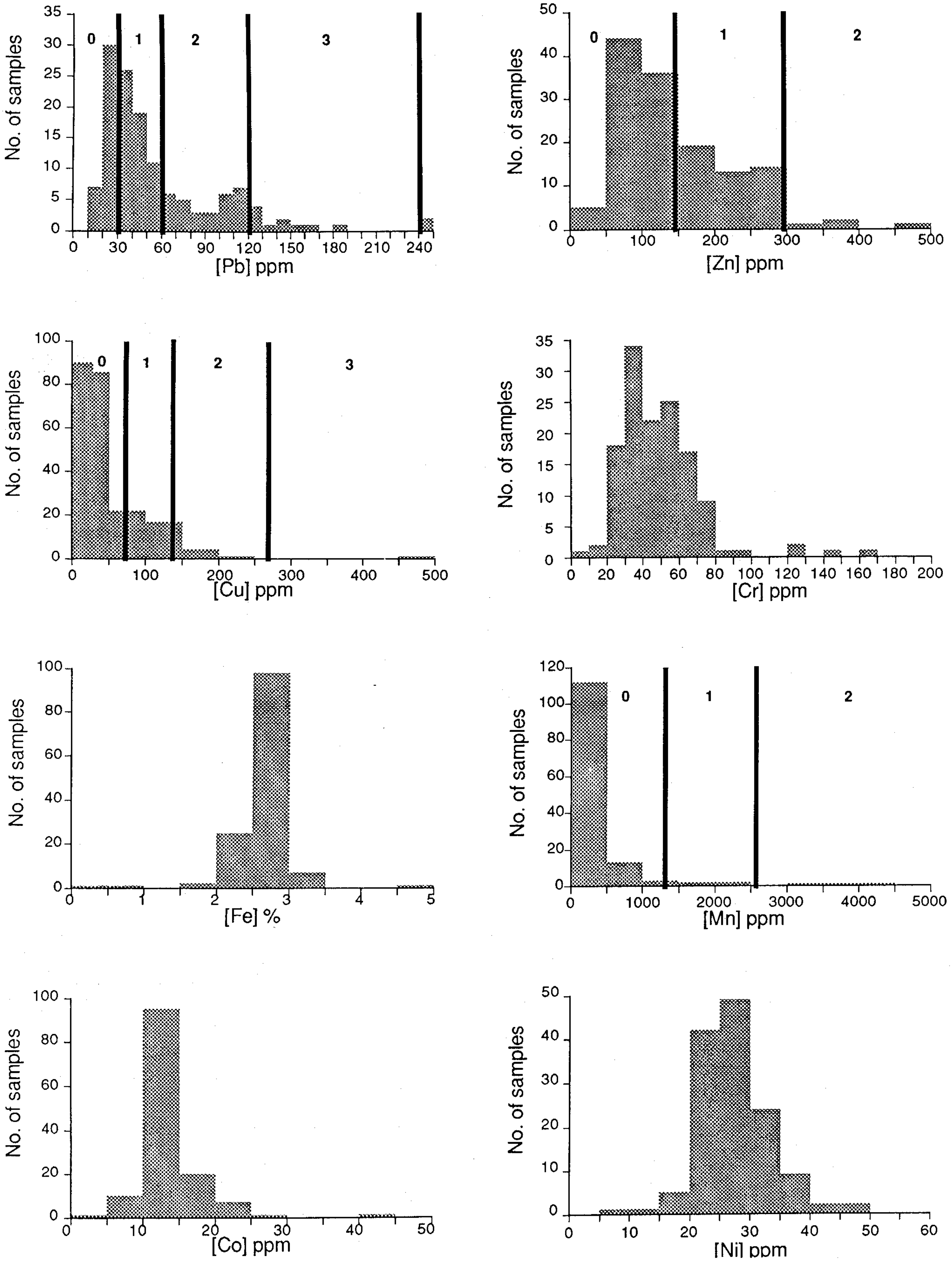


Fig. 4.3 Histograms of metal distributions in the < 20 μm sediment fraction. Data from Glasby et al 1988. Igeo index boundaries are solid lines and calculated assuming average shale as background (see text in Introduction). Data for Fe, Cr, Co and Ni are all in Igeo class 0.



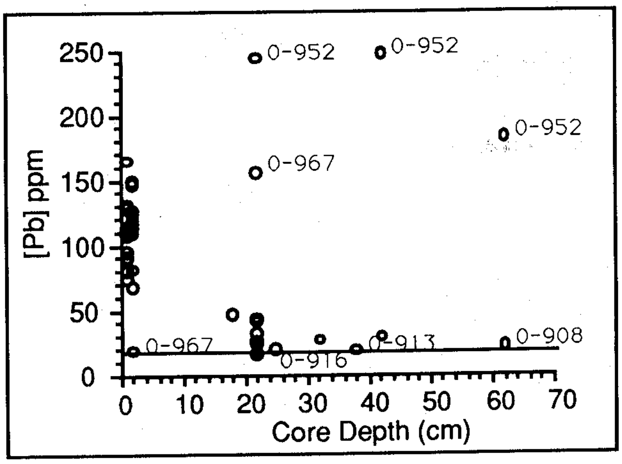


Fig. 4.4 Variation of Pb concentrations with depth in area A (Mangere Inlet). Solid line = calculated baseline concentration. Other elements and areas are shown in Appendix 3).

sediments than in subsurface sediments. Cr was significantly higher in one area but not in the other but its concentration remained in the uncontaminated category.

Four sites (0-877, 0-885, 0-952 and 0-967, Fig. 4.1) showed higher element concentrations in subsurface samples (Appendix 2). Sample 0-885 is located adjacent to the former MSPW-outlet, which has now been moved to the north side of Puketutu Island. This may explain why the surface sediment is less contaminated. Sample 0-877 is located in Big Muddy Creek on the northern side of the harbour. Two adjacent samples (0-876 and 0-878) do not have the same pattern as 0-877, and there is no obvious reason why this sample should be anomalous. Samples 0-952 and 0-967 are both located in Mangere Inlet where much effluent was discharged up to 1962. These exceptions to this general trend of decreasing concentration with depth could be due very high local sedimentation rates post-dating the onset of pollution. Two recent deep cores taken in Mangere Inlet also exhibit contamination to deeper levels in the sediment (1.4 m and 2.1 m) (Williamson et al. 1991). These were taken on the sides of channels and it is conceivable that high sedimentation rates (progradation) could occur there. Other possible mechanisms which may displace contaminants to greater depths in the sediment column such as sediment mixing (e.g. bioturbation) or water movement are considered highly unlikely to operate to such depths in the muddy, impermeable sediment.

Most depth profiles of element concentrations (Appendix 3) have a tendency to approach a "baseline" concentration at depth. This feature was utilised to estimate a background concentration of each metal in each studied area by taking the mean of the 5 lowest concentrations in sediments from areas A and C (e.g., Fig. 4.4), and the 4 lowest in sediments from areas C and D (because of fewer samples analysed). This mean was devised to reduce any bias from analytical error, although there were no outliers in these datasets. Results are listed in Table 4.1.

Average shale concentrations were much higher than 'background' concentrations (Table 4.1). Using average shale for background concentrations in the calculation of Igeo indices, as did Glasby et al. (1988), will give a conservative estimate of pollution. If actual background concentrations are used in the calculation, then this would give more contaminated categories for Zn and Cu pollution and Cr concentrations would also fall into moderate contamination categories.

Table 4.1 Baseline concentrations of elements in Areas A-D based on concentrations at depth in cores (Areas identified in Fig. 4.1). Average shale values given for comparison (after Turekian and Wedepohl 1961). All analyses in µg/g.

	Area A	**Area B**	**Area C**	**Area D**	**Shale**
Co	9	12	11	10	–
Cr	22	47	27	24	90
Cu	11	34	14	13	45
Fe	17420	23675	23940	17550	47200
Mn	70	205	225	140	850
Ni	17	28	21	21	68
Pb	18	39	23	23	20
Zn	46	106	62	49	95

Area B has higher background levels (Table 4.1) than the other areas (except for Mn and Fe) and this may be due to sedimentalogical changes accompanying the construction of the MSPW. The presence of walls enclosing the oxidation ponds no doubt changed the hydrological characteristics near Puketutu Island, and could have resulted in accelerated deposition of sediments. The other areas have similar concentration levels to one another - again except for Mn and Fe. In area A, C and D, Pb, Zn, Cu, Mn and Cr show decreasing concentrations with depth, whereas Ni and Co concentrations are more constant with depth. This suggests that Ni and Co are not discharged into the harbour in sufficient quantities to raise surface concentrations, or if they are, they do not accumulate in the sediments. Further evidence for this can found from examining the distributions of metal concentrations. Non-pollutants are often normally distributed while pollutants often appear to be positively-skewed, log-normally distributed, reflecting elevated concentrations at some sites due to pollutant inputs. In Fig. 4.3, the distributions of the non-pollutants (Fe, Co, Ni) are tightly grouped, possibly normally distributed. By contrast, the pollutants (Pb, Zn, Cu, Cr) appear to be log-normally distributed. Manganese is also log-normally distributed with large differences in concentrations. This may result from the fact that it is intensely cycled in sediments, undergoing reduction-dissolution at depth and oxidation-precipitation at the surface. Sometimes dissolved Mn can diffuse into the overlying waters before it is oxidized, leading to a loss of Mn. In other cases, Mn can be accumulate in the surface layer.

Longitudinal concentration profiles

The concentrations of elements were plotted on a number of longitudinal sections in the harbour (Fig. 4.5).

The trends along the north shore show that the highest levels of Pb, Zn and Cu in sediments are encountered in Mangere Inlet itself and that there is a steady decline in concentrations of these elements away from the inlet (Fig. 4.6). Although the most marked fall-off in concentrations has occurred within 10 km of the head of the inlet, background levels are still not encountered 20 km from there. This suggests a pervasive distribution of

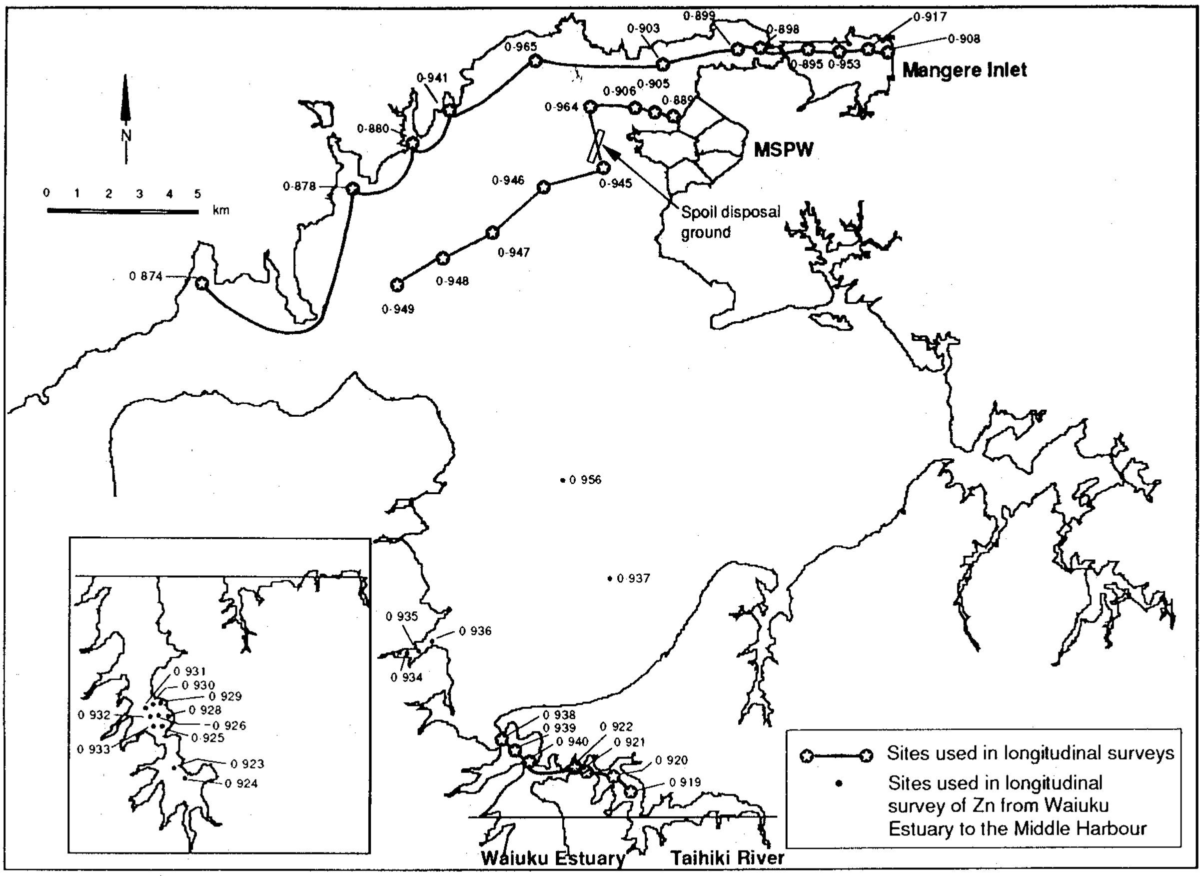


Fig. 4.5 Longitudinal concentration profiles.

these pollutants and that Mangere Inlet may be a source of much of the pollutants in the northern part of the harbour.

The trends of these elements from MSPW through the Purakau Channel is much more erratic and starts from much lower concentration levels (Fig. 4.7). Zn, Pb, and Cu are generally in the Igeo 1 class throughout the profile. There is some evidence of Pb, Cu, Cr and Zn enrichments within 2 km of the MSPW and at site 0-947 in Purukau Channel seaward of the spoil dumping ground. The enrichment may be due to inputs from Mangere Inlet and the presence of dumped spoil dredged from polluted sediments near Onehunga Wharf (Ports of Auckland 1990). The spoil is fine sediment. Under the relatively high energy at the dump site, it can be resuspended by waves and dispersed by currents. Drogue studies indicate that the predominant current directions are along the channel (Auckland Regional Authority Drainage Department 1989). The increase in concentration may mean that most spoil is dispersed by the ebb tide.

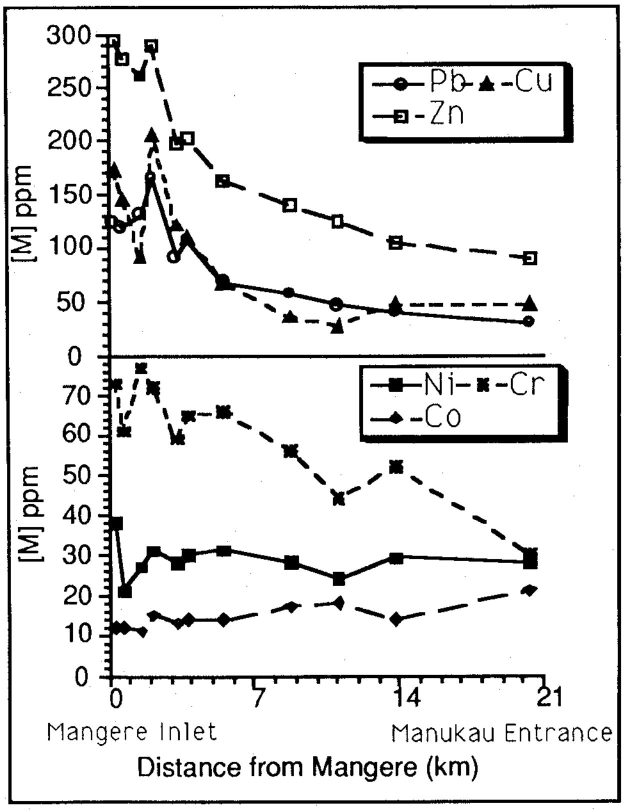


Fig. 4.6 Longitudinal survey along the north shore. Profile position is in Fig. 4.5.

Zn concentrations in sediments were also examined to see if there is any influence from the Steel Mill discharge in the Waiuku Estuary (Fig.4.8). There appeared to be a significant increase in Zn concentrations in some samples located within 1 km of the steel mill. Zn concentrations in the rest of the Waiuku Estuary and the Taihiki River displayed no obvious trends (Fig. 4.9). However, the concentrations in the surface sediments were high (about twice background - Table 4.1). This reflects the wide extent of Zn contamination of the <20 µm fraction throughout the Harbour.

The relationship between metal concentration and sediment texture

Glasby et al. (1988) eliminated differences in element concentration in sediments due to grain size by analysing the <20 µm fraction. We examined their data to see if

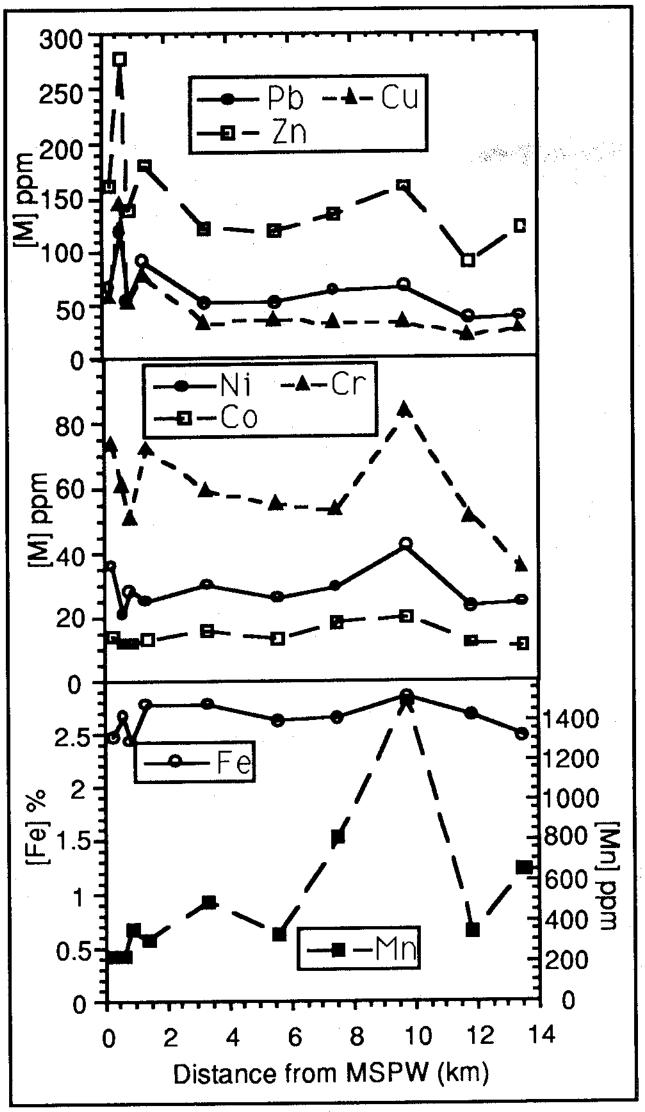


Fig. 4.7 Longitudinal survey from MSPW to Purakau Channel. Profile position is in Fig. 4.5.

there is a difference in metal concentrations in this fine sediment fraction due to the prevailing hydraulic conditions at sampling sites. For instance, sandy sites are a much less favoured for deposition of this fine sediment than are muddy sites. In addition, a far greater movement and flushing of sediments is expected from tidal and wave pumping than in muddy sediments, because of the difference in wave energy and sediment permeability. Well-flushed sediments would have more opportunity to lose metals through solubilisation and, if so, differences in concentrations would depend on sediment texture. This hypothesis was examined in the central harbour (Area C - Fig. 4.1) which has a wide range of sediment textures and the sites are fairly remote from sources of pollution. If the hypothesis was true, then the muddy bays would be expected to have a higher metal concentration in the <20 μm fraction than the well-flushed areas in the sandy banks and channels. Results of plotting metal concentration against mud content (Fig. 4.10 and Appendix 4) do not demonstrate any effects of sediment texture on concentrations. It is therefore concluded that the heavy metal composition of the fine particles (<20 μm) is independent of the hydraulic environment from which the sediments were collected.

Normalisation using iron concentrations

Normalisation with iron concentrations has been used to reduce the variation of metal concentrations in samples (Forstner & Whitman 1983). The rationale for doing this is that iron oxyhydroxides are one of the main sediment components which adsorb heavy metals. The possibility for reducing sample variance was examined by plotting Fe concentrations against other metal concentrations (Fig. 4.11 and Appendix 5). These plots gave no indication of any relationship. Fe concentrations are seen to lie within a narrow band indicating that the Fe content of the <20 μm fraction of the sediments is almost constant. It is therefore not surprising that this normalisation procedure has no effect for these samples. Isolating the < 20 μm fraction has removed those factors which cause a variation in the iron content, such as the sand (SiO_2) content.

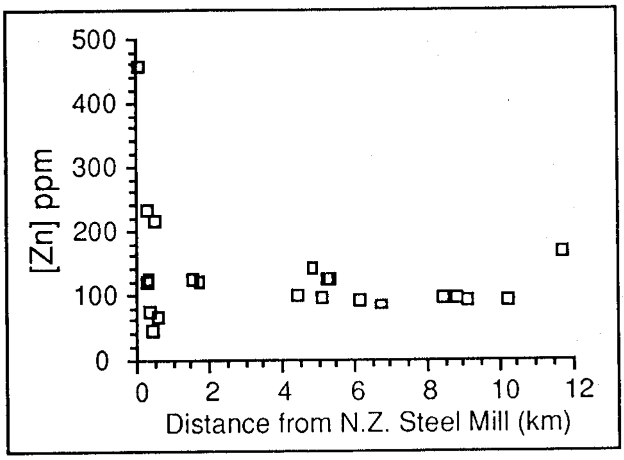


Fig. 4.8 Longitudinal survey of Zn in Waiuku Estuary and beyond. Site numbers identified in Fig. 4.5.

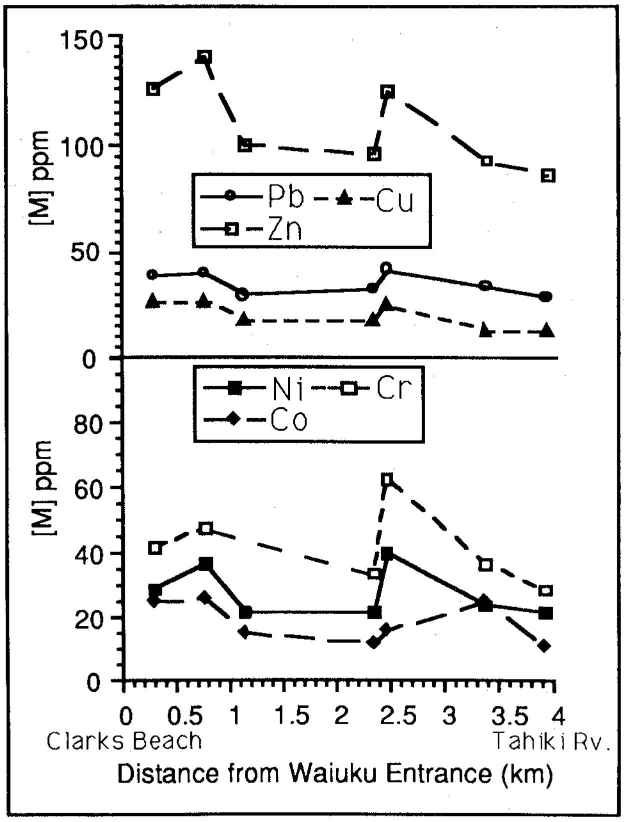


Fig. 4.9 Longitudinal survey in the Taihiki River. Profile position is in Fig. 4.5.

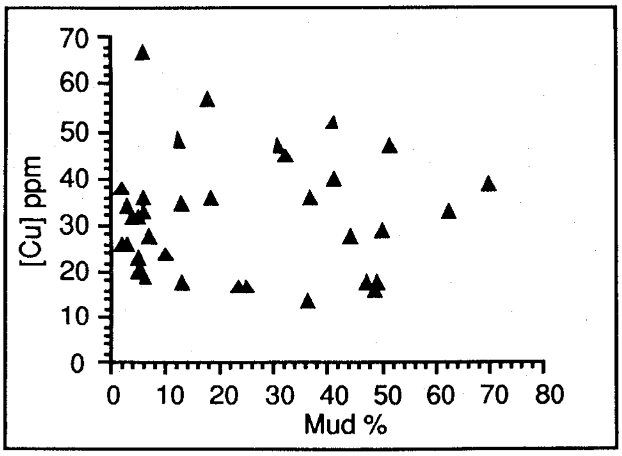


Fig. 4.10 The relationship between Cu concentration and mud content of the sediment before separation of the <20 µm fraction. Other elements are shown in Appendix 4.

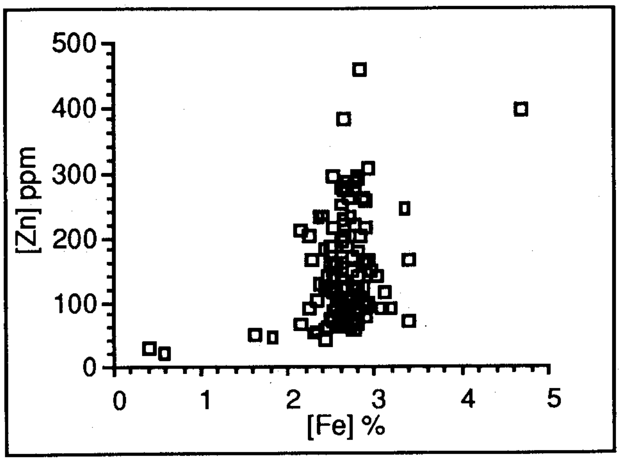


Fig. 4.11 Variation of Zn concentration with iron content. See Appendix 5 for other elements.

5 WAIUKU ESTUARY AND THE STEEL MILL DISCHARGE

5.1 The data base

History and sampling protocol

In May-June 1985, Bioresearches Limited started monitoring metals in shellfish and sediments within the mixing zones of the North and Southside outfalls of New Zealand Steel at Glenbrook. This monitoring has been carried out every year in May-June, with variations in the sampling programme from time to time. In the first two years, a total of ten sample stations were occupied, five on the Northside, four on the Southside and a control in the Taihiki River. In 1987, one of the Northside stations was excluded and, in 1989 and 1990 only one Northside, one Southside and the Taihiki Control sample were taken. The database is summarised in Table 5.1 and the locations of Bioresearches sample stations are shown in Fig. 5.1. One of the Southside stations (SS1) is located near a disused outfall.

Bulk sediments (excluding coarse shell) were collected. The metals analysed varied during the programme, but Fe, V, Mn, Cr, Zn, Pb, Cd, Ni, Cu and Al were analysed most years. These metals were extracted by digestion with conc. HNO_3 and determined by atomic adsorption spectrometry. This method will extract metals associated with ion-exchange sites, carbonates, amorphous and crystalline iron and manganese oxides, sulphides, organic material, and a small proportion of silicate-associated metal. CaO, SiO_2, TiO_2, Al_2O_3, MgO, P_2O_5, MnO, Na_2O, K_2O, Fe, Mn and Zn were determined by X-ray fluorescence (XRF). This presumably measures the total element concentration. In the following, results from the 2 methods for common elements Fe, Mn or Zn are distinguished by (HNO_3) and (XRF). Each sample site was a rectangular area measuring 50 m by 2.5 m lying with the long axis parallel to the high or low tide mark. Six replicates (or sub-samples) were taken randomly from the sites on each sampling occassion. Each sub-sample contained five surface cores 60 mm in diameter and 50 mm deep taken at the corners and in the centre of a quadrant. This sampling procedure was followed each year, except in 1985 when each replicate contained six surface cores taken on the circumference of a circle 0.5 m in diameter.

Table 5.1. Waiuku estuary database.

Year/site	1985	1986	1987	1988	1989	1990
NS1	✓	✓	✓	✓	✓	✓
NS2	✓	✓				
NS3	✓	✓	✓	✓		
NS4	✓	✓	✓	✓		
NS5	✓	✓	✓	✓		
SS1	✓	✓	✓	✓		
SS2	✓	✓	✓	✓		
SS7	✓	✓	✓	✓	✓	✓
SS8	✓	✓	✓	✓		
TC	✓	✓	✓	✓	✓	✓
ARWB						
Okohaka	✓	✓	✓	✓		
Kahawai	✓	✓	✓			
Karaka	✓	✓	✓			
TC	✓	✓	✓	✓		

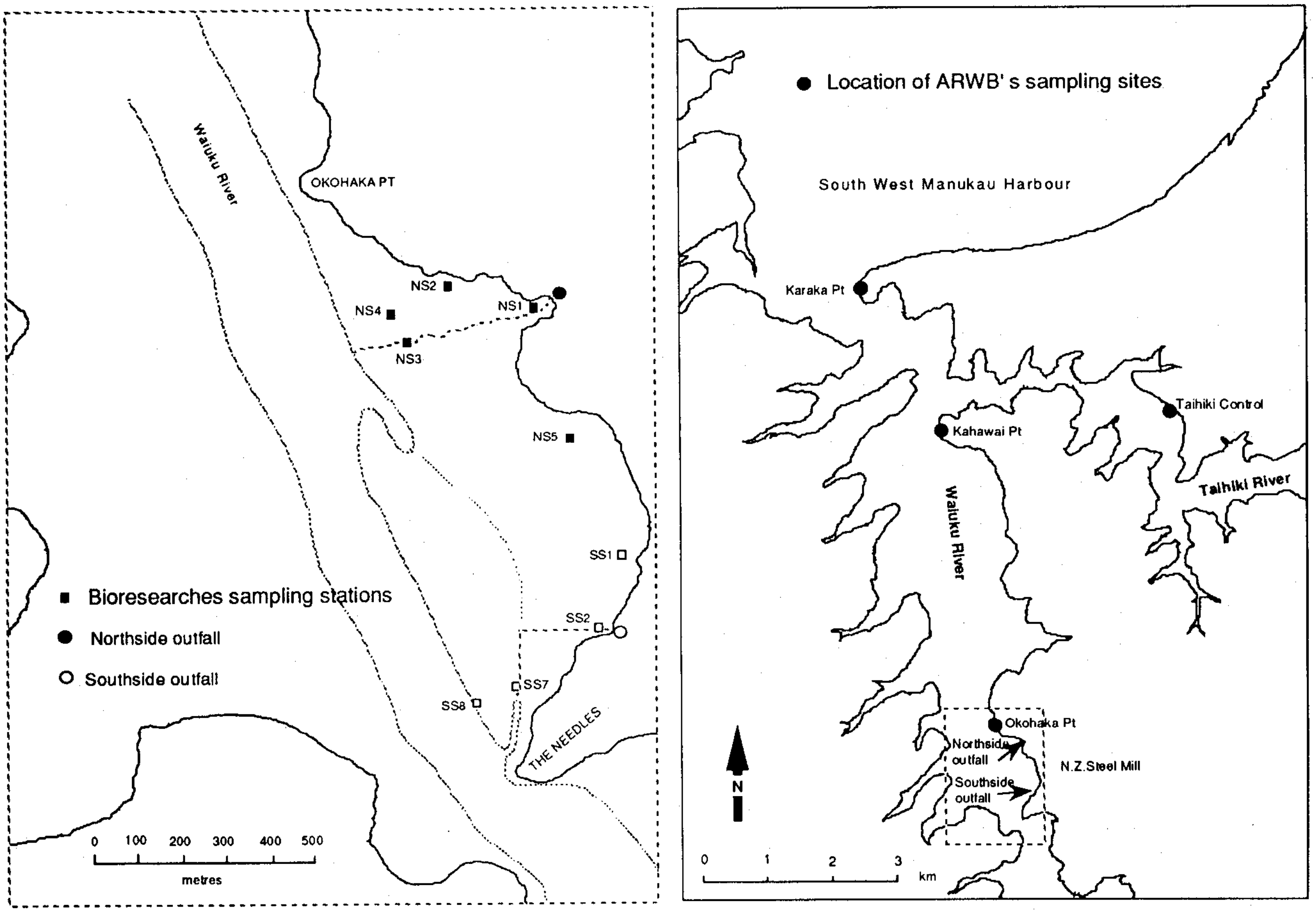


Fig. 5.1 Location of Bioresearches and ARWB's sampling stations.

The Auckland Regional Water Board also began monitoring Fe, Cr, Ni, Zn, Pb, Cu and Cd in sediments from the same estuary in 1985. Their sites are shown in Fig. 5.1 and the years and sites sampled in Table 5.1. Bulk samples were also analysed by atomic absorption following digestion with concentrated HNO_3 as above.

Both studies determined the particle size distribution on 1 composite sample from each site (i.e., they combined the 6 replicates before analysis).

The overall findings

The monitoring programme (Bioresearches 1985-1990) has demonstrated that many metals are highest at sites close to the mill and that there is a tendency for concentrations to fall off with distance from the outfalls. However, the patterns are complex and concentrations fluctuate about this general gradient. The Taihiki Control (TC) site almost always has lowest metal concentrations.

There has been a significant increase in Zn concentration at the NS1 site between 1985 and 1990 with a slight dip in 1986 but no increase at sites SS7 or TC. Copper concentrations often exhibit a significant difference between years, but there is no consistent trend. Up to 1988, none of the other stations showed a clear time trend in concentrations for any of the heavy metals with time.

The ARWB data (ARWB 1987a, 1987b, 1988) show no clear trends between site and with time.

5.2 The Steel Mill discharge monitoring programme (Bioresearches data)

Preliminary data analysis

A preliminary evaluation of the data found Cd concentrations were high when compared with equivalent data for the Waiuku Estuary obtained by ARWB (1987a) and Glasby et al. (1988) in 1985, and much higher than found in 1977 (Bioresearches 1977) and in 1981 (Bioresearches 1981). If they are correct, then they reflect very high contamination levels. Also, high Pb concentrations found in 1986 were probably the result of a higher detection limit that year. We omitted all Cd and these Pb results in the following data analysis.

Histograms (Fig. 5.2) show the distribution of the heavy metals. Natural concentrations of metals in sediments are usually normally distributed, while contaminated sediments frequently have positively-skewed log-normal (or similar) distribitions. Fig. 5.2 demonstrates that the Zn and Pb concentrations are positively skewed and are major contaminants when compared with calculated Igeo classes (see section 4.1 for an explanation of Igeo class). 48% of Zn analyses lie above the uncontaminated level (Igeo class 0) and the bulk of these are from sites closest to the outfalls (NS1, SS1). Vanadium has a wide positive skewness and also appears to be a contaminant. Concentrations of the other trace elements (Cu, Ni, Cr) are all relatively low compared with the <20 μm baseline or average shale (Table 4.1) or with catchment soil concentrations (Soil Bureau 1963) and displays relatively little positive skewness. They thus appear to be minor or insignificant components of the Steel Mill discharge.

Sediment Characteristics

The concentrations of parameters that reflect sediment characteristics: Mud%, SiO_2, Fe (HNO_3), Fe (XRF) and Al_2O_3 were examined in order to;

(1) investigate the relationship between these parameters,
(2) establish whether there are differences between sites,
(3) establish whether sediment characteristics change with time at any of the sites,
(4) establish the variability of sediment characteristics at the monitoring sites.

SiO_2 content increases with the sand content because sand particles are dominantly silica. Al_2O_3 is chiefly found in the clay fraction, and therefore increases with the amount of clay or mud (mud = clay + silt) in the sample. Fe occurs as unreactive silicates, crystalline iron oxide minerals, illmenite ($FeTiO_2$), and reactive amorphous iron oxyhydroxides. The latter, along with organic matter, are responsible for the binding most heavy metal contaminants. Fe (XRF) measures total iron while Fe (HNO_3) measures amorphous iron oxyhydroxides and an unknown proportion of the crystalline Fe.

These parameters were first plotted against each other and regression coefficients calculated (Fig. 5.3 and Appendix 6). This demonstrated medium to strong relationships, with Al_2O_3 giving the strongest correlation with other parameters. On this basis, it was decided that Al_2O_3 was the best parameter to normalise data to a constant sediment composition (reflecting the ability of mud to bind heavy metal contaminants).

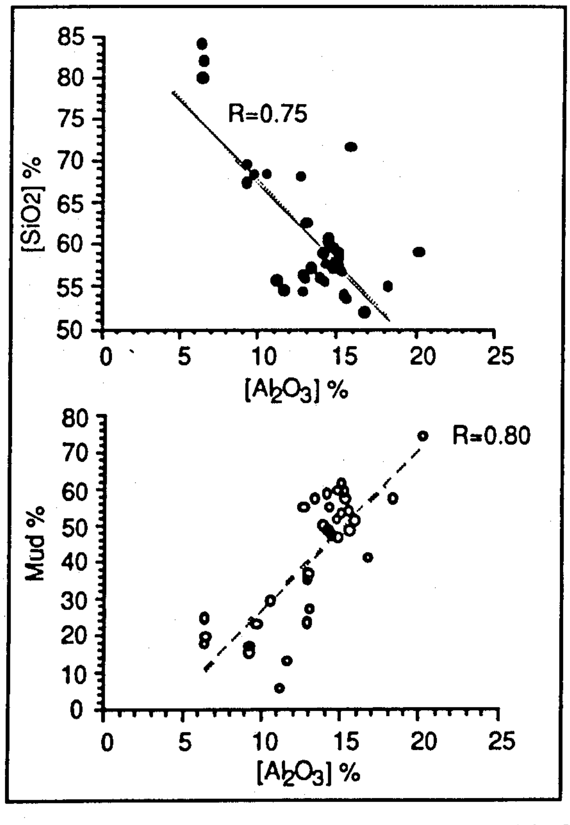
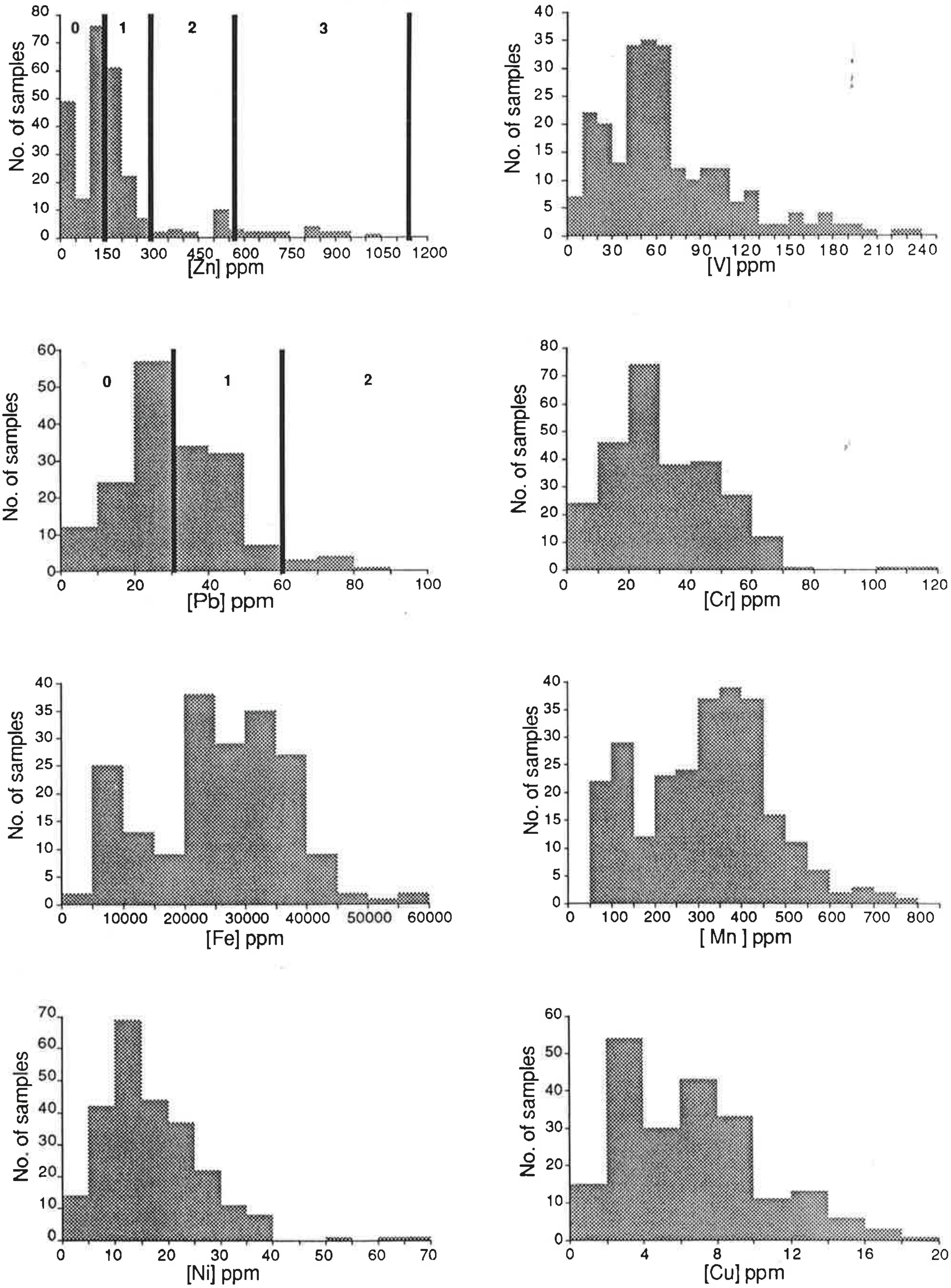


Fig. 5.3 The relationship between Al_2O_3 concentration and mud content or SiO_2 concentration. Other relationships between Al_2O_3, SiO_2, Fe and mud content are shown in Appendix 6.

Fig. 5.2. Histograms of metal distributions in total sediment from the Waiuku Estuary. Data from Bioresearches (1985-1990). Igeo index boundaries are solid lines and are calculated assuming average shale as background (see section 4.1).



Plots of Al_2O_3, SiO_2 and Fe concentrations at individual sites demonstrate that there are differences between sites and between years at any given site. These differences may mask trends and should be taken into account when carrying out time trend or intersite comparisons. Of particular note is the dominantly sand-like characteristics of the control site compared with the outfall sites.

Normalisation of concentrations

Normalisation was carried out by dividing all metal concentrations by Al_2O_3 concentrations. New confidence limits were estimated by dividing the original confidence limits[1] by Al_2O_3 concentrations. (New confidence limits from normalised data would need to be calculated for tests of significance, but these estimates are sufficient for our purposes in this report). It was expected that normalisation would have an effect on trend analysis because sediment characteristics vary with site and with time. In Fig. 5.4 and Appendix 7, it is seen that the concentrations of Al_2O_3, SiO_2, Fe and Mud% at the three sites vary with time and in different ways from site to site. Normalised and un-normalised data were compared for sites NS1, SS7 and TC for Zn and Cr. These show (Fig. 5.5 and Appendix 8)):

(1) A recent increase in Zn and Cr at the TC site, which is probably due to an increase in the mud content of sediment. After normalisation, the Zn and Cr concentrations are fairly constant at the TC site.
(2) An increasing Zn concentration with time at site NS1, which is reduced when concentrations are normalised.

All sites which have exhibit an increase in mean concentrations with time for Mn, Cr, V and Zn are listed in Table 5.2.

Table 5.2 Waiuku estuary sites which show an increase in mean concentrations with time.

Parameter/site	Mn	Cr	V	Zn
NS1			✓	✓
NS5				✓
SS1	✓	✓	✓	✓
SS2	✓	✓	✓	✓

The trends for site NS1 and SS2 may be understood in terms of their proximity to an outfall. However, site SS1 and NS5 are not closer than other sites and located between the 2 outfalls, near the location of a disused outfall. We do not understand why there should be increases at these 2 sites.

The normalised data were also plotted as a function of the distance from the northside outfall (Fig. 5.6). The plots confirm the general trends reported by Bioresearches (1985-1990) of a fall-off in metal concentration with distance from either the northside or southside outfall. Metals to exhibit this trend are Zn, Cr, Fe, and V. There appears to be no fall-off of Mn, Cu, Pb or Ni. Further work would be necessary to distinguish which trends are statistically significant .

The variance of data

In order to establish whether trends in element concentrations with time or within sample populations are significant, it is necessary to determine whether the trend in the concentration data exceeds random variability associated with e.g., sampling procedures or chemical analysis. In carrying out a trend analysis, it is necessary to collect replicate samples. In a well-designed study, the number of replicates depends on the perceived analytical variability, the statistical test used for the comparison, and the magnitude of differences that one is trying to detect.

The most common trend analysis is detecting a change in the influence of a discharge (as is being carried out in the monitoring programme at the NZ Steel outfalls). Examples of interesting changes are the effect of a discharge on sediment concentrations over time or over distance from the discharge. In sediments, variability will not only reflect analytical errors but may also reflect a difference in sediment properties that affect retention or mobilisation of heavy metals. For example, differences in texture between replicates would increase sample variance above that from analytical and sampling errors.

The extensive data available in the NZ Steel monitoring programme offered a unique opportunity to investigate the variance associated with analysis of sediments over a 50 x 2.5 m area. This sort of this area might be chosen for an experimental plot, or 50 m conceivably could be the limit in accuracy in re-sampling an unmarked site. We investigated the variability from:

- element to element
- year to year
- site to site.

For this exercise, the coefficient of variation (CoV) were examined. The CoV is calculated as:

CoV (%) = SD * 100 / mean

where SD is the standard deviation.

The range of CoV was compared for each parameter. For this purpose, data were combined irrespective of year or site and the results illustrated in Table 5.3 and Fig 5.7. For the XRF analyses, sediments in the monitoring plots (50 x 2.5 m) showed little variation in Al_2O_3 and SiO_2 concentrations on any sampling occasion (CoV ranged from 0 to 6%). This indicates that these plots are reasonably homogeneous in terms of sand and mud content. Fe and Mn content varied more widely (CoV range from about 1-20%), and we presume that this reflects both analytical error and variation in Fe and Mn concentrations throughout the sampling plot. The variation in Fe content, in turn, probably produces a corresponding variation in Zn concentrations (2-24%), because Zn is predominantly associated with Fe (Williamson & Hume 1990).

For HNO3 extracts, the most abundant trace metal Zn had CoV ranging from 2-40%. The other elements (Pb, Cd, Ni, Cr, Cu, V) had a wide range of CoV ≤35% for Pb to

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[1] Confidence limits = $t_{n,0.025}$ x SD / sqrt(n)
where n is the number of replicates.

Fig. 5.4 Variation of Al_2O_3 concentration and mud content at 3 sites, NS1, SS7, and TC. Note the differences in the Y-scales. Variation of Fe (XRF), Fe (HNO_3 extracted) and SiO_2 are shown in Appendix 7. Data from Bioresearches (1985-1990). The mud content was analysed on a composite of the replicates from each site.

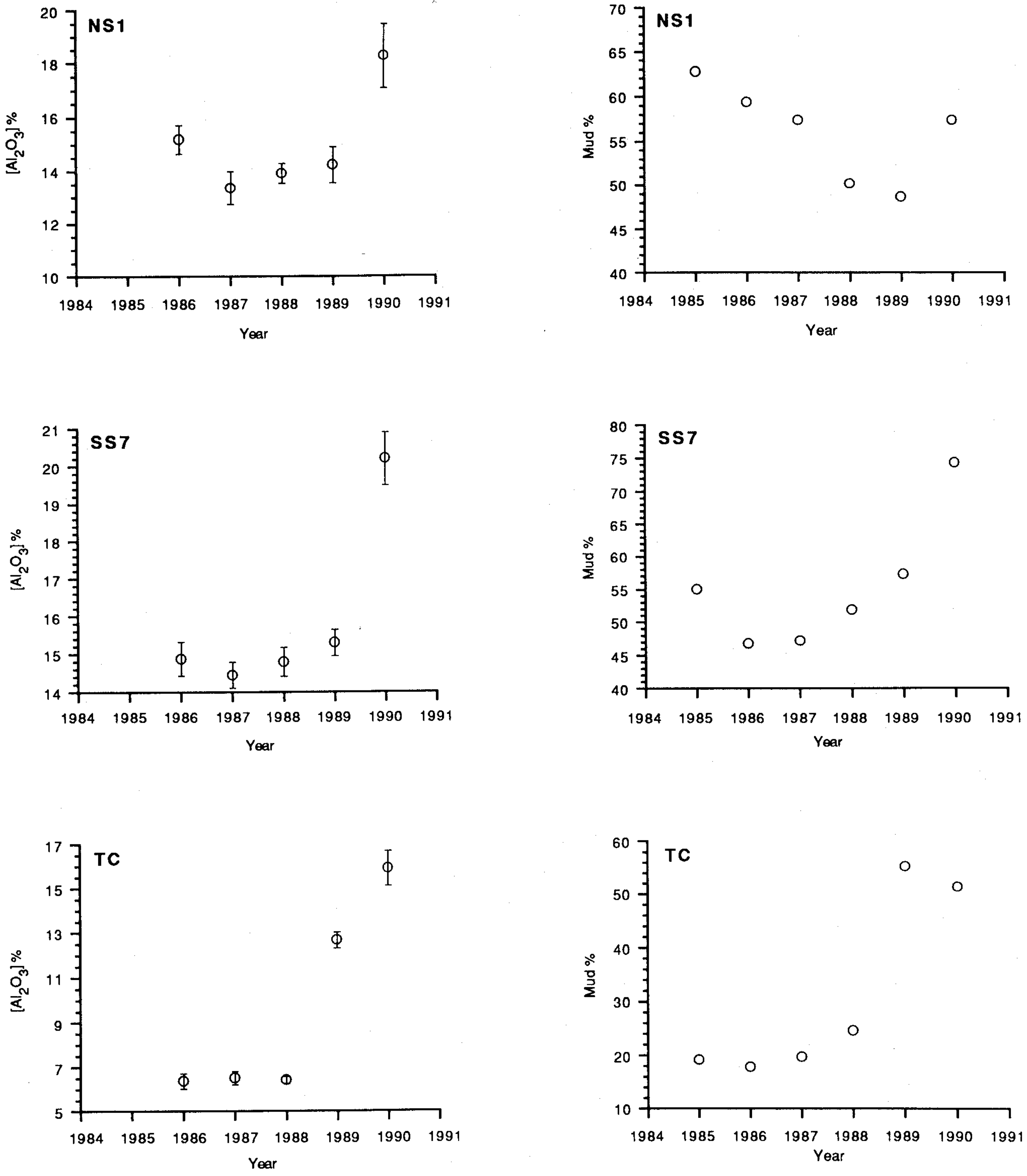


Fig. 5.5 Variation of Zn and Al_2O_3-normalised Zn concentrations at 3 sites, NS1, SS7, and TC. Note the differences in the Y-scales. Variation of Cr at these sites is shown in Appendix 8. Data from Bioresearches (1985-1990).

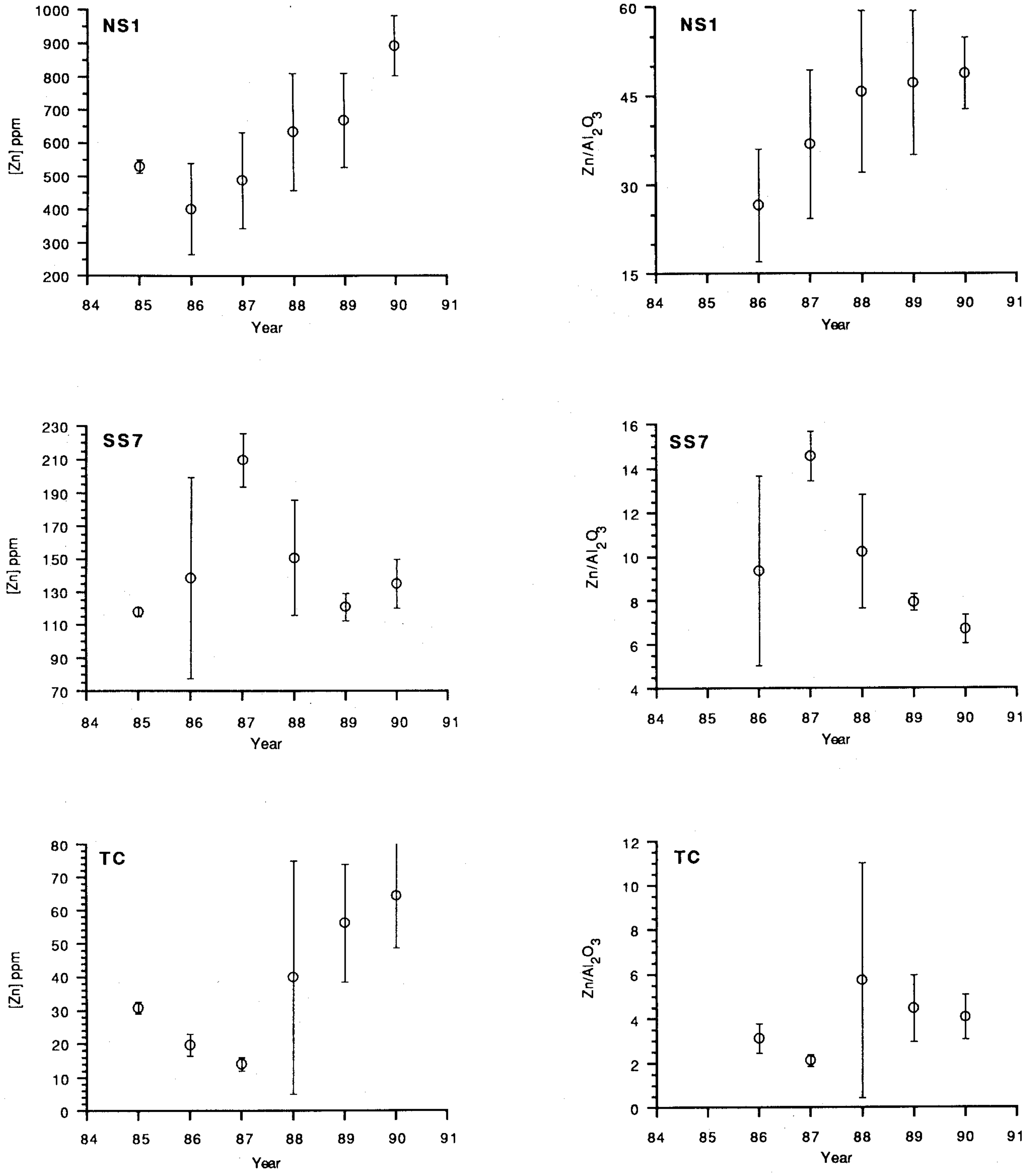


Fig. 5.6 Variation in Al_2O_3-normalised metal concentrations (1985-1990) with distance from the NZ Steel Mill discharge. Data from Bioresearches (1985-1990).

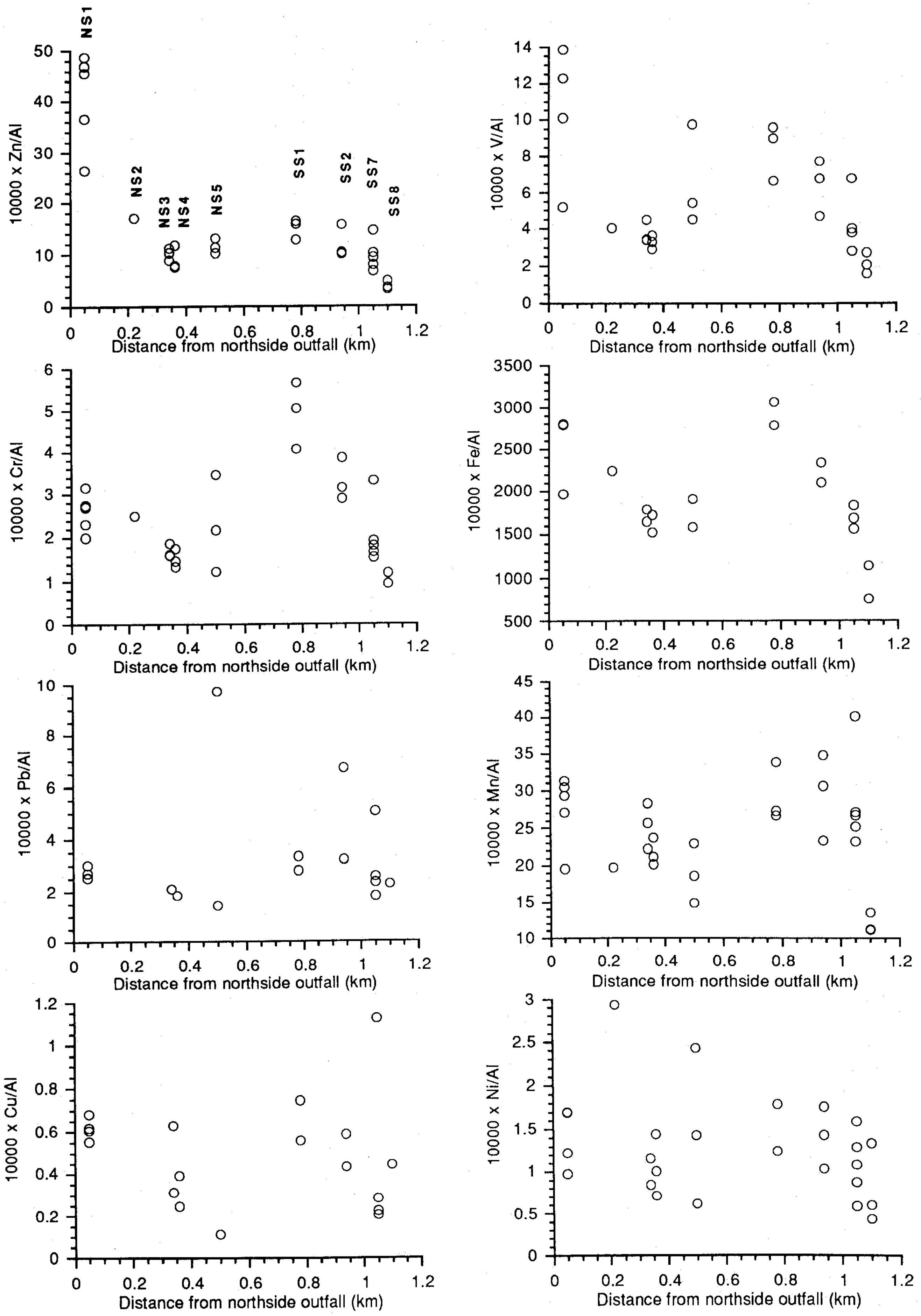


Table 5.3. The approximate range in the coefficient of variation (CoV) for analysed constituents in the Waiuku Estuary sediment. Each CoV was calculated from the 6 replicates taken from each site on each sampling occasion.

Metal	CoV
SiO_2, Al_2O_3	0-6 %
Fe (XRF, HNO_3)	0-20 %
Mn (XRF, HNO_3), Zn(XRF)	0-25 %
Zn, V, Cr, Cu, Ni	up to 35-50 %

≤50% for Cu. Thus the CoV found for major heavy metal components of the discharge (Zn and V) are similar to those which are minor components (Pb, Cr, Cu and Ni).

The variability from site to site and year to year indicated that variance was independent of site while some years have a greater range in CoV than other years (see Appendix 9). The reasons for this and for the wide range of CoV was investigated as described in Appendix 9.

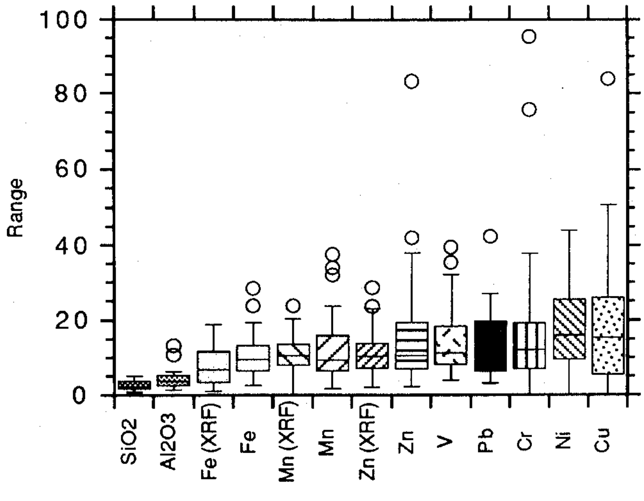


Fig. 5.7 The range in the coefficient of variation (CoV) for analysed constituents in the Waiuku Estuary sediment. Each CoV was calculated from the 6 replicates taken from each site for each year.

The CoV for Zn analysis by HNO_3 digestion were higher and only weakly related to the CoV for Zn analysed by XRF (Fig. 5.8). The concentrations determined by these methods are almost identical, as shown by the approximate 1:1 relationship in Fig. 5.9, so this suggests that HNO_3 method (for Zn) is inherently more imprecise, and that much of the CoV here is caused during the chemical analysis. Zn is difficult to analyse because of contamination problems, so we do not know if analytical errors are also a significant factor in the high CoV found for other trace metals. Analysis of Fe and Mn by HNO_3 extraction do not appear to be any more imprecise than by XRF.

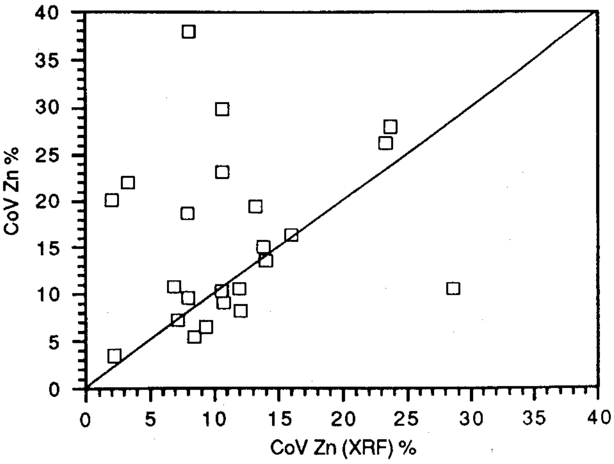


Fig. 5.8 The relationships between CoV for Zn analysis by HNO_3 digestion and by XRF.

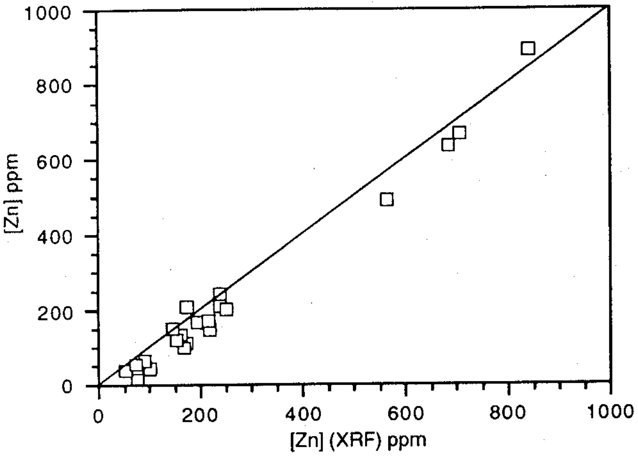


Fig. 5.9 The relationship between Zn concentrations determined by HNO_3 digestion and XRF.

In general summary, the following conclusions were made. No satisfactory explanation could be found for the source of the high CoV for trace metals. The high CoV could only be partly explained by differences in sediment characteristics as measured by the variation in SiO_2, Al_2O_3, Fe or Mn. Analytical precision appears to be a major factor for the high CoV for Zn extracted with HNO_3, and it may be important for other trace elements such as Pb, Cu and Ni, which occur in the sediments at concentrations near their detection limit. However, there is insufficient information to confidently suggest a way of reducing this variance, and this should be investigated in any future studies. It therefore appears that in the monitoring programme, there is a high variability in the trace heavy metal concentrations. If future work demonstrates this to be an intrinsic property of surface sediments over distances of 50m, then this will limit ability to detect trends in heavy metal pollution studies.

5.3 Waiuku Estuary monitoring programme (ARWB data)

Preliminary data analysis

Samples taken at Karaka Pt and Taihiki Control during 1985 show highly variable Zn concentrations. This was not observed in subsequent years or in the Bioresearches data for this and other years. Fe concentrations do not exhibit the same variation, and the % mud is similar to other years. These samples were therefore flagged as possibly contaminated. Coefficients of variance are displayed in Appendix 9.

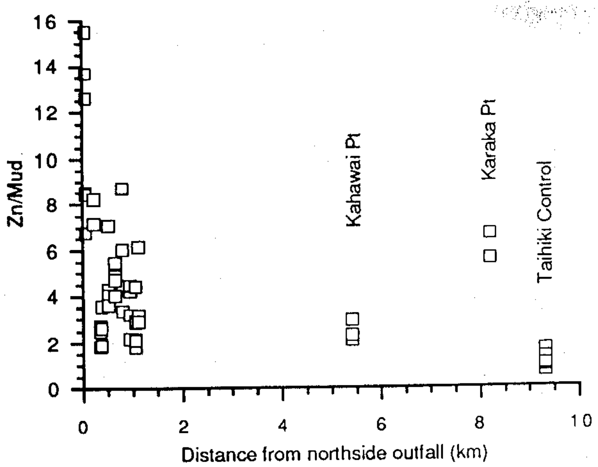


Fig. 5.10 Longitudinal trends of zinc (normalised with mud content) down the estuary. Other metals are shown in Appendix 10. Units on the y axis are ppm/%.

Longitudinal trends

The ARWB and NZ Steel data were combined to establish whether concentrations at the Bioresearches sites (in the proximity of the steel mill) are elevated relative to elsewhere in the estuary and to examine concentration trends down the estuary. Longitudinal trends of metals are shown in Fig. 5.10 for Zn and in Appendix 10 for the other metals. Because Al_2O_3 concentrations were not measured in the ARWB study, metal concentrations were normalised (i.e., divided) by mud content (%) of the total sediment.

High metal mud ratios were found at Karaka Point for 2 years, but this was due to the very low measured mud content (3%) on both occasions. The mud content is only an approximate estimate of some factors (e.g., surface area) that control metal concentrations. At low mud content, the metal concentration in the sand fraction becomes more important and the normalisation procedure is no longer useful.

From an examination of these plots, the following generalisations could be made :

(1) There was good agreement between concentrations of metals analysed in both studies at the "control' site (Taihiki Control). This site always had the lowest concentrations for Zn.

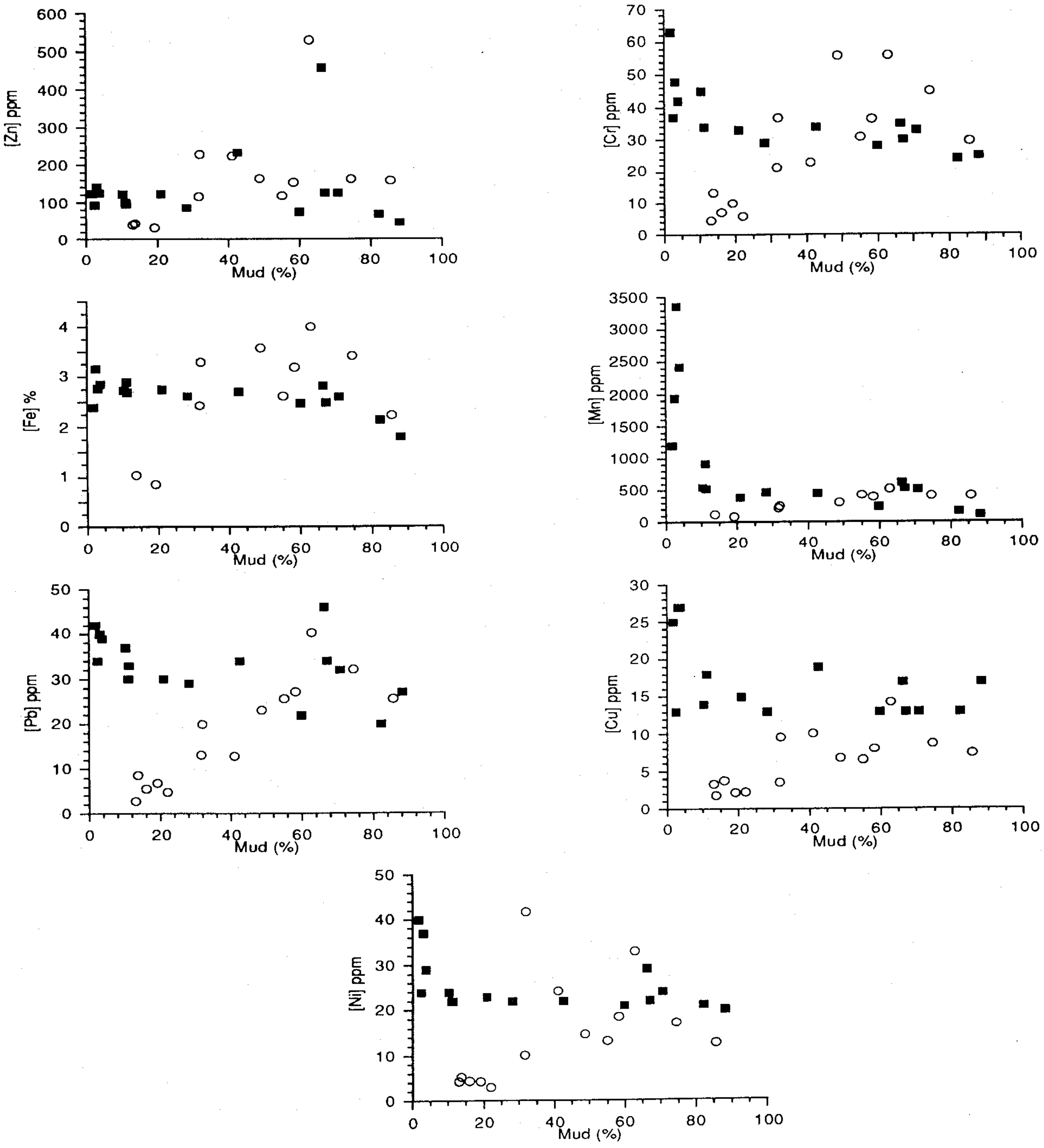
(2) For the other metals (V, Fe, Cu, Ni, Cr, Mn), low concentrations could be found both near and far from the Steel Mill outfalls, which confirms conclusions drawn for other longitudinal surveys (Fig. 4.6, 5.6), that the concentrations fall to baseline levels quite close (within 300m) to the mill outfalls.

6 COMPARISON OF <20 μM FRACTION AND TOTAL SEDIMENT CONCENTRATIONS

The data of Glasby et al. 1988 were collected in mid-1985 and their Waiuku estuary data were compared with data from Bioresearches (1985) and ARWB (1985), collected about the same time. Plots of heavy metal concentration against mud (<63 μm) concentration were prepared (Fig. 6.1. In the data of Glasby et al. 1988, we used the original mud concentration found in the sediment before the <20 μm fraction was separated. Plots show a remarkable similarity in concentrations at about 40% mud or greater, but not at low mud concentrations. These results are consistent with ARWB results (Fig. 5.9) comparing the <63 μm fraction and total sediment.

Higher concentrations are expected in finer sediments and this is demonstrated when comparing <20 μm fraction with total sediments which are predominantly sand. (Glasby et al. 1988 data also shows some very high concentrations at low mud concentration, but this is not found for the harbour as a whole (Appendix 4)). The similarity between <20 μm and total fractions at high mud concentration demonstrates that the concentration differences between different-sized mud particles are not great and/or that <20 μm particles make up a large proportion of the mud.

Fig.6.1 Comparison of <20 μm fraction (filled circles) (Glasby et al 1988) and total sediment concentrations (unfilled circles) (Bioresearches 1985, ARWB 1987a).



7 CONCLUSIONS

This report evaluates published information to obtain a better understanding on the fate of heavy metal pollutants in sediments of Manukau Harbour. The information comes from a survey of the heavy metal content of the <20 µm fraction from sediments throughout the harbour (Glasby et al. 1988) and from receiving water sediment monitoring programmes for the Glenbrook Steel Mill discharge (Bioresearches 1985-1990, ARWB 1987a. 1987b, 1988). The former allowed reappraisal of harbour-wide contamination, while the latter allowed the study of localised heavy metal inputs.

1 Proximity to pollution source

Glasby et al (1988) identified localised areas of pollution, using an index of pollution (Igeo class) of the <20µm fraction of the surface sediments. Their data additionally indicated that surface sediments from the whole harbour had low levels of Pb, Zn, Cu and Cr pollution. Longitudinal concentration profiles of their data exhibited a decline in contamination with distance from a severely polluted area (Mangere Inlet) or from the point of discharge (MSPW or Glenbrook Steel Mill). The decline was initially rapid but did not reach background levels. A longitudinal profile from the MSPW indicated that the MSPW is a far less important source of heavy metals than Mangere Inlet. In addition, a deviation from the generally linear trends occurred in Pb, Zn, Cu and Cr concentrations in the Purakau Channel. This increase may have been due to the dumped spoil from Onehunga Wharf (which in turn is contaminated by sediments from Mangere Inlet), but the increase in concentrations occurred some distance from the dumping ground. Longitudinal profiles in the Waiuku Estuary showed that high Zn concentrations near the Steel Mill outfall declined rapidly (within a few hundred metres) and thereafter, concentrations were indistinguishable from those found elsewhere in the Waiuku Estuary or indeed elsewhere in the harbour.

Concentrations of metals in total sediment samples (Bioresearches 1985-1990) exhibited a definite decrease (particularly in Zn, Cr, V, and possibly Pb) away from the Steel Mill outfalls. This decrease occurred over very short distances (<300 m), and further away, the longitudinal surveys down the estuary (ARWB 1987a. 1987b, 1988) did not show any indication of decreasing concentrations with distance or increasing concentrations with time. The survey of total and the <20 µm fraction of the surface sediments were therefore in good agreement.

2 Depth trends

The data of Glasby et al. (1988) show that the metals associated with pollution (Pb, Zn, Cu, Cr) decreased in concentration with depth in the sediment column while non-pollutant metals (Fe, Co, Ni) show no change with depth. There is a tendency for the metal concentrations in most sediments to approach the baseline concentration at shallow depth, although exceptions to this trend are found, particularly in Mangere Inlet. Estimates of baseline concentrations are given in Table 4.1. Similar baseline concentrations were found in area A (Mangere Inlet-Onehunga), C (middle harbour) and D (Waiuku Estuary), while area B (MSPW-Puketutu Is) had higher concentrations at depth, possibly related to changes in the hydraulic regime associated with the building of the Manukau Sewage Purification Works.

Comparison of surface sediment and baseline concentrations demonstrated widespread, low-level contamination by Zn, Pb, Cu and possibly Cr throughout the harbour.

3 Other factors controlling heavy metal concentrations

Glasby et al. (1988) data showed that away from major sources (Mangere Inlet, MSPW, Glenbrook Steel Mill) concentrations of Zn, Cu, Cr and Pb in the <20 µm fraction approached a reasonably constant, low level of contamination. The heavy metal contents in these samples was independent of whether they originated from high energy (sandy banks and channels) or low energy environments (muddy, sheltered sub-estuaries). It was therefore concluded that the composition of the fine silt and clay particles has been little affected by the hydraulic environment. Further, the iron, cobalt and nickel concentrations of the <20µm fraction were very similar throughout the harbour. These findings point to a consistency in composition of the fine silt and clay particles.

Bioresearches' monitoring programme demonstrated that there were differences in major sediment components Al_2O_3, SiO_2, total Fe concentrations, and in the particle size, between sites and between years at any given site. This suggests that the data should be normalised to constant sediment characteristics before comparing concentrations between years and between sites. Al_2O_3 appeared to be the best parameter for normalisation. The effects of normalising was examined at three sites which had increasing Zn and Cr concentrations with time. At two of the sites remote from the current discharge point, the change in heavy metal concentration was correlated with a change in major sediment characteristics. Normalising with Al_2O_3 removed these trends.

The results from the 3 studies were compared where they had each sampled the same area at about the same time. Similar concentrations were found when the original sediment sample contained >40% mud, irrespective of the difference in size fraction analysed (<20 µm or total). This suggests that in the muddy (>40% mud) sediments of the Manukau Harbour, particle size effects on metal concentrations are relatively minor, and it may be possible to compare results from the 3 studies.

4 Sample variance

The replicated sampling of sediments in the Waiuku estuary allowed us to examine sample variance for major sediment components (Al_2O_3, SiO_2, Fe) and for the heavy metals (Zn, Pb, Cd, V, Co, Mn, Cr, Ni). Sediments in the monitoring plots (50 x 2.5 m) showed little variation in Al_2O_3 and SiO_2 concentrations on any sampling occasion (Coefficient of variance (CoV) ranged from 0 to 6%). This indicated that these plots are reasonably homogeneous in terms of sand and mud content. The content of other major sediment components, Fe and Mn, varied more widely (CoV range from 0-25%). If this CoV range reflected a difference in sediment characteristics rather than analytical error, it probably produced a corresponding variation in trace metal concentrations, because a major proportion of these elements are often associated with Fe and Mn oxides.

For the trace-metals, the most abundant metal, Zn, had CoV ranging from 0-40%. The other elements (Pb, Cd, Ni, Cr, Cu, V) had a wide range of CoV from 0-35% for Pb to 0-50% for Cu. Therefore the CoV of major and minor contaminants were similar. CoV for the trace elements did not vary systematically with location, proximity to mill, magnitude of concentration, nor could be explained by changes in major sediment components such as Al_2O_3 and SiO_2. It is possible that analytical error is a major source of variation, but we were unable to confirm this. Therefore, no satisfactory explanation could be found for the source of the high CoV for trace metals, and we could not confidently suggest a way of reducing this variance e.g., through normalisation or alternative sampling techniques. It therefore appears that in the NZ Steel Mill and Waiuku Estuary monitoring programmes, there is a high variability in the trace heavy metal concentrations at sites. If future work demonstrates this to be an intrinsic property of surface sediments over distances of 50m, then this will limit ability to detect trends in heavy metal pollution studies.

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APPENDIX 1 Glasby et al. (1988) data base.

Stn	Latitude/Longitude	Depth cm	Pb	Zn	Cu	Ni	Fe	Co	Cr	Mn	Cd	Gravel	Sand	Mud	Silt	Clay
0-873	37°00.3'/174°34.1'	0-2	42	95	36	26	2.91	16	41	214	<0.5	3	78.8	18.2	8.8	9.5
0-874	37°00.6'/174°34.1'	0-2	30	90	47	28	3.07	21	30	271	<0.5	9	60.1	30.9	26.3	4.6
0-876	36°58.35'/174°37.15'	0-2	44	105	33	26	2.84	12	46	254	<0.5	1	36.6	62.4	41.8	20.6
0-877	36°58.6'/174°37.3'	0-2	32	80	45	26	2.58	17	25	387	<0.5	0	68.0	32.0	9.9	22.1
0-877	36°58.6'/174°37.3'	16-18	40	118	44	29	3.11	16	40	248	<0.5					
0-878	36°58.9'/174°37.44'	0-2	40	105	48	29	2.79	14	52	270	<0.5	16	71.4	12.6	4.8	7.8
0-878	36°58.9'/174°37.44'	14-16	27	70	29	24	2.67	14	34	289	<0.5					
0-879	36°57.62'/174°38.7'	0-2	42	109	36	31	2.8	13	53	218	<0.5	17	46.5	36.5	33.2	3.3
0-879	36°57.62'/174°38.7'	18-20	24	58	23	26	2.71	12	40	234	0.7					
0-880	36°58.00'/174°38.8'	0-2	44	105	39	26	2.8	14	35	327	<0.5	0	30.0	70.0	39.9	30.1
0-880	36°58.00'/174°38.8'	20-22	25	61	26	26	2.46	14	32	281	<0.5					
0-881	36°55.9'/174°42.2'	0-2	73	137	52	29	2.5	13	54	235	<0.5	7	52.1	40.9	36.8	4.1
0-881	36°55.9'/174°42.2'	20-22	26	66	21	28	2.8	14	36	279	<0.5					
0-882	36°55.9'/174°42.2'	0-2	60	120	47	24	2.54	12	42	233	<0.5	3	45.6	51.4	32.9	18.5
0-882	36°55.9'/174°42.2'	20-22	25	71	23	27	2.5	15	33	421	<0.5					
0-883	36°55.9'/174°42.6'	0-2	78	151	57	27	2.72	13	53	245	<0.5	10	72.0	18.0	11.3	6.7
0-883	36°55.9'/174°42.6'	8-10	39	96	30	28	2.92	15	46	262	<0.5					
0-884	36°58.46'/174°44.6'	0-2	57	159	58	33	2.51	15	70	215	0.6	1	12.9	86.1	61.1	25.0
0-884	36°58.46'/174°44.6'	10-10	43	108	39	31	2.53	14	64	261	<0.5					
0-885	36°58.65'/174°44.7'	0-2	61	171	65	34	2.59	14	75	216	<0.5	0	64.0	36.0	15.8	20.2
0-885	36°58.65'/174°44.7'	14-16	59	396	131	40	4.68	23	67	390	<0.5					
0-886	36°58.7'/174°44.4'	0-2	48	138	53	33	2.6	14	59	258	<0.5	0	32.0	68.0	42.2	25.8
0-887	36°58.9'/174°44.7'	0-2	56	160	61	37	2.5	14	79	215	<0.5	2	67.6	30.4	18.8	11.5
0-887	36°58.9'/174°44.7'	8-10	32	99	32	33	2.88	16	41	278	<0.5					
0-888	36°57.62'/174°44.85'	0-2	75	234	75	36	2.34	14	127	194	<0.5	0	5.0	95.0	71.2	23.7
0-889	36°57.5'/174°44.9'	0-2	66	163	56	36	2.47	14	73	224	0.6	9	4.5	86.4	58.8	27.7
0-890	36°57.2'/174°45.1'	0-2	35	104	39	35	2.79	16	46	243	<0.5	0	37.0	63.0	42.2	20.8
0-891	36°57.1'/174°45.2'	0-2	82	203	92	49	2.23	17	94	197	1.0	1	7.3	91.7	66.9	24.7
0-892	36°56.5'/174°47.9'	0-2	107	204	106	31	2.81	15	63	296	<0.5	6	55.5	38.5	22.5	15.8
0-893	36°56.7'/174°48.1'	0-2	108	219	101	38	2.76	15	63	289	<0.5	31	28.3	40.7	26.5	14.2
0-894	36°56.5'/174°48.2'	0-2	114	217	114	35	2.89	15	71	325	<0.5	19	39.7	41.3	26.8	14.5
0-895	36°56.12'/174°47.85'	0-2	165	290	205	31	2.78	15	72	385	<0.5	0	53.0	47.0	24.4	22.6
0-896	36°55.9'/174°48.6'	0-2	128	252	196	32	2.59	13	64	255	<0.5	0	3.0	97.0	66.9	30.1
0-897	36°55.8'/174°48.6'	0-4	149	186	93	28	2.49	11	72	178	<0.5	0	2.0	98.0	59.8	38.2
0-897	36°55.8'/174°48.6'	20-24	44	167	22	25	2.25	12	34	158	<0.5					

(Continued)

Stn	Latitude/Longitude	Depth cm	Pb	Zn	Cu	Ni	Fe	Co	Cr	Mn	Cd	Gravel	Sand	Mud	Silt	Clay
0-898	36°56.1'/174°46.82'	0-2	91	197	121	28	2.59	13	59	404	<0.5	0	7.0	93.0	48.4	44.6
0-899	36°56.1'/174°46.20'	0-2	107	202	110	30	2.63	14	65	387	<0.5	31	42.1	26.9	12.6	14.3
0-900	36°55.9'/174°46.2'	0-2	74	163	75	30	2.55	12	56	259	<0.5	7	33.5	59.5	35.7	23.8
0-901	36°55.7'/174°46.2'	0-2	80	169	61	30	2.73	13	67	281	<0.5	43	22.8	34.2	25.0	9.2
0-902	36°56.35'/174°46.2'	0-2	90	222	81	35	2.63	16	63	347	<0.5	4	33.6	62.4	42.4	20.0
0-903	36°56.5'/174°44.6'	0-2	68	162	67	31	2.59	14	66	338	<0.5	1	93.1	5.9	3.1	2.9
0-904	36°56.8'/174°44.6'	0-2	51	137	52	31	2.51	12	54	235	<0.5	0	47.0	53.0	40.8	12.2
0-905	36°57.35'/174°44.55'	0-2	54	140	53	28	2.43	12	51	363	<0.5	2	28.4	69.6	53.6	16.0
0-906	36°57.22'/174°44.3'	0-2	91	181	76	25	2.78	13	72	309	<0.5	42	53.4	4.6	2.9	1.7
0-907	36°55.93'/174°49.55'	0-4	81	183	85	32	2.4	12	50	221	<0.5	5	0.9	94.0	49.8	44.2
0-907	36°55.93'/174°49.55'	16-20	47	43	42	31	2.42	41	20	40	<0.5					
0-908	36°56.10'/174°49.65'	0-4	124	295	173	38	2.52	12	73	252	<0.5	2	19.6	78.4	48.6	29.8
0-908	36°56.10'/174°49.65'	20-24	42	130	21	30	2.34	12	38	176	<0.5					
0-908	36°56.10'/174°49.65'	40-44	29	87	16	28	2.75	13	45	236	<0.5					
0-908	36°56.10'/174°49.65'	60-64	22	58	13	28	2.76	12	29	277	<0.5					
0-909	36°56.25'/174°49.65'	0-4	117	278	143	26	2.61	12	59	246	0.6	0	24.0	76.0		
0-910	36°56.40'/174°49.65'	0-4	126	158	91	30	2.54	11	58	148	<0.5	0	37.0	63.0		
0-910	36°56.40'/174°49.65'	20-24	27	72	17	26	3.39	20	33	172	<0.5					
0-911	36°56.50'/174°49.65'	0-4	68	165	53	34	3.37	20	42	512	<0.5	3	42.7	54.3		
0-911	36°56.50'/174°49.65'	20-24	24	77	15	38	2.61	17	30	120	<0.5					
0-912	36°57.5'/174°49.6'	0-4	113	289	130	33	2.66	12	64	207	<0.5	0	12.0	88.0		
0-912	36°57.5'/174°49.6'	24-26	20	29	7	32	0.41	4	8	17	<0.5					
0-913	36°56.9'/174°49.1'	0-4	127	309	110	10	2.92	14	59	277	<0.5	0	41.0	59.0		
0-913	36°56.9'/174°49.1'	20-24	26	60	15	33	2.71	12	31	162	<0.5					
0-913	36°56.9'/174°49.1'	36-40	19	61	13	30	2.62	11	30	208	<0.5					
0-914	36°56.65'/174°49.4'	0-4	109	288	103	26	2.75	12	64	234	<0.5	0	17.0	83.0		
0-914	36°56.65'/174°49.4'	20-24	32	104	17	21	2.32	13	34	155	<0.5					
0-915	36°56.45'/174°49.35'	0-2	110	261	107	25	2.85	14	58	320	<0.5	1	61.4	37.6		
0-916	36°56.25'/174°49.3'	0-4	112	273	131	26	2.63	11	50	272	<0.5	10	27.9	62.1		
0-916	36°56.25'/174°49.3'	20-24	17	61	11	20	2.59	10	29	235	<0.5					
0-917	36°56.00'/174°49.30'	0-4	119	277	145	21	2.66	12	61	230	0.7	0	12.0	88.0		
0-918	36°56.40'/174°48.9'	0-4	116	295	117	18	2.77	14	64	369	0.8	0	16.0	84.0		
0-918	36°56.40'/174°48.9'	20-24	16	58	12	15	2.42	12	27	212	<0.5					
0-919	37°09.61'/174°44.50'	0-2	29	86	13	22	2.63	11	29	473	<0.5	15	56.9	28.0		
0-920	37°09.30'/174°44.10'	0-2	34	93	13	24	3.17	25	37	1941	<0.5	22	75.7	2.3		

(Continued)

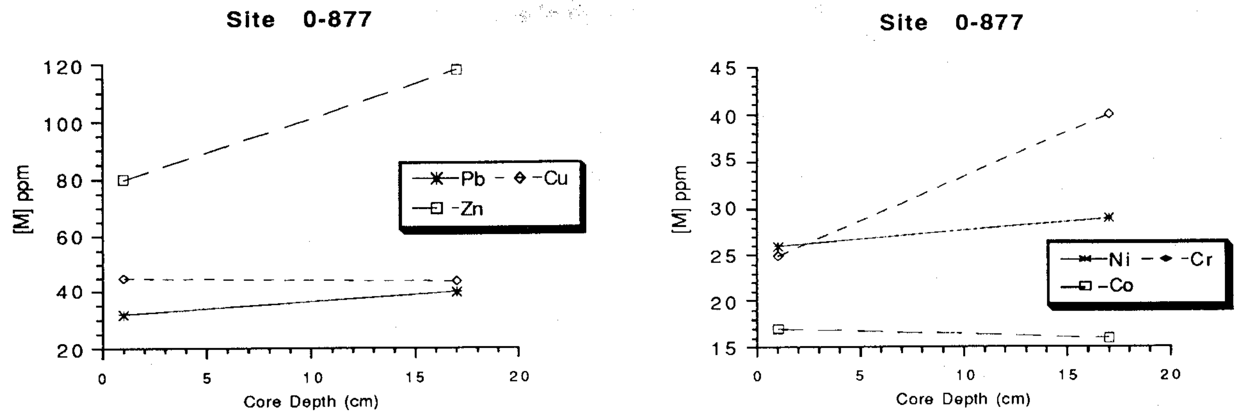
Stn	Latitude/Longitude	Depth cm	Pb	Zn	Cu	Ni	Fe	Co	Cr	Mn	Cd	Gravel	Sand	Mud	Silt	Clay
0-921	37°09.20'/174°43.1'	0-2	42	125	25	40	2.4	16	63	1202	0.9	89	9.3	1.6		
0-922	37°09.20'/174°43.1'	0-2	33	96	18	22	2.7	12	34	522	<0.5	21	67.9	11.1		
0-923	37°13.85'/174°43.7'	0-4	34	126	13	22	2.5	12	30	528	<0.5	3	30.1	66.9		
0-923	37°13.85'/174°43.7'	19-23	26	22	17	22	0.57	12	20	41	<0.5					
0-924	37°13.6'/174°43.55'	0-2	37	123	14	24	2.74	21	45	547	<0.5	7	82.8	10.2		
0-925	37°12.9'/174°43.25'	10-14	34	217	14	23	2.51	12	42	242	<0.5	1	71.23	27.7		
0-925	37°12.9'/174°43.25'	20-24	32	87	13	24	2.76	13	38	300	<0.5					
0-926	37°12.25'/174°43.18'	0-4	32	126	13	24	2.61	12	33	513	<0.5	2	27.4	70.6		
0-926	37°12.25'/174°43.18'	20-24	25	63	11	22	2.55	11	33	331	<0.5					
0-928	37°12.70'/174°43.35'	0-4	34	234	19	22	2.71	13	34	452	<0.5	15	42.5	42.5		
0-928	37°12.70'/174°43.35'	24-28	30	110	15	22	2.54	12	29	300	<0.5					
0-929	37°12.50'/174°43.28'	0-4	46	459	17	29	2.83	14	35	618	<0.5	13	20.9	66.1		
0-929	37°12.50'/174°43.28'	20-24	24	66	14	23	2.63	13	29	255	<0.5					
0-930	37°12.52'/174°43.05'	0-2	30	123	15	23	2.76	14	33	388	<0.5	1	78.2	20.8		
0-931	37°12.58'/174°42.90'	0-2	22	75	13	21	2.49	10	28	245	<0.5	2	38.2	59.8		
0-932	37°12.73'/174°43.00'	0-2	27	45	17	20	1.81	9	25	110	<0.5	0	12.0	88.0		
0-933	37°12.92'/174°43.10'	0-2	20	68	13	21	2.15	10	24	166	<0.5	1	16.8	82.2		
0-934	37°07.28'/174°39.50'	0-4	27	92	14	20	2.54	11	30	232	<0.5	10	54.0	36.0		
0-934	37°07.28'/174°39.50'	20-24	28	83	14	24	2.78	13	34	272	<0.5					
0-935	37°07.20'/174°39.40'	0-4	36	95	16	22	2.66	12	36	3542	<0.5	10	45.9	44.1		
0-935	37°07.20'/174°39.40'	20-24	18	56	12	18	2.32	10	33	2379	<0.5					
0-936	37°07.00'/174°39.65'	0-4	34	97	17	21	2.68	12	34	387	<0.5	27	49.6	23.4		
0-936	37°07.00'/174°39.65'	10-14	23	69	15	24	2.58	12	36	407	<0.5					
0-937	37°05.95'/174°44.07'	0-2	39	92	20	25	2.22	13	24	406	<0.5	25	69.7	5.2		
0-938	37°08.7'/174°41.4'	0-2	39	126	27	29	2.86	25	42	2422	<0.5	27	69.3	3.6		
0-939	37°08.92'/174°41.80'	0-2	40	141	27	37	2.78	26	48	3358	<0.5	26	71.0	3.0		
0-940	37°09.10'/174°42.06'	0-2	30	100	18	22	2.91	15	325	911	<0.5	68	21.1	10.9		
0-941	36°57.4'/174°39.62'	0-4	46	124	28	24	2.76	18	44	689	<0.5	0	93.0	7.0		
0-942	36°56.05'/174°41.40'	0-4	102	164	40	26	2.89	17	55	488	<0.5	2	56.8	41.2		
0-942	36°56.05'/174°41.40'	20-24	23	72	17	24	2.61	12	40	285	<0.5					
0-943	36°58.74'/174°44.08'	0-4	45	113	26	26	2.71	12	51	412	<0.5	0	43.0	57.0		
0-944	36°58.52'/174°43.50'	0-4	43	115	28	23	2.51	11	50	389	<0.5	0	56.0	44.0		
0-944	36°58.52'/174°43.50'	20-24	43	106	22	27	2.68	11	56	350	<0.5					
0-945	36°58.36'/174°42.84'	0-2	51	119	35	26	2.62	13	55	328	<0.5	8	79.1	12.9		
0-946	36°59.03'/174°41.66'	0-2	62	135	32	29	2.64	18	53	808	<0.5	16	79.0	5.0		

(Continued)

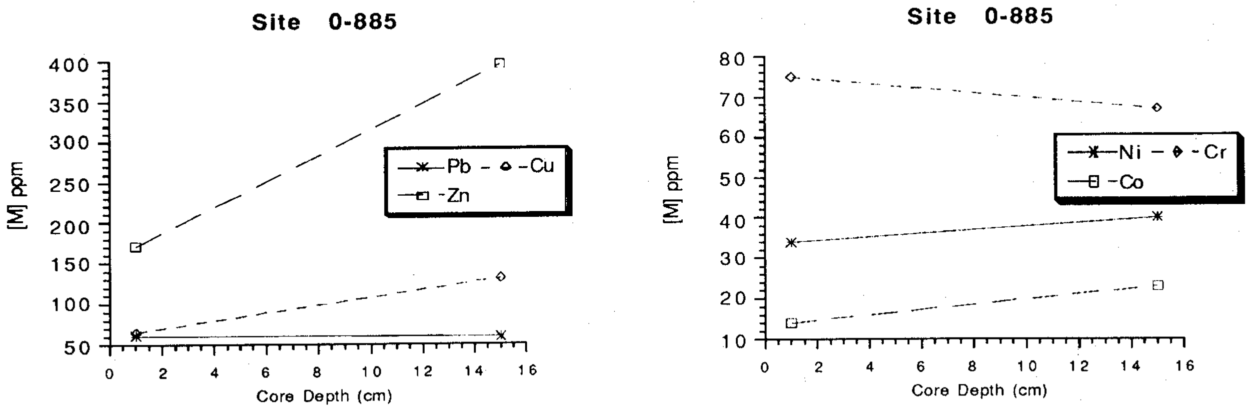
Stn	Latitude/Longitude	Depth cm	Pb	Zn	Cu	Ni	Fe	Co	Cr	Mn	Cd	Gravel	Sand	Mud	Silt	Clay
0-947	36°59.85'/174°40.42'	0-2	66	161	32	42	2.84	20	83	1500	<0.5	2	94.1	3.9		
0-948	37°00.25'/174°39.10'	0-2	36	89	19	23	2.67	12	51	347	<0.5	12	81.8	6.2		
0-949	37°00.70'/174°38.04'	0-2	37	122	26	24	2.47	11	35	648	<0.5	3	95.1	1.9		
0-950	37°00.00'/174°43.53'	0-2	44	246	38	29	3.33	12	51	426	<0.5	9	89.2	1.8		
0-951	37°00.77'/174°42.04'	0-2	53	258	34	31	2.88	15	49	560	<0.5	0	97.0	3.0		
0-952	36°55.9'/174°48.97'	0-4	147	235	453	30	2.38	10	60	190	0.7	5	26.6	68.4		
0-952	36°55.9'/174°48.97'	20-24	244	276	88	30	2.63	11	125	293	1.2					
0-952	36°55.9'/174°48.97'	40-44	247	276	104	32	2.77	11	144	367	1.7					
0-952	36°55.9'/174°48.97'	60-64	182	214	168	30	2.13	10	162	284	1.4					
0-953	36°56.13'/174°48.4'	0-2	131	261	92	27	2.69	11	77	275	<0.5	0	22.0	78.0		
0-954	36°56.42'/174°48.58'	0-2	95	188	113	29	2.67	11	55	332	<0.5	12	16.7	71.3		
0-955	36°56.58'/174°48.6'	0-2	111	228	125	27	2.62	10	67	209	<0.5	16	19.3	64.7		
0-956	37°04.20'/174°43.15'	0-4	49	168	29	29	2.91	22	43	4482	<0.5	0	50.0	50.0		
0-956	37°04.20'/174°43.15'	20-24	27	77	17	26	2.87	13	40	119	<0.5					
0-957	37°03.63'/174°49.90'	0-4	33	93	18	25	2.79	13	38	297	<0.5	0	87.0	13.0		
0-957	37°03.63'/174°49.90'	20-24	27	69	15	23	2.73	12	34	317	<0.5					
0-958	37°01.53'/174°51.23'	0-4	39	122	18	25	2.74	12	31	514	<0.5	0	51.0	49.0		
0-958	37°01.53'/174°51.23'	30-34	29	86	15	22	2.52	10	28	230	<0.5					
0-959	37°01.93'/174°51.20'	0-4	38	112	18	24	2.73	12	33	340	<0.5	0	53.0	47.0		
0-959	37°01.93'/174°51.20'	20-24	26	78	16	23	2.67	11	35	331	<0.5					
0-960	37°01.11'/174°45.80'	0-2	40	99	20	26	2.6	16	41	1316	<0.5	0	95.0	5.0		
0-961	37°01.3'/174°45.45'	0-2	45	112	23	34	2.79	18	48	488	<0.5	0	95.0	5.0		
0-962	37°01.45'/174°44.80'	0-2	30	81	17	23	2.66	12	36	328	<0.5	0	75.0	25.0		
0-963	37°01.70'/174°44.05'	0-2	52	149	26	33	2.94	24	49	1610	<0.5	0	97.0	3.0		
0-964	36°57.30'/174°42.65'	0-2	51	123	33	30	2.78	16	59	490	<0.5	12	81.8	6.2		
0-965	36°56.60'/174°41.50'	0-2	57	140	36	28	3.01	17	56	754	<0.5	0	94.0	6.0		
0-966	36°58.40'/174°40.50'	0-2	45	101	24	41	2.78	14	60	411	<0.5	1	89.1	9.9		
0-967	36°57.22'/174°49.05'	0-4	19	52	13	50	2.3	16	42	43	<0.5	0	11.0	89.0		
0-967	36°57.22'/174°49.05'	20-24	155	384	188	28	2.63	12	66	257	0.7					
0-967	36°57.22'/174°49.05'	31-33	27	49	17	24	1.62	9	28	128	<0.5					

APPENDIX 2 Depth profiles

Distribution of heavy-metal contents with depth in sediments at 4 sites (0-877, 0-885, 0-952 and 0-967) which showed higher concentrations in subsurface samples. Data from Glasby et al. (1988).


Site 0-877

Site 0-877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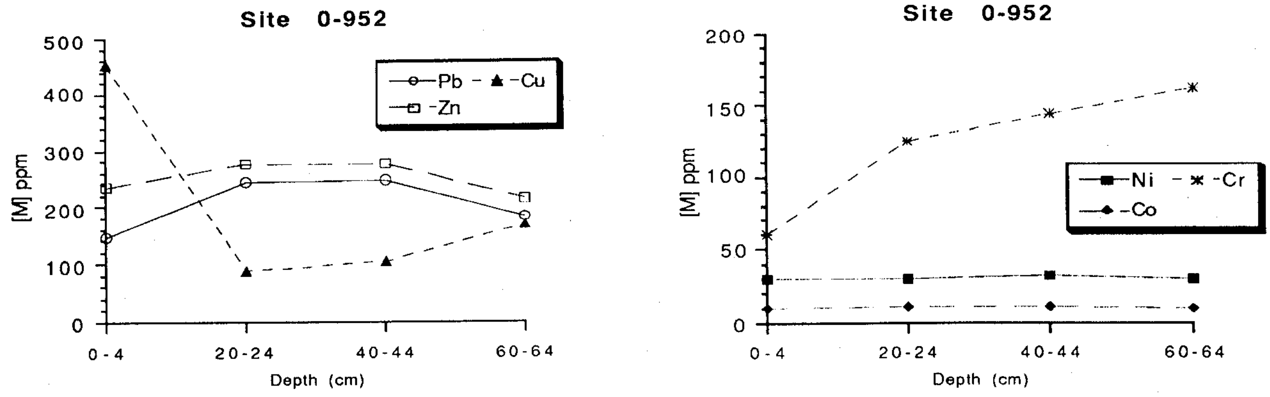
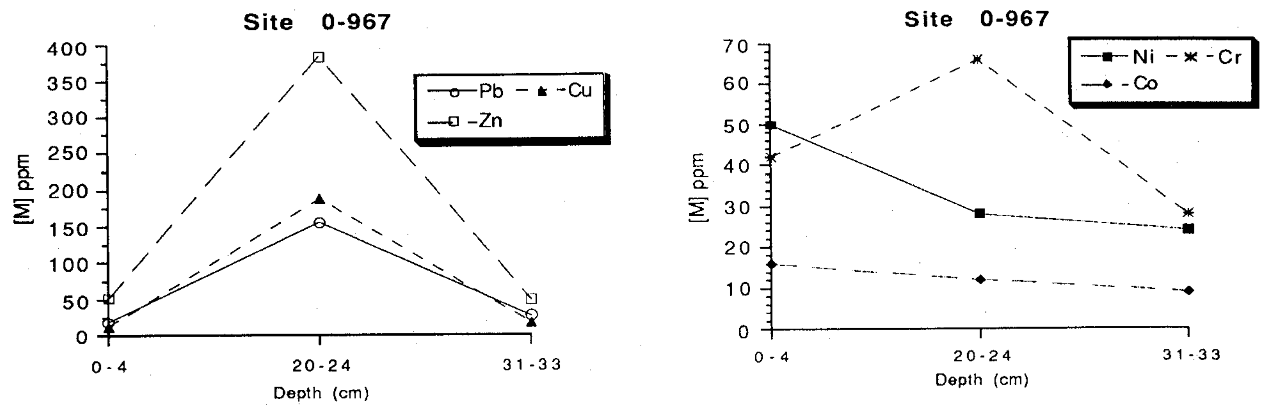
Site 0-885


Site 0-952

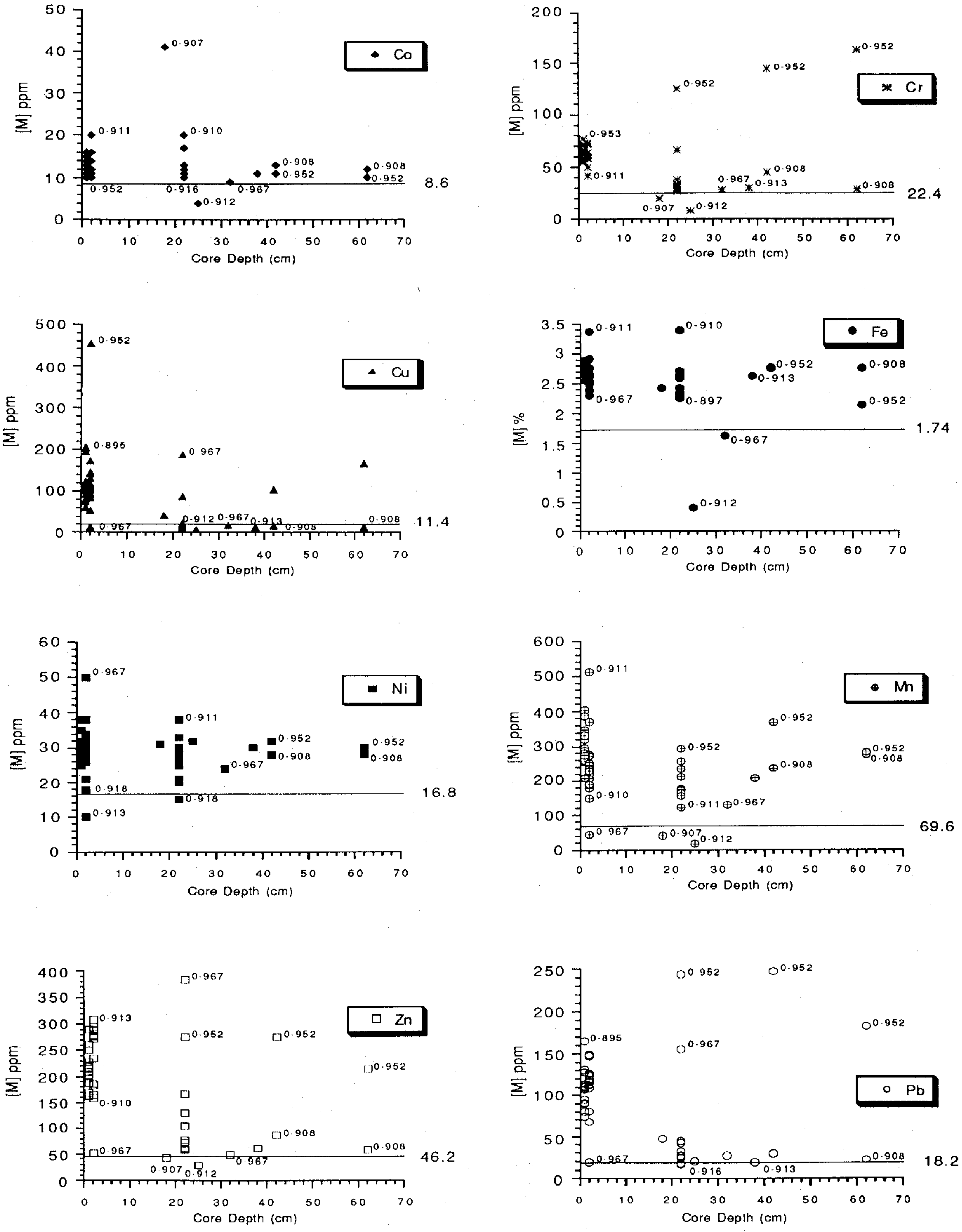
Site 0-952


Site 0-967

Site 0-967

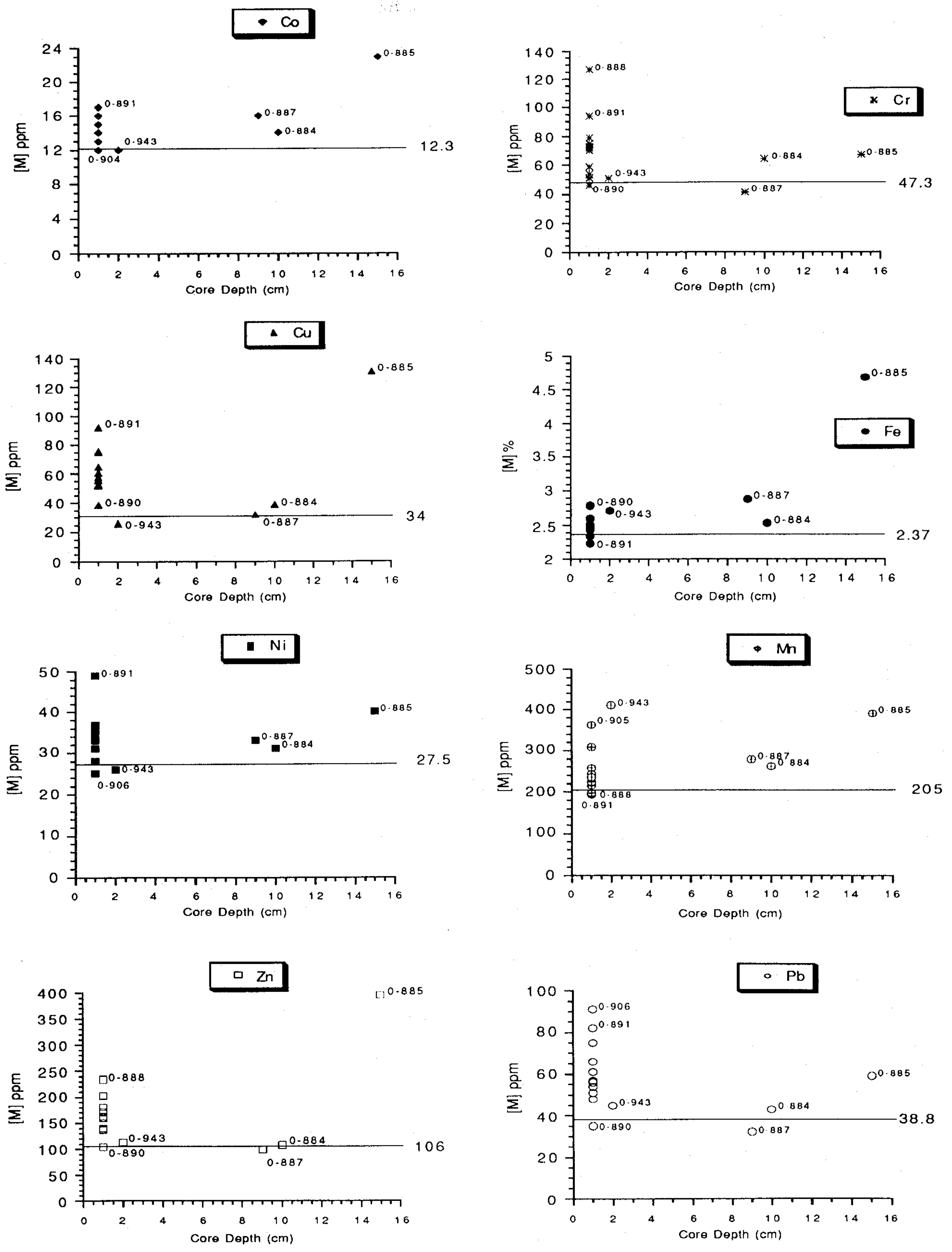
APPENDIX 3A Depth profiles Area A

Distribution of heavy-metal contents with depth in sediments in Area A. Solid line = calculated baseline concentration. Data from Glasby et al. (1988). Some individual cores are identified by station number



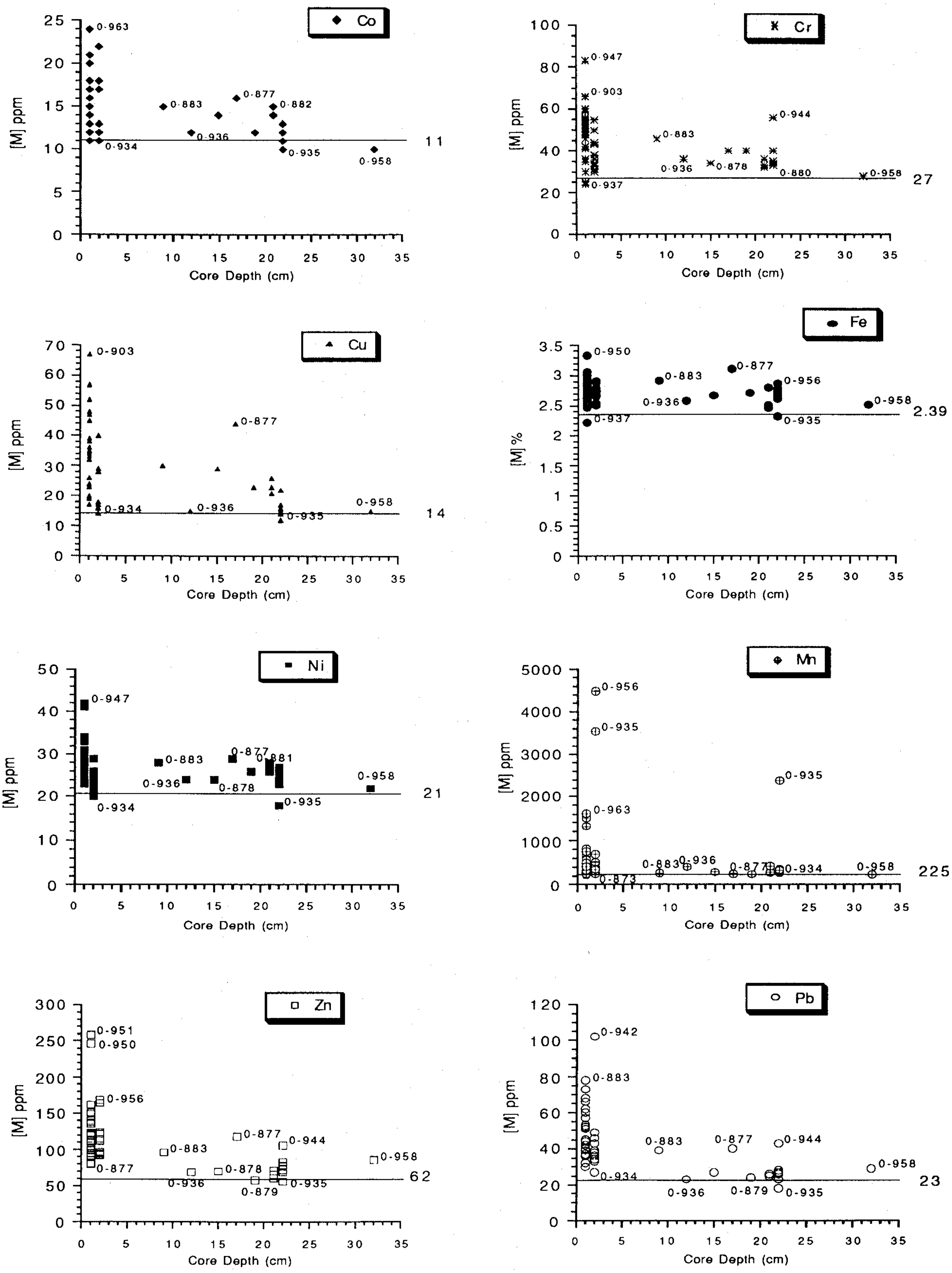
APPENDIX 3B Depth profiles Area B

Distribution of heavy-metal contents with depth in sediments in Area B. Solid line = calculated baseline concentration. Data from Glasby et al. (1988). Some individual cores are identifiedby station number.



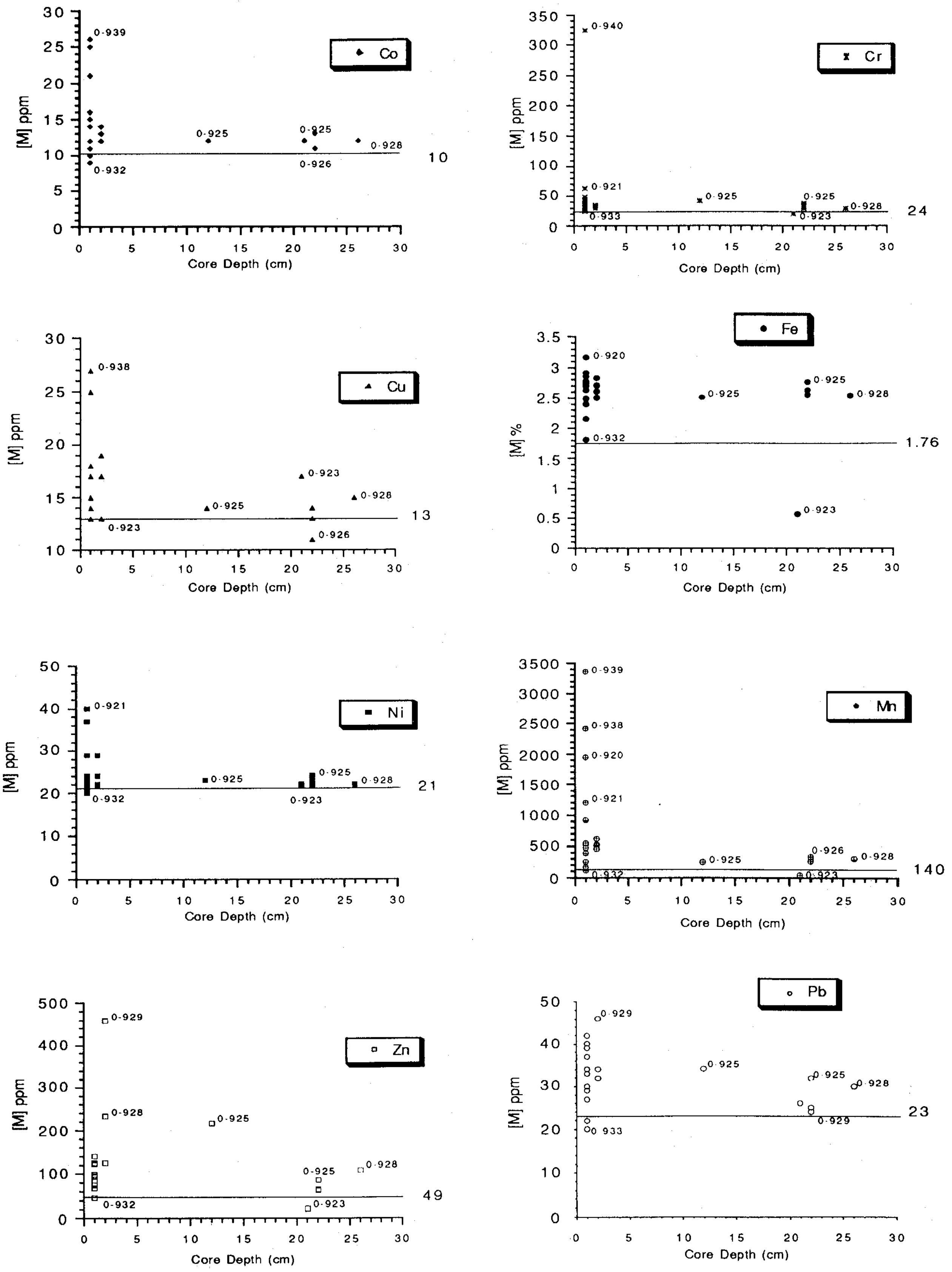
APPENDIX 3C Depth profiles Area C

Distribution of heavy-metal contents with depth in sediments in Area C. Solid line = calculated baseline concentration. Data from Glasby et al. (1988). Some individual cores are identified by station number.



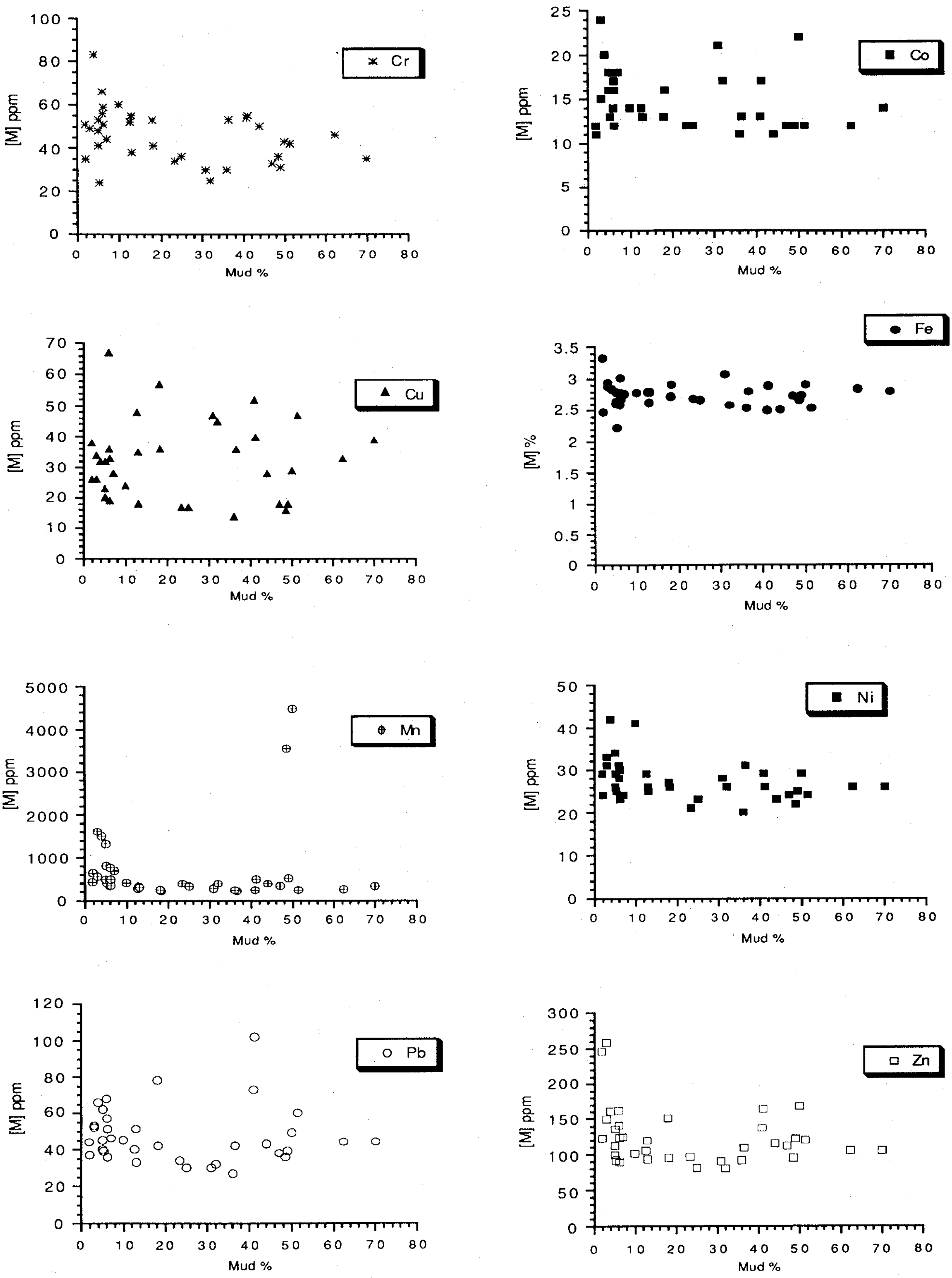
APPENDIX 3D Depth profiles Area D

Distribution of heavy-metal contents with depth in sediments in Area D. Solid line = calculated baseline concentration. Data from Glasby et al. (1988). Some individual cores are identified by station number.



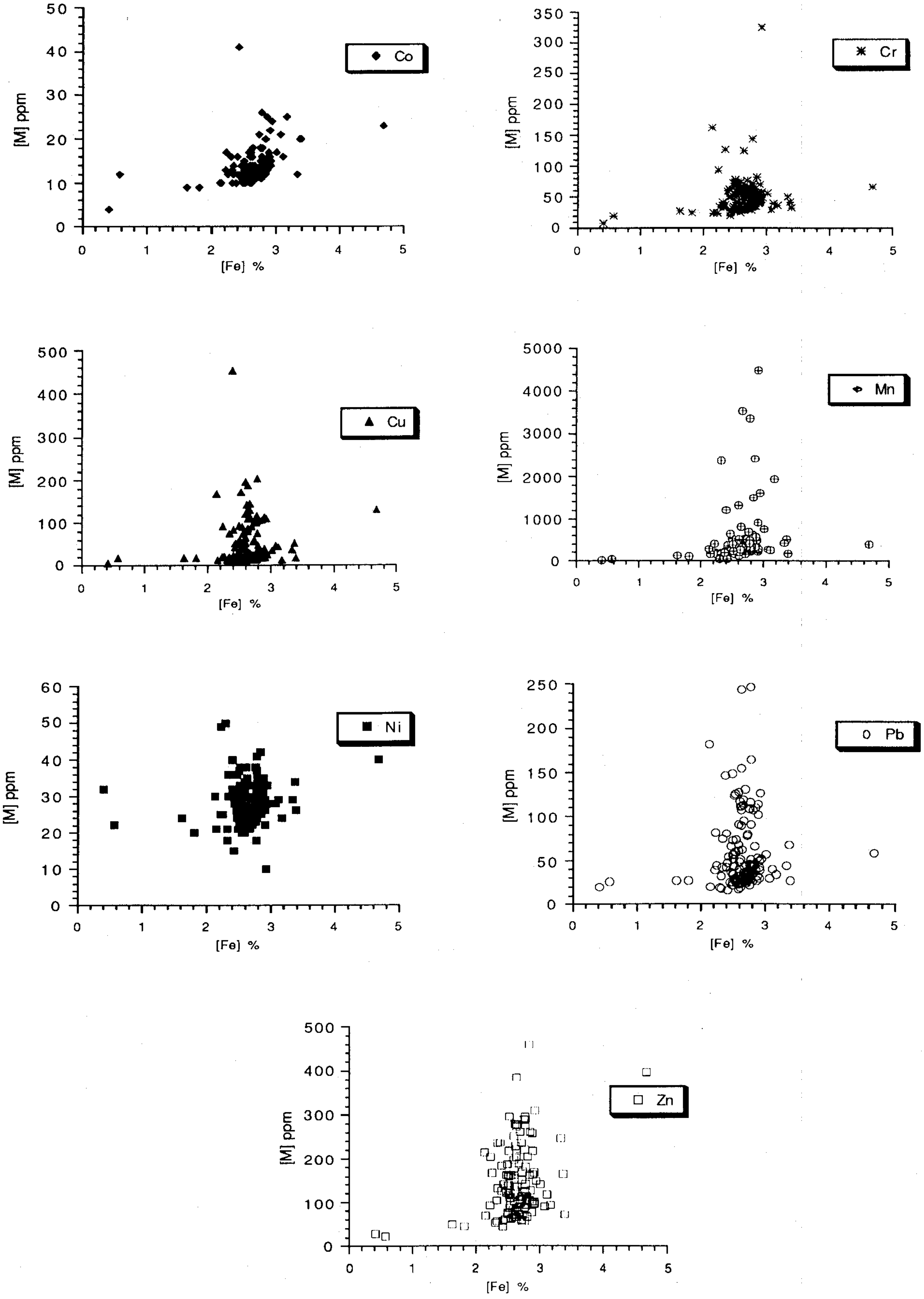
APPENDIX 4 Heavy-metal versus mud content

Heavy-metal contents in the <20µm fraction of the sediments as a function of the mud content in the total sediment in samples. Data from Glasby et al. (1988).



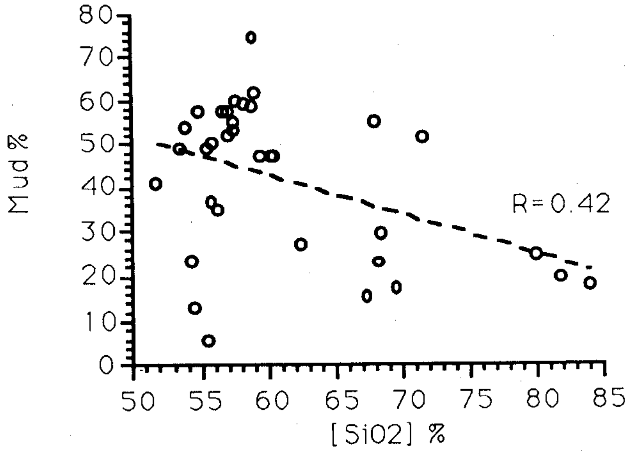
APPENDIX 5 Heavy-metal versus Fe concentration

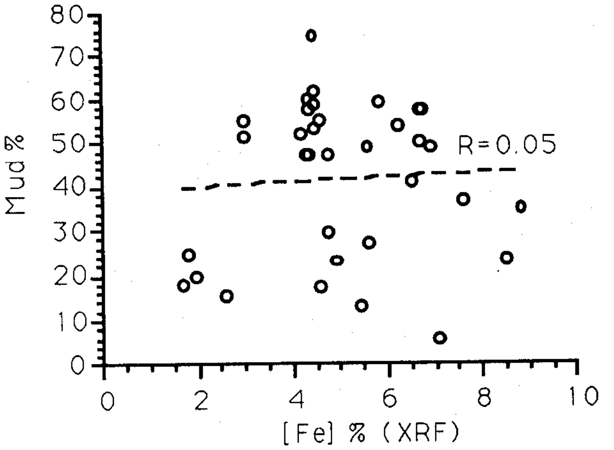
Relationship between heavy-metal contents and Fe in the <20 µm fraction of sediments from the whole harbour. Data from Glasby et al. (1988).

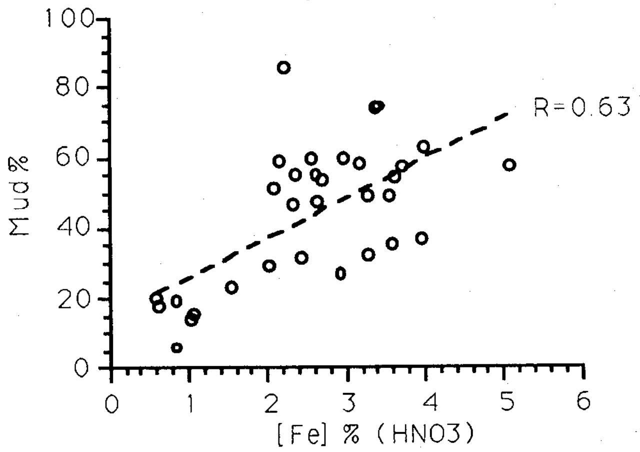


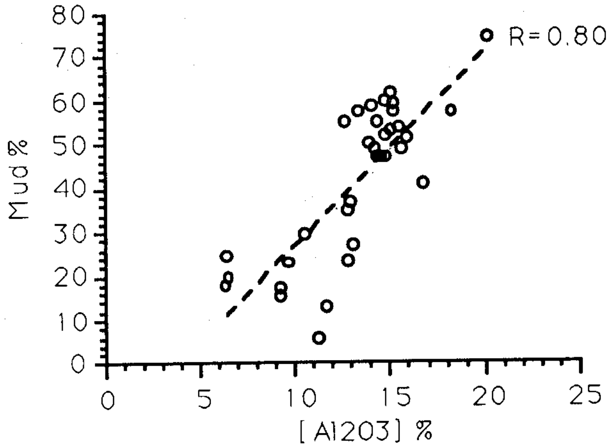
APPENDIX 6 Sediment composition relationships

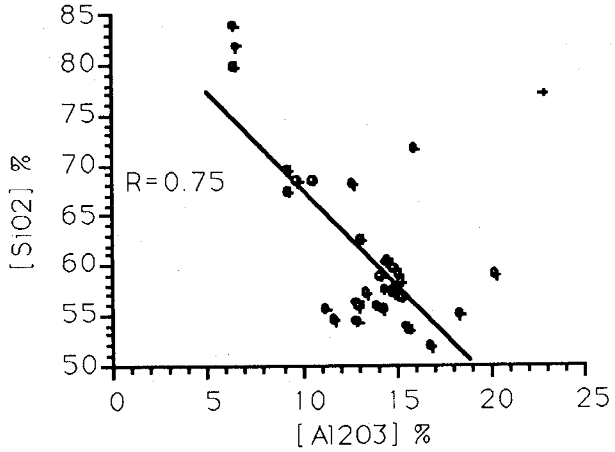
Plots of relationships between various major sediment parameters in the Waiuku Estuary. Data from Bioresearches (1985-1990).





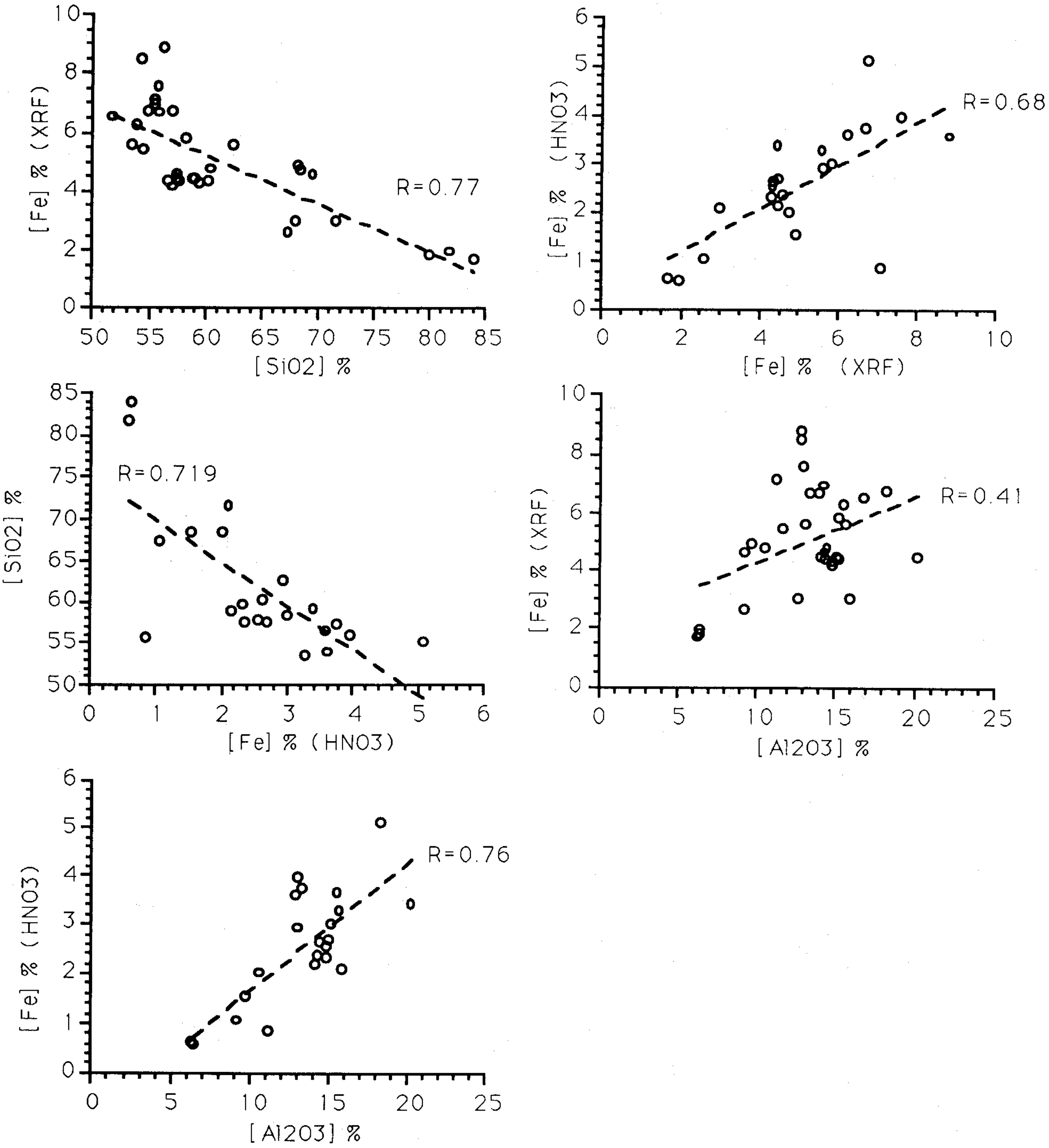






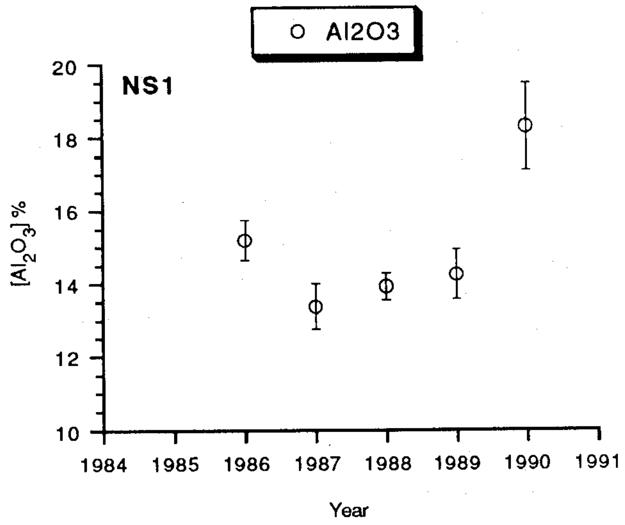
APPENDIX 6 (cont.)

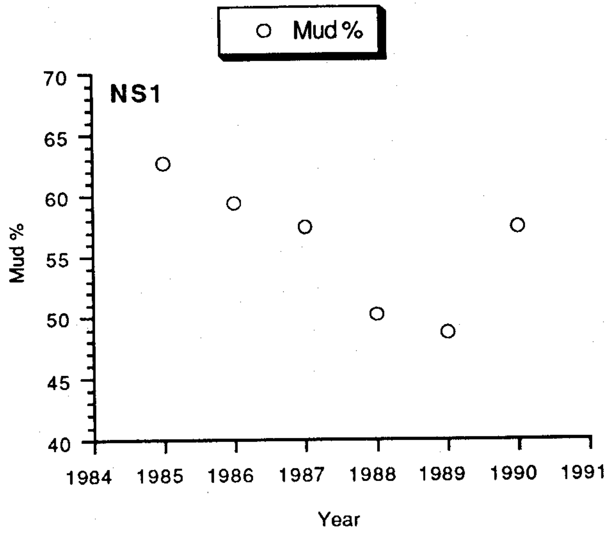
Plots of relationships between various major sediment parameters in the Waiuku Estuary. Data from Bioresearches (1985-1990).

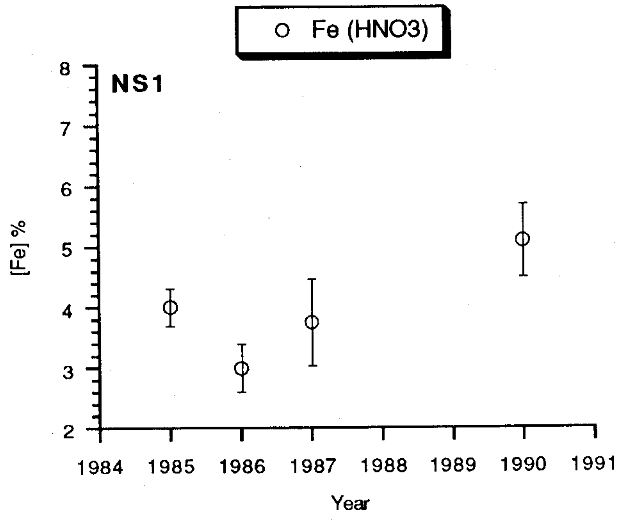


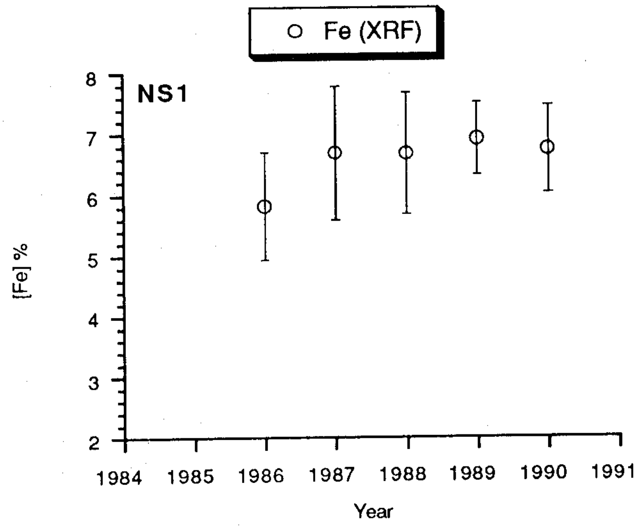
APPENDIX 7A Time trends in sediment composition

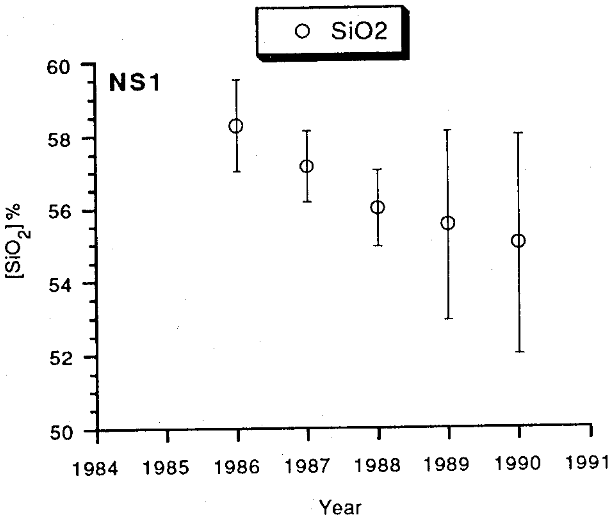
Variation with time of major sediment parameters Al_2O_3, SiO_2, Fe (XRF), Fe (HNO_3 digest) and mud content at site NS1. Data from Bioresearches 1985-1990.





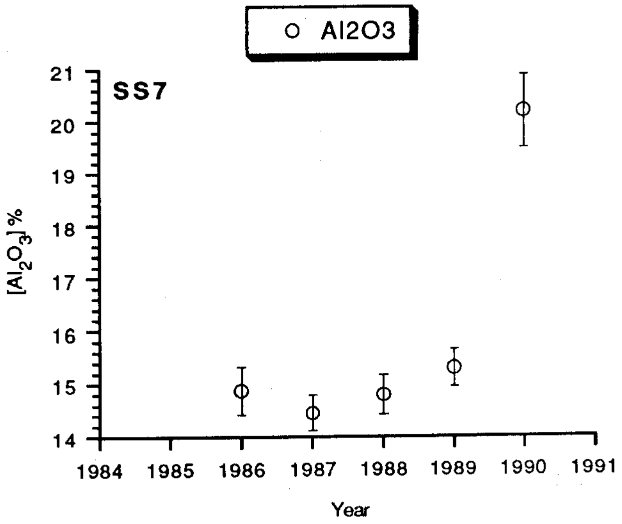


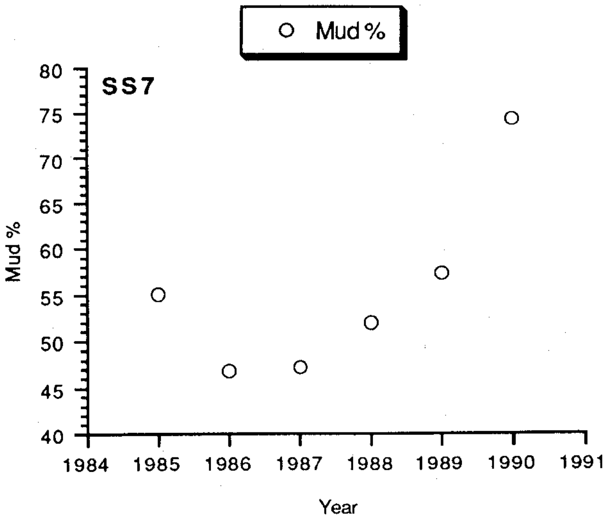


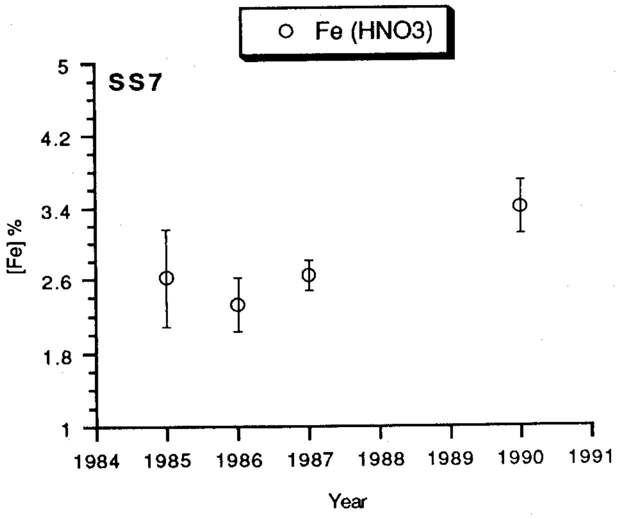


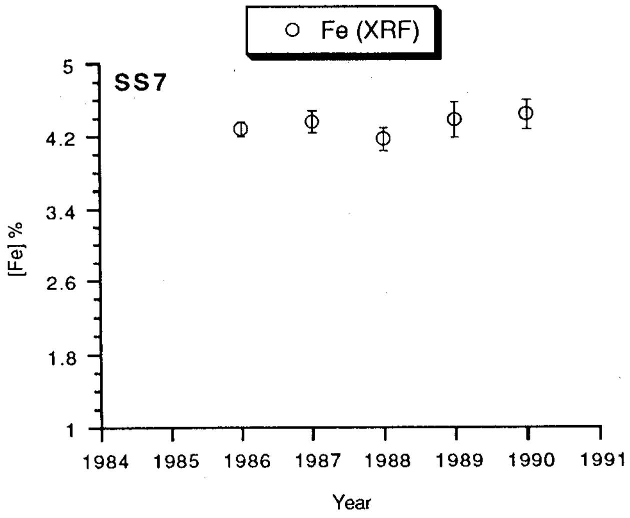
APPENDIX 7B Time trends in sediment composition

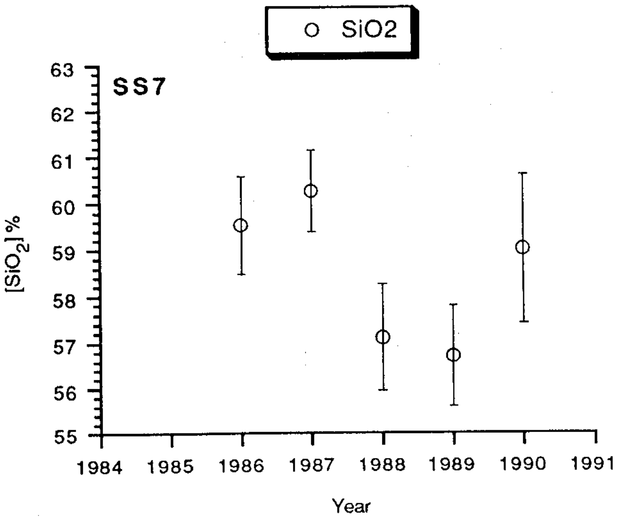
Variation with time of major sediment parameters Al_2O_3 , SiO_2, Fe (XRF), Fe (HNO_3 digest) and mud content at site SS7. Data from Bioresearches 1985-1990.





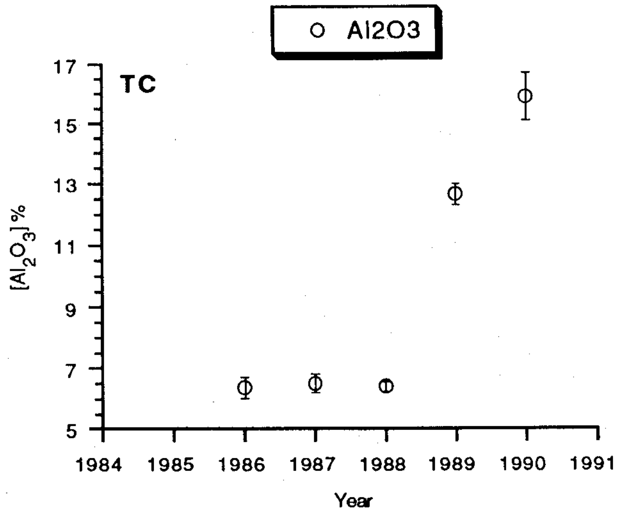


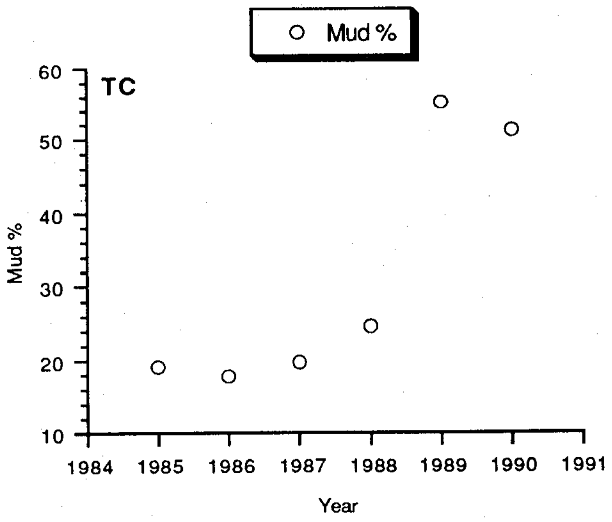


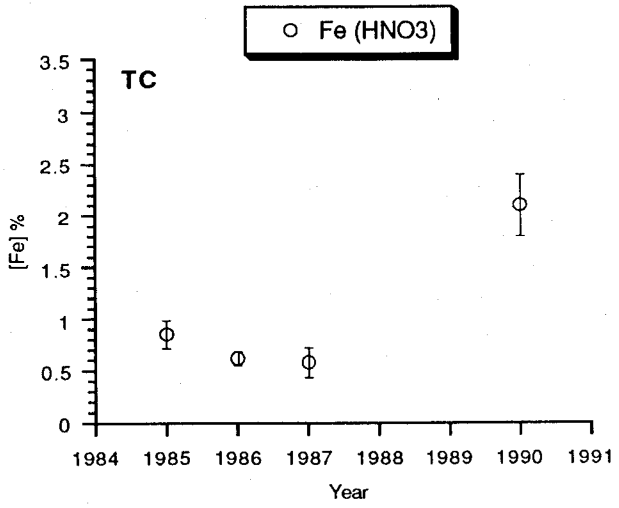


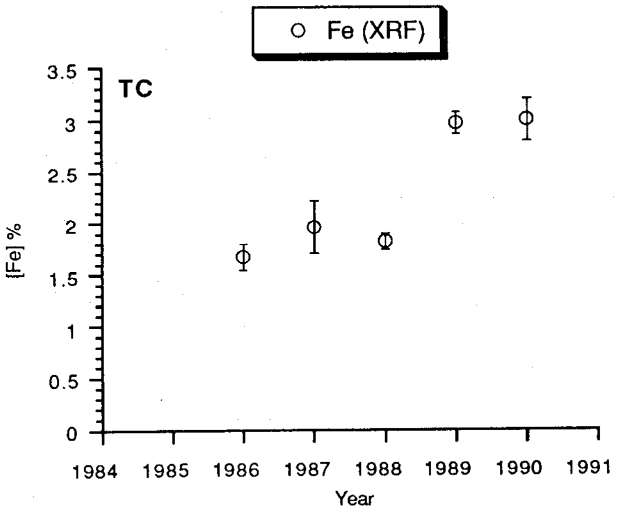
APPENDIX 7C Time trends in sediment composition

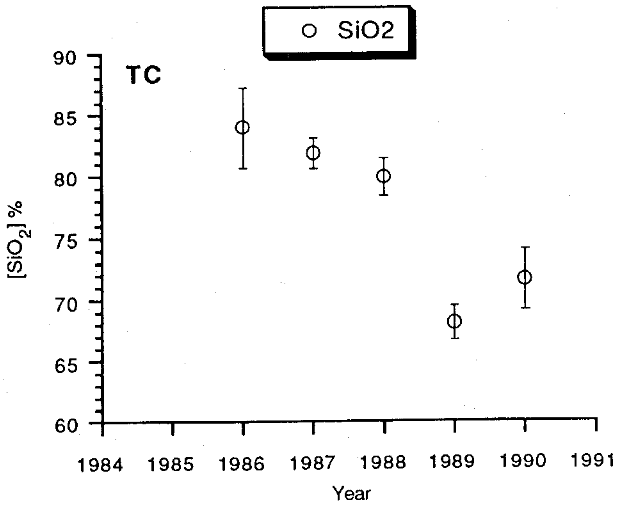
Variation with time of major sediment parameters Al_2O_3 , SiO_2, Fe (XRF), Fe (HNO_3 digest) and mud content at site TC. Data from Bioresearches 1985-1990.





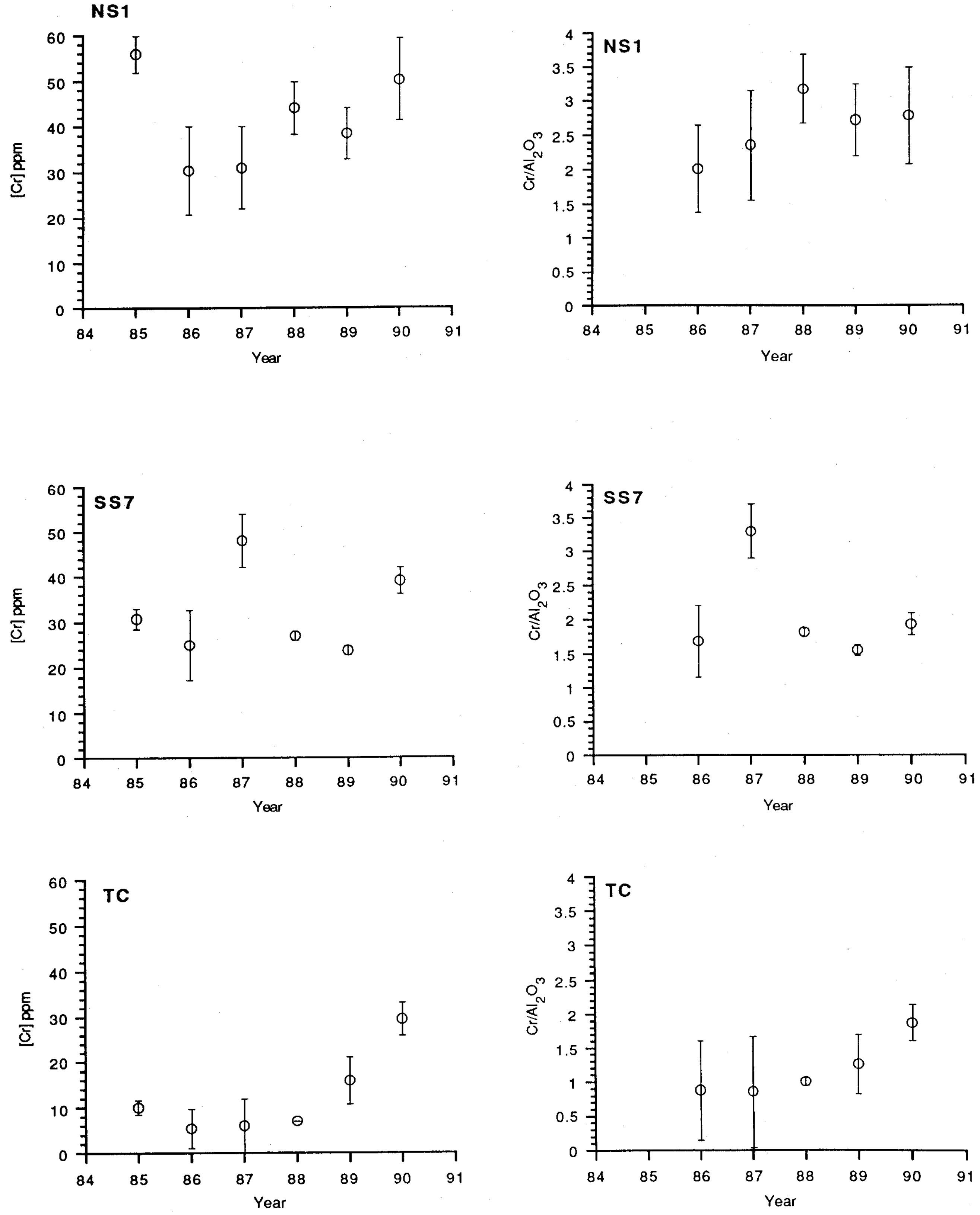






APPENDIX 8 Time trends in chromium concentrations

Variation with time of chromium and Al_2O_3 normalised chromium concentrations at site NS1, SS7 and TC. Units of Cr/Al_2O_3 are ppm/%. Data from Bioresearches 1985-1990.



APPENDIX 9 Sample variability

Coefficients of variation (CoV) was plotted against years and against sites (Figs A9.1 and A9.2) for each element. The following generalisations can be made:

(1) In any year, no site showed consistently high or low CoV. For example, the variance at TC (the most remote site) is no less than the variance at NS1 (the closest to the discharge from the mill, Fig. 5.1). A reasonable hypothesis is that a higher variance would be found at a site close to a discharge, because sediments in different parts of the 50m x 2.5m sampling plot would be exposed to different metal concentrations in the overlying water. The fact that it does not could mean:

(a) CoV is independent of site, in which case there is no spatial variability in discharge over the sampling site.

(b) Spatial variability in discharge does occur at sites close to discharges, but other factors are controlling CoV at more remote sites.

(2) Some years show a greater variation in CoV than other years (i.e., the spread in the variances is not consistent from year to year). For example, the CoV in 1985 are generally lower than those in 1986 (Fig. A9.1). This might be due to variations in analytical accuracy and/or precision from year to year. However, the possibility of a widespread difference in sediment characteristics in the Waiuku Estuary from year to year cannot be ruled out (e.g., conditions favouring greater benthic algal biomass).

(3) At any one site for a given year, there seems to be a weak correlation between CoV values for different heavy metals, (e.g. in 1987, the CoV for site SS1 are high for all the metals). This reduces the possibility that high CoV are caused by contamination of the samples during analysis, because if contamination was the cause of this high variance, the samples would have to have been contaminated by all the metals analysed. However, the overall correlation is weak to moderate.

(4) CoV should increase at low element concentrations because analytical errors increase as concentrations approach the detection limit. However, there was a poor relationship between CoV and mean concentrations, although any relationship could have been obscured by other factors (e.g., see (1) above) or by the fact that detection limits varied from year to year.

The coefficients of variance for ARWB and Bioresearches data were compared as shown in Fig A9.3. Generally, precision is lower in the ARWB study for Fe, Zn and Pb while slightly greater for Cr, Ni and Cu.

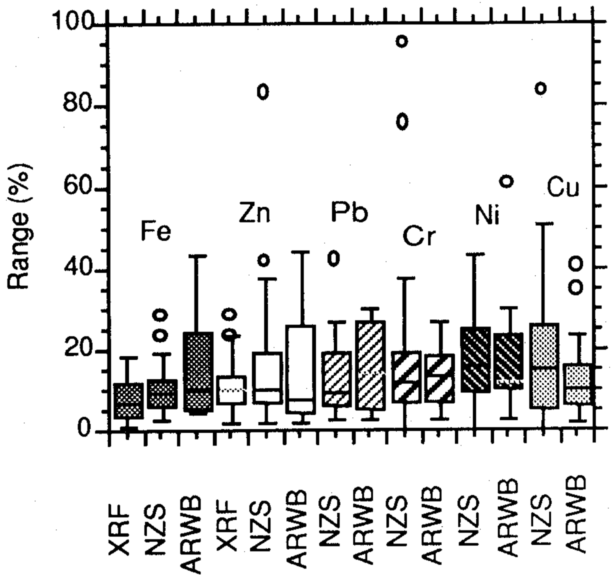


Fig. A8.3 The coefficients of variance for ARWB and Bioresearches data. XRF denotes total metals determined in Bioresearches' study. Elsewhere metals were determined after HNO3 digestion.

Fig. A9.1 Coefficient of variance (CoV) for heavy-metal contents (extracted with HNO_3) plotted against year. The CoV were calculated for 6 replicates from each site. Site numbers have been reformulated for plotting, e.g., SS1 = 1SS. Data from Bioresearches (1985-1990).

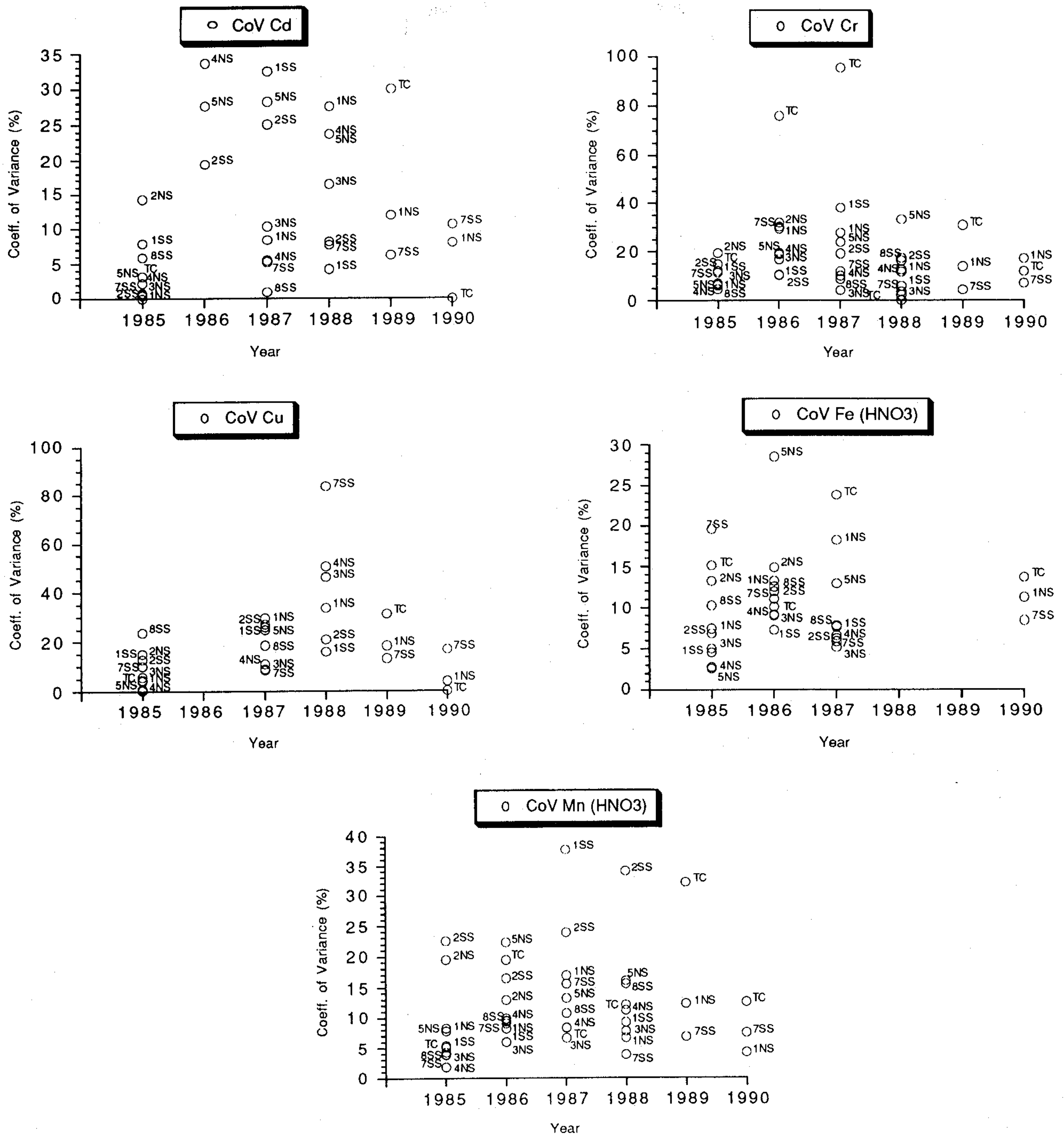


Fig. A9.2 Coefficient of variance for sediment concentrations plotted against site. The CoV were calculated for 6 replicates from each site. Years are indicated by last 2 digits e.g., 1988 = 88. Data from Bioresearches (19985-1990).

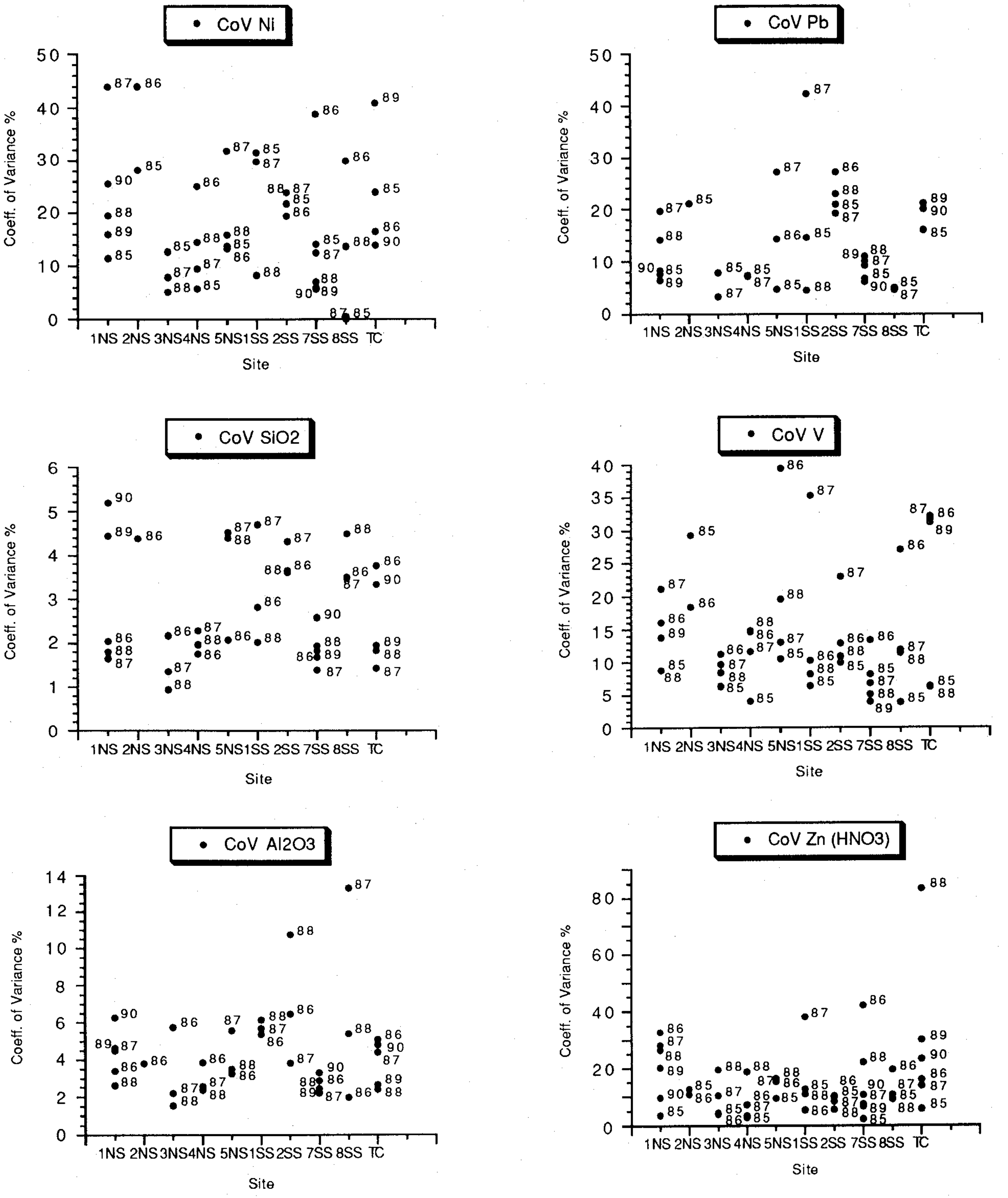
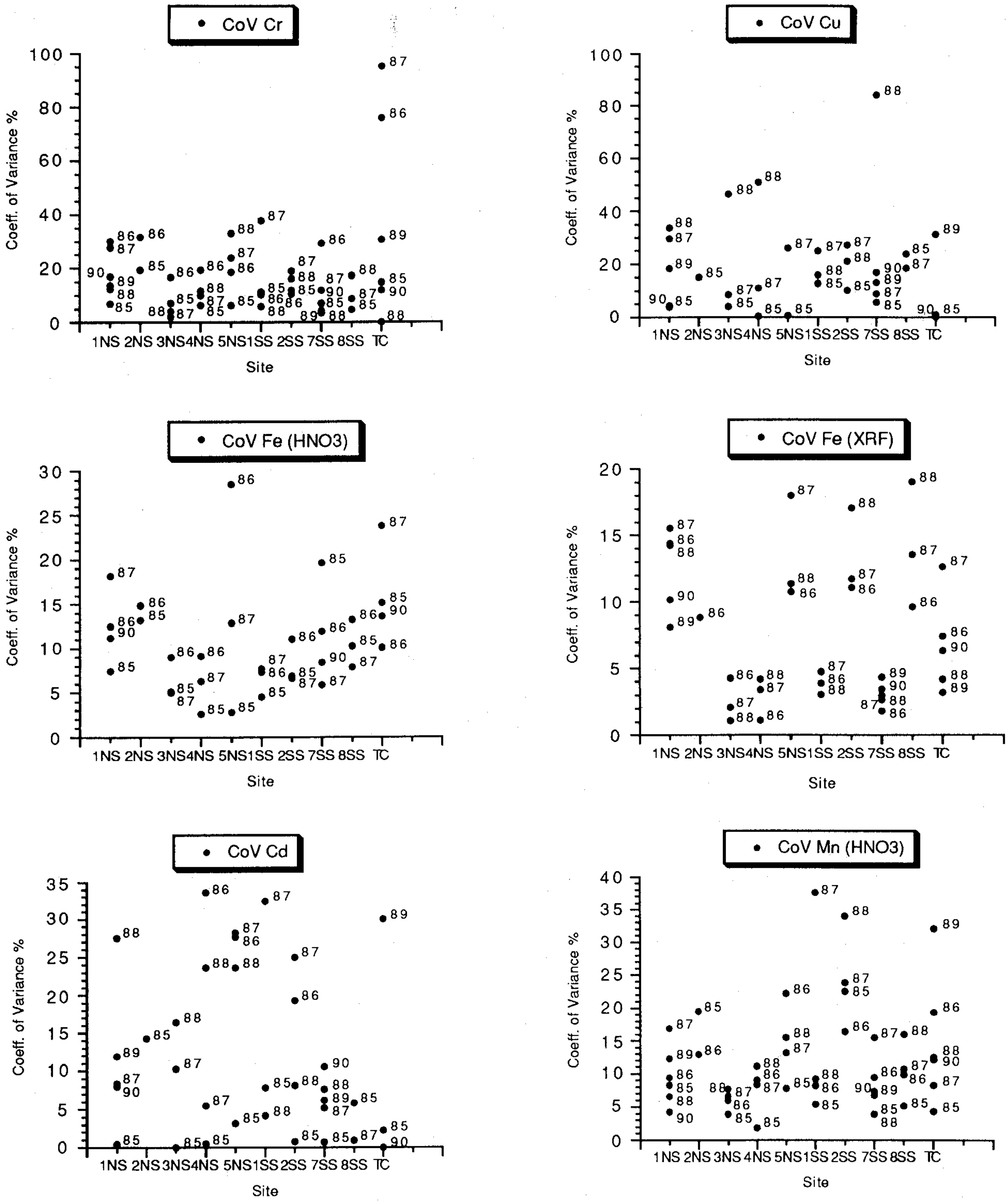


Fig. A9.2 (cont.)



CoV Cr
CoV Cu
CoV Fe (HNO3)
CoV Fe (XRF)
CoV Cd
CoV Mn (HNO3)
Coeff. of Variance %
Site
1NS 2NS 3NS 4NS 5NS 1SS 2SS 7SS 8SS TC

APPENDIX 10 Longitudinal concentration trends

Variation in metal concentrations (normalised to mud content) with distance from the NZ Steel Mill northside outfall. Units of the Y axis are in ppm/%