NIWA

Taihoro Nukurangi

The Distribution and Fate of Contaminants in Estuarine Sediments

Recommendations for environmental monitoring and assessment

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The Distribution and Fate of Contaminants in Estuarine Sediments

Recommendations for environmental monitoring and assessment

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prepared for
Environment and Planning
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1 INTRODUCTION

This report summarises progress made in understanding the fate of contaminants in estuarine sediments, with particular reference to studies carried out in the Manukau Harbour from 1989-1993. This work was funded by the Auckland Regional Council and the Foundation for Science Research and Technology.

The report summarises information on:

- Distribution of contaminants
- The processes controlling their concentration and effects in sediments
- The processes controlling recovery (self-cleansing) of sediments

The report makes recommendations on:

- Which contaminants should be routinely analysed in the Auckland region
- Other contaminants that need further investigation of their occurrence
- Other parameters that must be measured when studying contaminants
- Procedures for conducting studies on estuarine contaminants, including:
  —Design
  —Sampling
  —Laboratory analysis

The report is divided into two sections:

- A summary of the Sediment Recovery Programme, along with recommended procedures for future work.
- Specific guidelines for sediment analysis, which can be used without reference to the summary report.

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 million 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 were 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. Despite routing of effluents to the MSPW, 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. Fox et al.1988; Glasby et al. 1988; Roper et al. 1988; ARWB 1990, Williamson et al 1992) 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 is summarised in Table 2.1, which was taken from Williamson et al 1992).

In addition to discharges from point sources, there is runoff from urban and rural areas. The urban runoff carries PAH, Pb, Cu and Zn to the harbour. Rural runoff includes diffuse source pollutants from pasture (e.g., DDT Hume et al 1989) and a 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.

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 industrialised areas in New Zealand (Linge 1959,). 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, and these may serve as time markers for pollution events in the harbour. While this table may not be comprehensive, it does give an idea of the time frame of development. The history and nature of the sewerage systems in the region is summarised in Table 2.2, also taken from Williamson et al 1992.

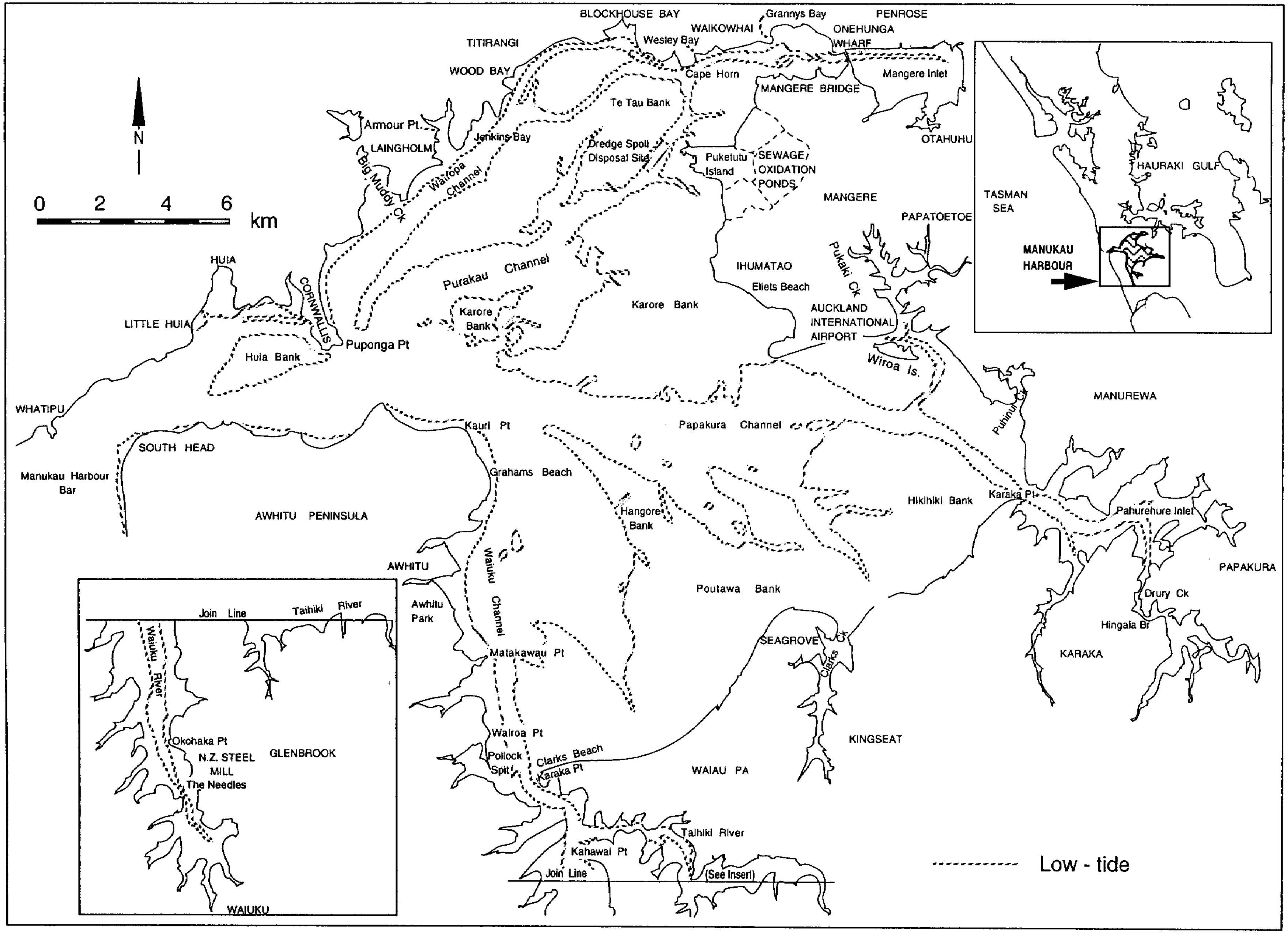

Fig. 2.1 Manukau Harbour location map.

Table 2.1. Development of the Manukau Harbour catchment by decade since European settlement (Williamson et al 1992).

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; NZ. Iron and Steel Company set up and closed down in Onehunga (1883-1886).
1890s	Fellmongery in Onehunga
1900s	First trials with artificial fertiliser at Papakura.
1910s	NZ. 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 fertiliser 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 manufacturing steel at Glenbrook.

Table 2.2. Summary of sewerage systems in areas adjacent to Manukau Harbour (Williamson et al 1992). 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, 7,850 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 per year. The 5 day BOD load was estimated to be 27,000 kg per year (equivalent to a population of 400,000 people).

3 SEDIMENTARY DYNAMICS

3.1 Scope

Sediment type and dynamics strongly affects contaminant concentration and fate. Our understanding of contaminant behaviour is considerably improved by understanding sediments dynamics.

3.2 Sediment zones

Within an estuary it is useful to distinguish 3 zones based on 3 types of processes (Hakanson 1982):

(1) Areas of accumulation (deposition) where fine materials are continuously being deposited.

(2) Areas of transportation where fine materials are deposited discontinuously, i.e, the periods of accumulation are interrupted by periods of mobilisation (generally of short duration and associated with storms).

(3) Areas of erosion where there is little deposition of fine materials.

Areas of erosion are characterised by bare rock, gravels and sands, while sediments in areas of transportation are diverse; ranging from muds to sands. The deposits within areas of accumulation are generally muddy, with a high water and organic content. In the Manukau, we distinguish the 3 zones by sediment texture and by hydrological environment. For example, Fig. 3.1 shows the mean particle size. Here, areas of accumulation are distinguished by muddy sediments found in sheltered sub-estuaries, especially Mangere, Pahurehure and Waiuku. Areas of erosion are the exposed sandy banks and major channels in the main parts of the harbour, where resuspension of fine material by waves occurs in shallow waters and by strong currents in the deeper channels. Between the areas of erosion and accumulation are areas of transportation. They are also found in parts of the main harbour on some of the sheltered banks (e.g., near Puponga Point, around Puketutu Is). The concept of sediment zones is consistent with other studies (Luoma 1990) which report that fine particles seek their preferred sites of deposition (accumulation zones) regardless of point of introduction.

The above discussion presents an idealised

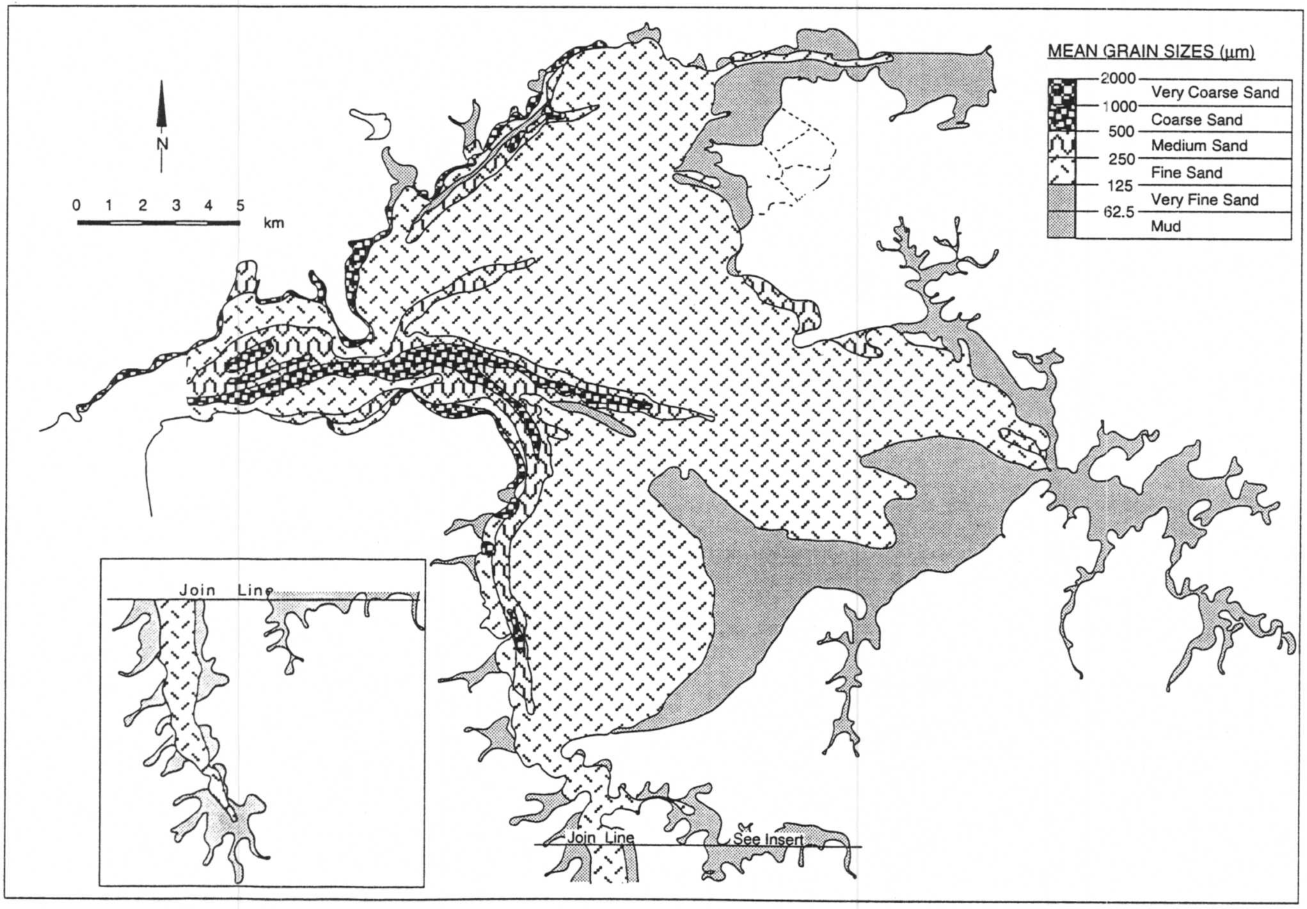

Fig. 3.1 Principle sediment types in the Manukau Harbour (from Tonkin & Taylor 1986).

PROCEDURE FOR ESTABLISHING THE BASIC SEDIMENT ENVIRONMENT.

1 Familiarise oneself with basic hydrology, morphology and wind exposure, using charts and maps.

2 Obtain particle size information from sieve analysis of surface sediments.
Collect samples from the top 1 cm (muds), 2 cm (sands) (as reasonably representative of recent history).
Measure the proportion of gravel, coarse, medium, fine sand, mud.
Note large changes in deeper sediment textures that may typify some transport zones.

3 Summarise, estimate or measure currents, especially in channels.

4 Map inputs of contaminants and sediments.

5 Identify and map sediment type (see Section 3.2) based on particle size, exposure (as judged from wind fetch) and currents.
Erosion zones are (1) exposed intertidal areas or (2) channels and are dominated by gravel (especially shell hash), or coarse and medium sand.
Accumulation zones are usually sheltered with muds or sandy mud.
Transport zones are partly sheltered, and predominantly muddy sands or muds.

An example of many of the steps given in this procedure can be found in Vant et al (1993).

picture. In reality, the characteristics that a particular site may exhibit in the accumulation—erosion 'gradient' will depend on the time scale of observation. For example, we expect that sediment in accumulation zones will still be moved around the zone during storm events, and sediment texture will vary as a result.

An example of an accumulation zone
The small estuaries around the Manukau Harbour act as very efficient traps for fine sediments. Here there is shelter from wave and tidal energy and the areas act as settling basins for suspended material that originates both from the catchment or from the main body of the harbour. In contrast, in the main body of the harbour, wind/wave action will resuspend fine sediments. For example, the sediment flux in and out of Mangere inlet (Vant 1990) for both windy and calm days are shown in **Fig. 3.2**, along with calculated inputs from the urbanised catchment surrounding Mangere Inlet. On the calm day, export and import of sediments balance, while on the windy day, the inlet appears to be a sink of suspended sediment. (Also note that the estimated annual catchment input is small compared with the amounts of sediment transported in and out of the inlet during one tidal cycle).

Examples of transportation zones
On Wiroa Is sand flats, the grain size characteristics of surficial sediments in the upper tidal flats change with time, between neap HW and spring HW. It appears that during calm periods, muds settle out from suspension in the shallow areas. The mud is temporarily stable here because tidal currents are too weak to resuspend the sediment. The mud is stable even during storm events on a neap tide when the water is so shallow that the waves break further offshore, sheltering the nearshore zone from disturbance. However during storms coinciding with spring tides, when the water is

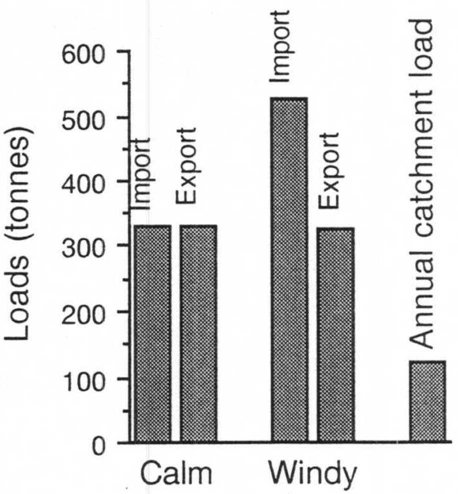

Fig. 3.2 Sediment loads in ebb and flood tides for Mangere Inlet (Vant 1990), and estimated annual sediment load from the surrounding catchment.

on average 0.7m deeper than for neap tides, high orbital velocities associated with wave activity resuspend the finer mud fraction and disperse it away from the area. In summary, mud is washed into the area, stored temporarily high on the tidal flats, some is mixed into the sand but most is transported away to areas of low environmental energy, such as that of the Pukaki Creek inlet.

Also at Wiroa Is, westerly and south-westerly storms push sand into Pukaki Creek, causing lenses of sands overlying muddier sediments. During calmer periods, mud can deposit on these sands, so the particle size characteristics of sediments vary widely in this area.

An example of a erosion zone

From 1975 to 1989, some 130000 m^3 of dredge spoil has been disposed at the Purakau Dredge Spoil Disposal Site (about 10000 m^3 per annum). This site is in the Purakau channel in the exposed outer harbour (Fig. 2.1) and has a relatively high energy environment because of waves and currents. The predominantly fine sediment dredge spoil is resuspended and dispersed from this zone (Ports of Auckland 1989, Ryan and Healy 1991), along with its associated contaminants.

3.3 Sediment dynamics

Physical mixing of sands

The Manukau Harbour is shallow with extensive intertidal areas (43% of total harbour area at spring low tide) and is largely devoid of vegetation. Large areas of sediment are subject to the action of wind-generated waves. In the main body of the harbour winds fetch up to 22 km in places, and can generate quite large waves (Tonkin & Taylor 1986). Sand flats are thus a very dynamic system, in which sediment is continually reworked. Over most of the tidal flats, waves turn-over the top few centimetres of sediment continually, forming small ripples (height = 1-2 cm, wavelength = 10-15 m). Large amounts of sediment and juvenile shellfish are shifted as bedload during windy periods (S. Thrush, NIWA-Ecosystems, unpubl. data) In those areas exposed to greater wave fetch, multiple bars form on low gradient intertidal flats (Fig. 3.3). The vertical distance between bar crest and trough is typically 10-25 cm. Sporadic storm events shift the bars at scales of decimeters and meters. These bars occur over 70% of the eastern harbour shore so the process is important on a harbour-wide basis. The bars gradually rework the sediment to 10-25 cm depth over large areas along the eastern harbour shore which is close to the sources of contaminants. Reworking may be a major factor in contaminant cycling by flushing the interstitial waters and winnowing fines from the sands. The low levels of pollutants in the sands are due to this constant reworking.

Bioturbation

Many studies overseas have shown that bioturbation strongly affects the physical, chemical and biological properties of sediments (Rhodes and Young 1970, Rhoads et al. 1978, Lee and Swartz 1980, Aller 1982, Rhoads and Boyer 1982, Aller et al. 1983). It is likely that biological mixing is more important in muddy sediments than sandy sediments, where strong physical forces occur. Two distinct groups of animals can be distinguished on the basis of the magnitude of sediment disturbance. Large individual predators, such as rays, flounders and crabs, may shift large amounts of sediment in their search for food. In contrast, smaller animals such as worms and gastropods which burrow and ingest sediment, shift only small amounts of sediment, but may be important in sediment turnover because of their high population densities.

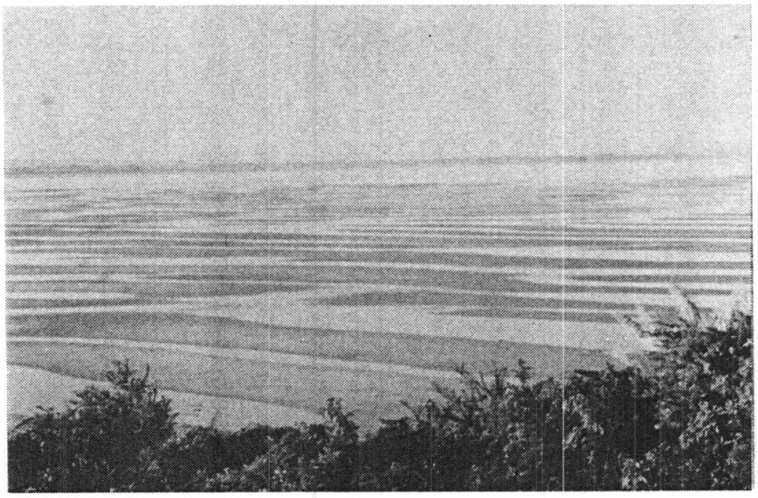

Fig. 3.3 Multiple bars on the eastern shore of the Manukau Harbour.

Ecological studies on Manukau intertidal sands have shown that ray feeding is a major factor in sediment turnover (Thrush et al 1991). Measurements made on sand flats near Wiroa Is and Te Tau Bank found an average rate of disturbance of 1.4 %/day of the area studied (Fig. 3.4). The average pit formed by this disturbance had a depth of 12 cm and diameter

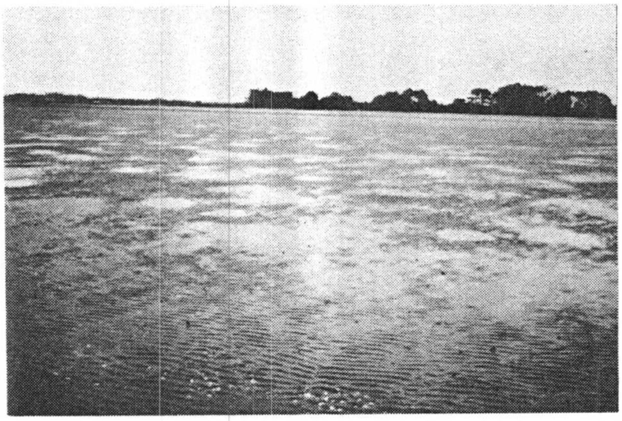

Fig. 3.4 Stingray pits on intertidal sand flats. Most of the pits were formed on the previous high tide, reflecting a high rate of sediment mixing.

of 80 cm. At this rate, an area would be turned over every 70 days. Casual observation suggests that this process is widespread, although not continuous at each site.

Bioturbation has a strong impact on the chemistry of muddy sediments. In unbioturbated sediments, oxygen penetration is very restricted and the redox boundary occurs a few mm below the surface. In bioturbated muddy sediments, oxygen can be transported deep within the sediments via burrows, which typically extend 10-25 cm below the surface, but can be as deep as 60 cm on banks. Oxic sediments line the walls of these burrows, so the 'mud' profile is a 'hotch-potch' of oxic and anoxic environments (Fig. 3.5).

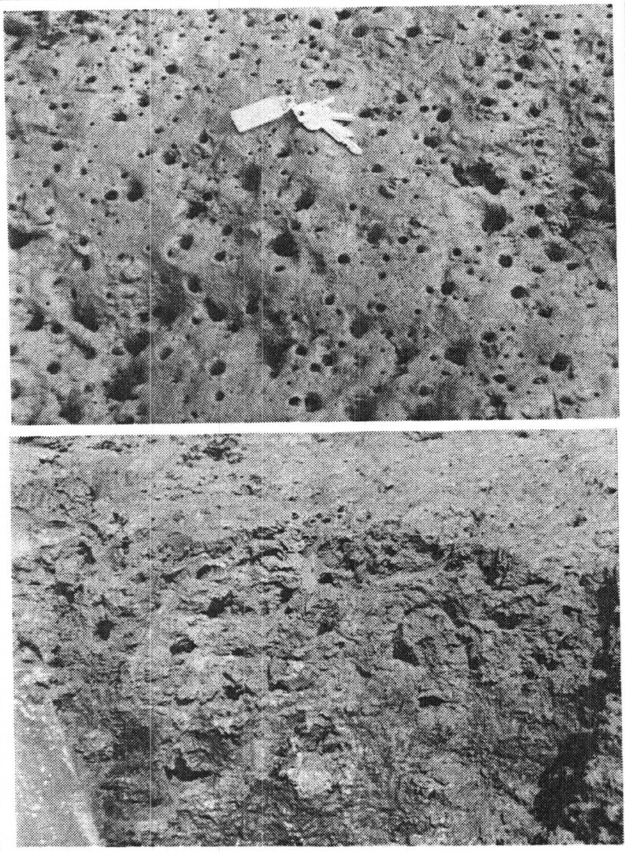

Fig. 3.5 Bioturbation in Manukau Harbour muddy sediments.

Resuspension processes

Sediments are resuspended by 3 processes.

1 On subtidal or submerged intertidal banks, high orbital velocities associated with waves will suspend fine sediments and even temporarily suspend coarse sand particles. On windy days the waters become very turbid because winds, which fetch 22 km in places, generate waves which throw large quantities of fine sands and muds into suspension. For example, on muddy banks in the Manukau Harbour, small wavelets up to 5 cm high raised nearshore turbidity 12-fold in the shallow overlying water (Fig.3.6), compared with deeper water just offshore. The turbidity is due mainly to larger (rapidly settling) particles, and in deeper waters immediately off-shore, turbidity drops to about 15-30 NTU (Fig 3.6). This short-lived resuspension in shallow water is an important re-distribution mechanism for muddy surface sediments.

In sandy sediments, we suspect that fine sediments are constantly being reworked and resuspended. Wave action also shifts a large amount of sand as bedload in the process.

2 In major subtidal channels strong currents

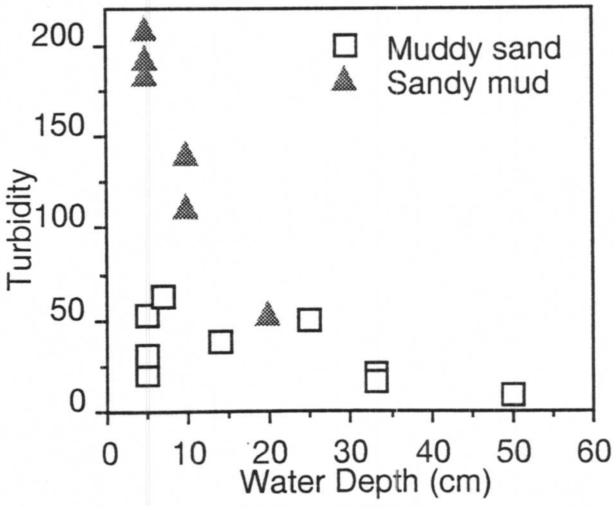

Fig 3.6 Turbidity (NTU) generated by small waves (3-5 cm crest-trough) breaking onto muddy shores near Pukaki Creek in the Manukau Harbour

keep fine sediments in suspension.

3 At low tide, surface water draining from an intertidal bank may be concentrated into channels, and flows may be high enough to erode channel banks and beds. For example, near Wiroa Is, intertidal sandy areas drain to the low tide channel through muddy areas. Flows are concentrated into small very mobile channels ('rills') as well as large 'streams'. In the process, the banks and beds erode, so that turbidity in the drainage waters varies from <10 NTU on intertidal sands, up to 570 NTU in the muddy areas.

Tidal pumping

During low tide, surface water drains over the intertidal areas after they are exposed. On sandy banks, surface drainage occurs as sheet runoff or is channelised in the broad shallow troughs. In addition to surface flow, the 'sands', although compacted, are highly permeable, so there is relatively little impediment to interstitial water flow. Here, sediment permeability is probably increased by bioturbation, in particular the feeding action of *Macomona liliana*, a surface-feeding mollusc found in high numbers down to 10 cm depth (Pridmore et al. 1990), which dominates the benthic community in the some sandy environments. Most other bioturbation does not leave many visible structures (e.g., burrows) through the 'sand' profile. Because of the large tidal range (4 m on a spring tide) there may be a reasonable head of water over the sand flats at low tide, and therefore a nett movement of interstitial water seawards seems likely.

In contrast muddy banks are unconsolidated and impermeable. However, bioturbation from abundant polychaetes (e.g., *Heteromastus filiformis*) and crabs (e.g., *Macrophthalmus hirtipes*) (Roper et al. 1988), extensively honeycombs the profile (Fig. 3.5). During low tide we observed that surface water draining over the mud flats continuously siphons through many burrows and galleries to ~15-50 cm depth, thus providing regular low-tide irrigation of burrow water. This occurs in addition to the expected burrow irrigation by some animals to

The importance of resuspension processes in the Manukau Harbour

The mass of sediment in suspension throughout the whole Manukau Harbour was calculated for 'average' (reasonably calm) conditions and for very windy conditions (Williamson et al 1991). Under relatively calm conditions, the average suspended sediment concentration throughout the harbour is 22.5 g/m^3, which is equal to a mass of about 18,000 tonnes (**Fig. 3.7**). During the storm, the average suspended sediment concentration was approximately 300 g/m^3. If this is representative of the whole harbour then about 240,000 tonnes were in suspension. Spread evenly over the harbour these loads equate with 0.04 and 0.6 mm thickness of sediment.

Tonkin and Taylor (1986) estimated the suspended solids load to the harbour to be of the order of 46,000 tonnes/year, although they acknowledged that it may be twice this. These calculations show that the annual stream input to the Manukau is very small compared with the instantaneous mass of sediment in suspension in the harbour at any one time (Fig. 3.7). In fact, the amount of sediment in suspension in the Manukau under average conditions is equal to the estimated average annual load delivered to the harbour from freshwater inputs over about 5 months! The large amounts of sediment in suspension at any one time is evidence of very substantial reworking of surficial sediment in the Manukau Harbour.

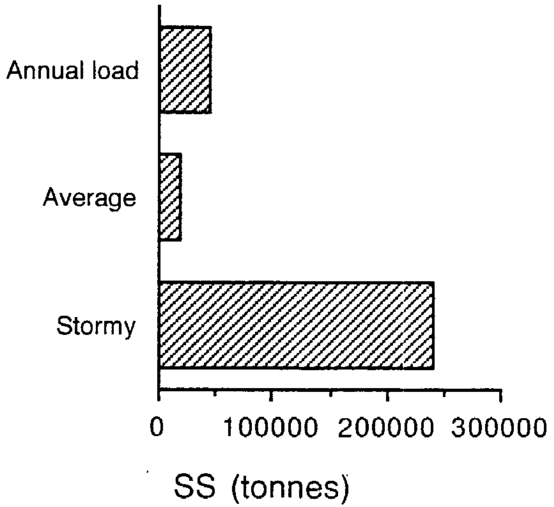

Fig 3.7 The estimated mass of sediment suspended in the Manukau Harbour under different conditions compared with the annual catchment load of sediments to the harbour.

maintain oxic conditions when tidal flats are submerged. Hence low-tide drainage will probably greatly facilitate the exchange of solutes between the sediment and overlying waters.

Sedimentation and burial

Sediment accumulation rates have been measured using radiocarbon and pollen dating techniques at a number of places in the Manukau by Murray-North Ltd (1988) and by Hume *et al.* (1989) in Drury Creek and in this study at Mangere Inlet (Fig. 3.8). They are highest in the muddy tidal creeks that drain the headwaters and low on the exposed sandy areas in the main body of the harbour. Sedimentation in the tidal creeks, which comprise about 20% of the total harbour area, is highest because they are usually close to the source of catchment inputs and, being sheltered from wave action, they tend to act as traps for particulates from a considerably wider area. On a harbour-wide basis, stream inputs of freshwater and sediment are too small to dilute polluted sediments significantly or cause the nett transport of estuarine sediments out to sea. Input of 46,000 tonnes per year is equivalent to 0.55 mm if all deposited in the sheltered tidal creeks, which is far less than measured rates of accumulation (Fig. 3.8).

3.4 Summary

A summary of the characteristics of the three types of sediment zones and the implications for the fate, effects and analysis of contaminants is given in Table 3.1.

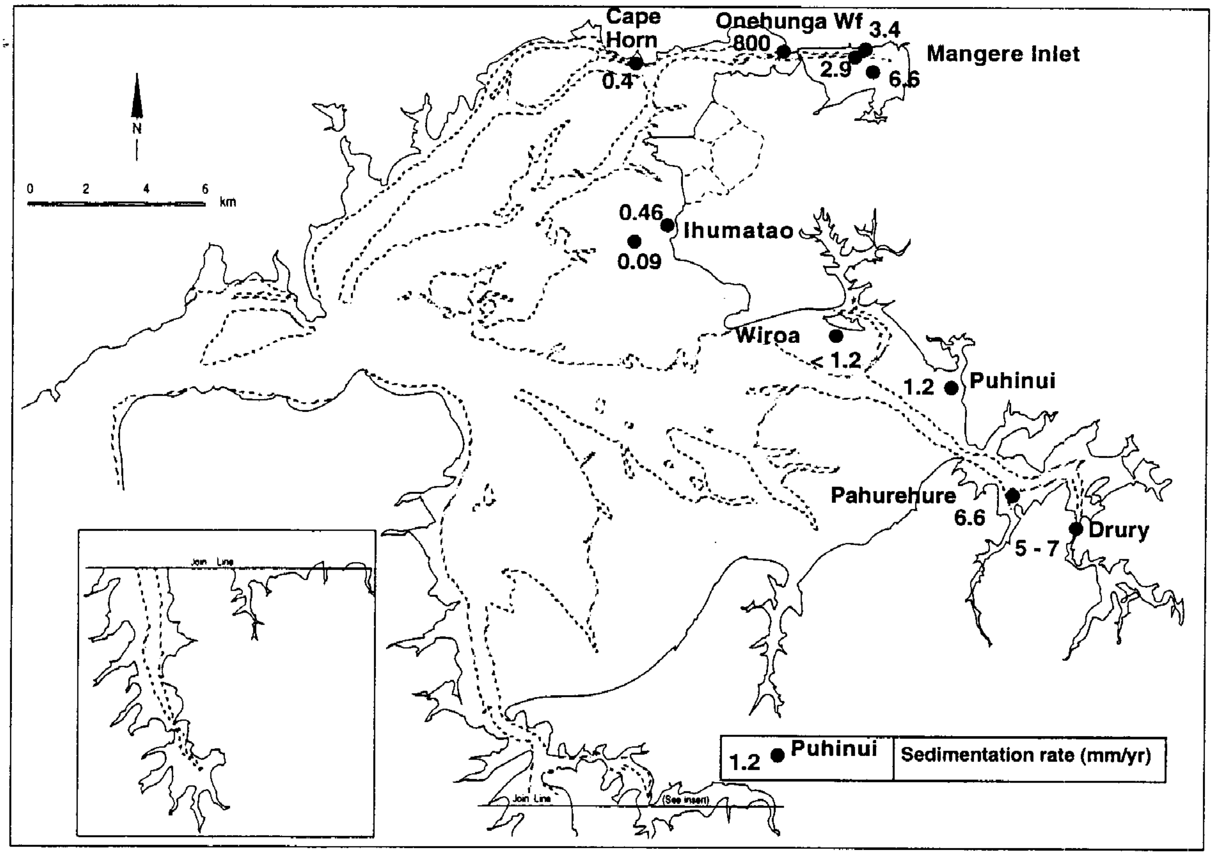

Fig. 3.8 Sedimentation rates in the Manukau Harbour.

Table 3.1 The implications for the fate, effects and analysis of contaminants in sediment zones

Erosion zones	**Transport zones**	**Accumulation zones**
Sediment texture		
Coarse sediments. Fine sediments will be reworked, resuspended and dispersed	Characterised by large changes in sediment texture	Fine sediment texture
Contaminant accumulation		
Little accumulation of contaminants because there is little fine material. Contaminants are flushed away because of winnowing of fines and interstitial water exchange	Range between erosion and accumulation zones.	Sediment is effective in adsorbing many contaminants and high concentrations can be accumulated.
Susceptibility to contamination		
Very susceptible to spills of toxic substances because there is relatively little to ameliorate toxicity. However, any spilled toxic substance will be flushed out relatively quickly	Range in susceptibility to contamination between erosion and accumulation zones.	Sediment is effective in ameliorating the toxicity, so they are less susceptible to the immediate impact of spills of toxic substances. However, spilled material will remain in sediment for a long time.
Analysis		
Difficult to interpret analyses. The low content of mud particles, which control contaminants in accumulation zones, may have different characteristics in this environment. Analyses of the mud fraction to reduce particle size effects need to be interpreted cautiously.	Sediment type depends on previous conditions such as season, tide, storms, therefore repetitive sampling exercises will need to carefully consider sampling conditions	Wide range of methods available to reduce the effects of variation in sediment texture on contaminant concentrations.

4 TRACE ELEMENTS

4.1 Trace elements of concern and their distribution in the Manukau Harbour

Introduction

There are many trace elements whose concentrations are increased by human activity (ARWB 1989 p1-9). Of these, the ones of most concern are those identified as priority pollutants by the United States Environmental Protection Agency (Table 4.1). Trace elements of potential concern in the Manukau are those that exceed natural concentrations (see section 4.2) and sediment quality criteria (see section 4.4).

Lead, Zinc and Copper

Of all the trace elements, Pb, Zn and Cu more frequently exceed sediment 'criteria'. Concentrations near some industrial stormwater discharges can exceed sediment concentrations known to be acutely toxic by many times. Concentrations throughout Mangere Inlet and Onehunga Bay are high enough to be of concern (Fig. 4.1). Concentrations throughout the harbour as a whole are often 2-3x greater than background (Fig 4.1, 4.2), which suggests a widespread distribution of contamination, although not necessarily to toxic levels. The trends along the northern 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. 4.3). 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. Concentrations in Mangere Inlet were much higher in the past (Fig. 4.4). They continue to be discharged to the harbour via stormwater and sewage disposal.

Interstitial water concentrations of Pb and Cu in Mangere Inlet (Fig. 4.5) are close to or exceed marine water quality criteria.

Chromium

Chromium concentrations are also elevated in Mangere Inlet compared with background, but here concentrations are lower than criteria (Fig.

Table 4.1 Priority (USEPA) trace elements and their distribution in the Manukau Harbour.

Trace element	Localised	Widespread	Comment
Ag-Silver	?	?	Never measured, but has limited use around, and is discharged to the Manukau.
As-Arsenic	Yes	No	High concentrations close to some industrial stormwater drains
Be-Berylium	?	?	Never measured, unlikely problem
Cd-Cadmium	Yes	No	Some high concentrations found in Mangere Inlet
Cr-Chromium	Yes	No	High concentrations close to some industrial stormwater drains. High concentrations found deep within sediments of Mangere Inlet
Cu-Copper	Yes	Yes	High concentrations found throughout Mangere Inlet and Onehunga Bay
Hg-Mercury	Yes	No	High concentrations close to some industrial stormwater drains
Ni-Nickel	Yes	No	High concentrations close to some industrial stormwater drains
Pb-Lead	Yes	Yes	High concentrations found throughout Mangere Inlet and Onehunga Bay
Sb-Antimony	No?	No	Low concentrations in Waiuku Estuary
Tl-Thallium	?	?	Never measured, unlikely problem
Zn-Zinc	Yes	Yes	High concentrations found throughout Mangere Inlet and Onehunga Bay

4.1). Interstitial water concentrations are also low compared with Water Quality Criteria (Fig. 4.5). The source of this chromium is sewage and past industrial pollution. In the past, Mangere Inlet received much higher loads of Cr as evidenced by the high concentrations deep within the sediments. (Fig. 4.4). As with Pb, Cu and Zn there is a pollution gradient along the North shore (Fig. 4.3). Concentrations can be very high locally near some industrial stormwater discharges.

Cadmium

Cadmium concentrations are elevated in surface sediments in Mangere Inlet (Table 4.2) compared with background (Ports of Auckland 1989) but concentrations are less than sediment criteria. Cadmium concentrations are low in the Waiuku estuary (Williamson et al 1992). It seems likely that there are locally high cadmium concentrations from past industrial pollution in Mangere Inlet, and recent industrial stormwater runoff.

Mercury

Concentrations of these can be locally very high near some industrial stormwater drains, but contamination does not appear to be widespread because detailed studies in the Waiuku Estuary, Mangere Inlet or the main body of the harbour have found only low concentrations (Table 4.2). Because Hg is so toxic, there is a need for more information on its distribution, especially near stormwater outfalls, because elevated concentrations of Hg have been reported in Auckland stormwater sediments (ARC 1992).

Nickel

Nickel is a major contaminant of MSPW effluent (ARC 1989) yet does not appear to have accumulated in sediments around the effluent discharge or Mangere Inlet. Concentrations in the <20 µm sized particles throughout the harbour have concentrations (Fig. 4.2) similar to background. It does not appear to have been a historical pollutant in the Mangere area, because concentrations throughout deep cores (Fig. 4.4) are similar to background levels. It is, however, relatively high in interstitial waters in Mangere Inlet (Fig. 4.5), and future research will focus on the source and fate of this nickel. It is possible that Ni is highly mobile and does not accumulate in the sediments.

Arsenic

Arsenic concentrations are low compared with sediment criteria and similar to that expected from background (Table 4.2). Historically, arsenic concentrations have not been high (Fig. 4.4).

Beryllium, Selenium, Antimony, Thallium

Antimony has been measured at 15 sites in the Waiuku Estuary and found to be <1 µg/g (Bioresearches 1977) compared with a WDOE criteria of 150 µg/g and ER-L of 2 µg/g (see section 4.4). Selenium has been measured in 11 sediment samples from Waiuku Estuary, and all were < 0.5 µg/g (Bioresearches 1977). For the other toxic elements on USEPA Priority Pollutant list there is no data for the Manukau Harbour. Of these, Ag is a potential problem, because it is sewage-derived and is known to be a problem in San Fransisco Bay, which is similar in a number of respects to Manukau Harbour.

Summary

Concentrations of many elements (As, Cr, Cu, Ni, Hg, Pb, Zn) are very high near drains from some industrial areas. Some (Cu, Pb, Zn) are high and of concern through Mangere Inlet, Onehunga Bay and small parts of the Waiuku Estuary and Pahurehure Inlet. These elements are also elevated above natural levels throughout a large part of the harbour, but concentrations are low compared with criteria. Thus, concentrations of many trace elements are at levels of concern in the muddy, urbanised or industrialised inlets and estuaries. Concentrations in the muddy sand and sands in the main body of the harbour are low compared with sediment criteria.

Priorities for future work are:

- Fate and effects of the major contaminants Cu, Pb and Zn.
- Survey of Hg distribution near stormwater drains.
- Fate of Ni discharged form the MSPW.
- Preliminary surveys of Ag, Sb, Be, Tl and Se in Mangere Inlet and Onehunga Bay.
- Further surveys of Cd and As in industrialised estuaries.

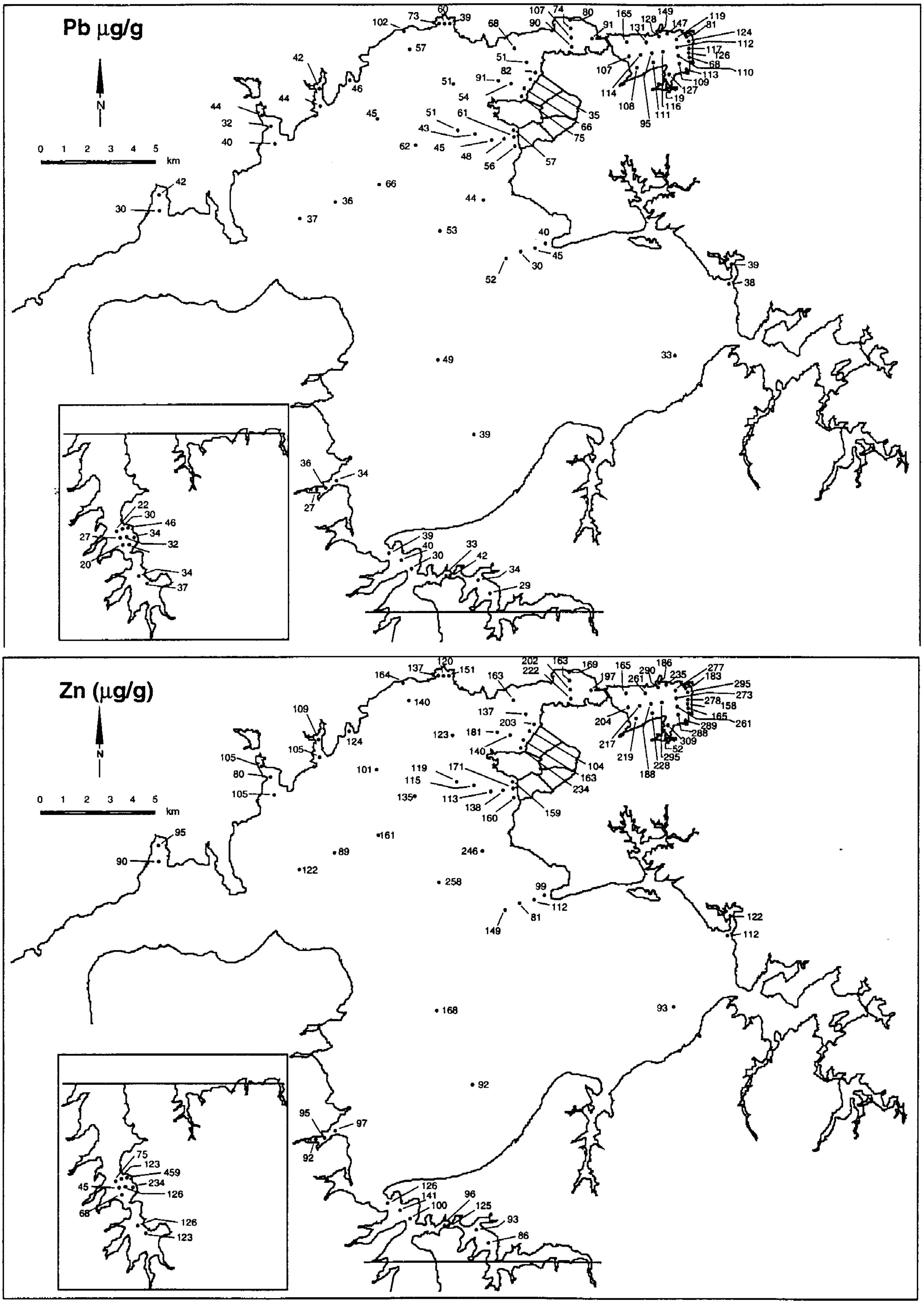

Fig. 4.1 Concentration of Pb, Zn, Cu and Cr in the <20 µm sized-fraction of surface sediments of the Manukau Harbour.

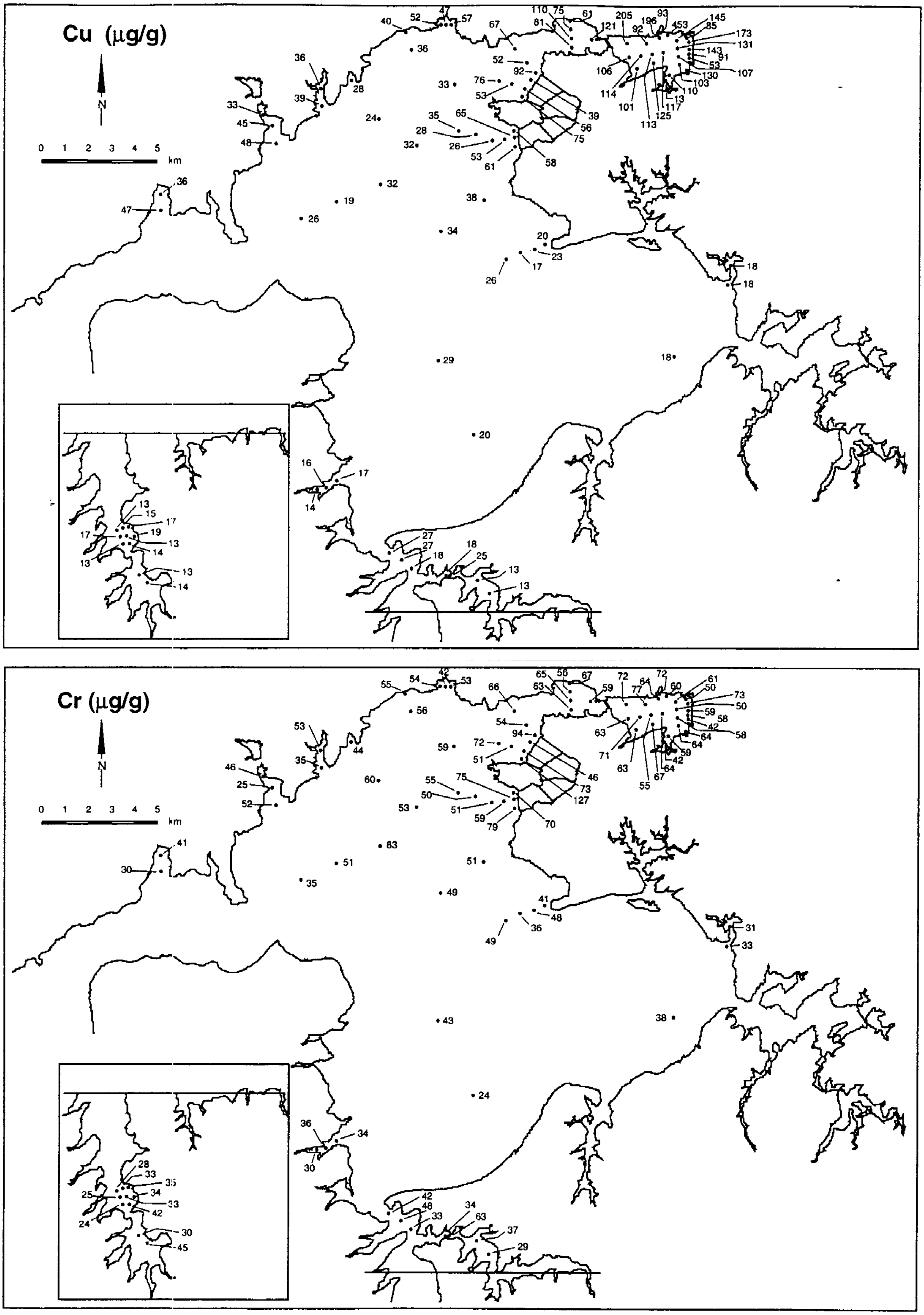

Fig. 4.1(continued) Concentration of Pb, Zn, Cu and Cr in the <20 µm sized-fraction of surface sediments of the Manukau Harbour.

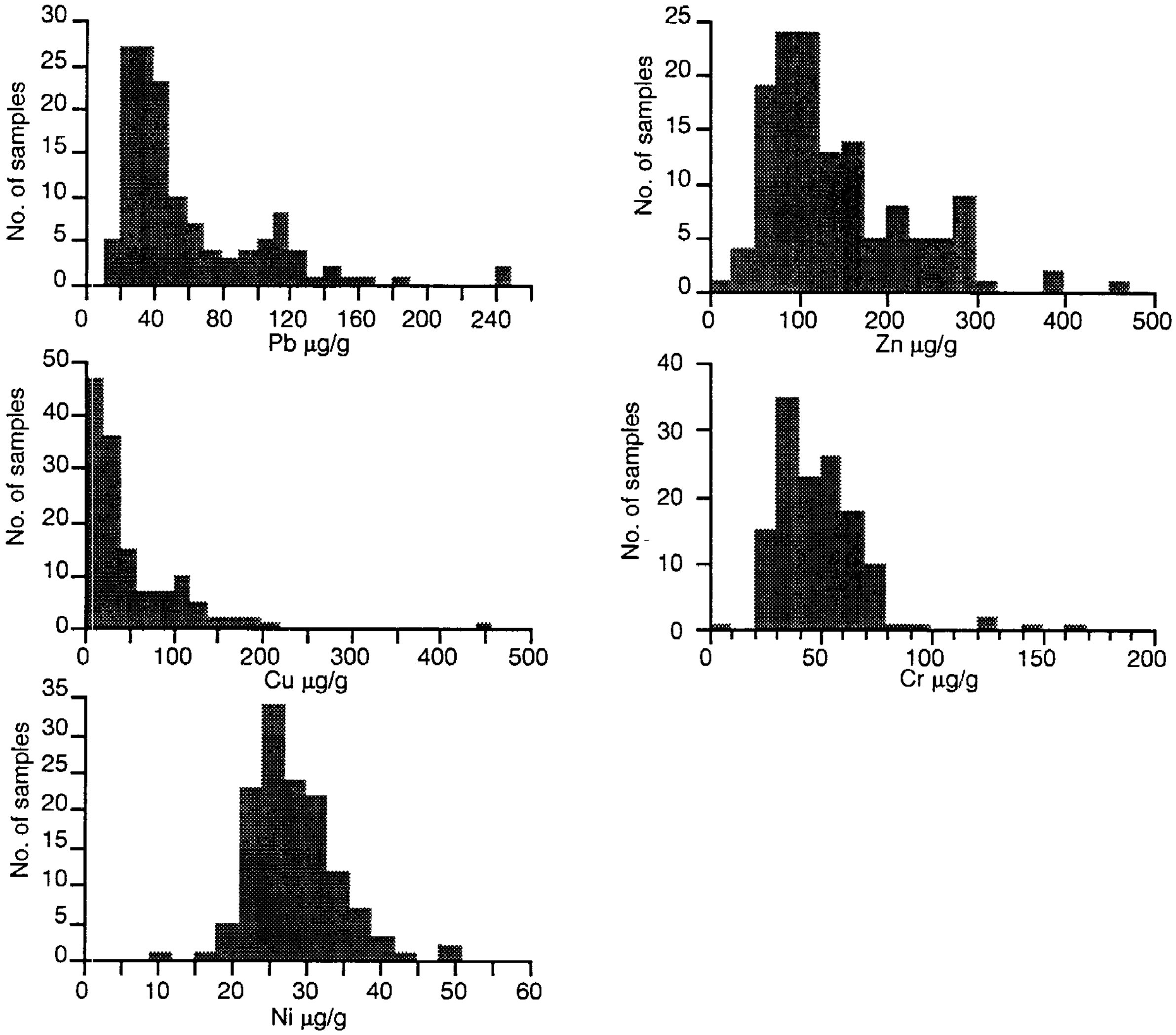

Fig 4.2 Distributions of Pb, Zn, Cu, Cr and Ni concentrations in the < 20 µm particle size fraction throughout the Manukau Harbour. Data from Glasby et al (1992). Sediment pollution by Pb, Zn and Cu is clearly evident from the high concentrations and log-normal distribution. Pollution by Cr is less pronounced, while there is little pollution by Ni.

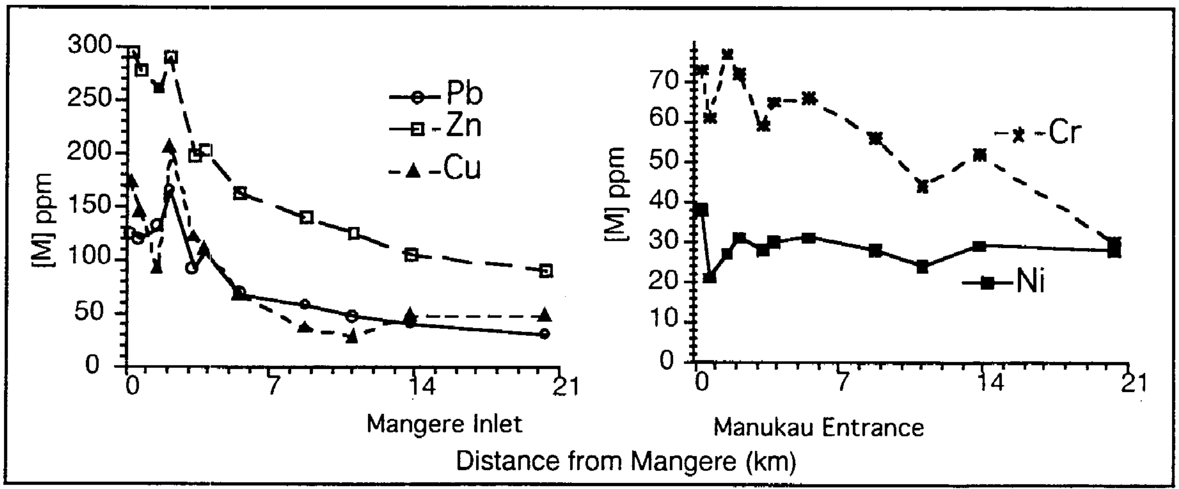

Fig. 4.3 Concentration gradients along the northern Manukau Harbour (from Williamson et al 1992). The units ppm=µg/g.

Table 4.2 Median (and range) of As, Cd and Hg sediment concentrations (µg/g) found by Kingett Mitchell and Associates (Ports of Auckland 1989). As and Cd were determined on 0.5 M HCl extracts, while Hg was determined after digestion with HNO_3/H_2SO_4 and persulphate/permanganate.

Location	n	As	Cd	Hg
Mangere Inlet northern shore	5	2.2 (1-4)	0.5(0.3-2.6)	0.11 (0.07-0.13)
Onehunga Wharf	6	1.8 (1.2-2.1)	0.2	0.11(0.11-0.12)
MSPW outfall	2	0.75	0.7	0.16
Intertidal sand flats and channels of main harbour (Purakau, Papakura Channels, Motukaraka, Te Tau, Karore Banks)	28	0.5 (0.1-0.9)	<0.1	0.01 (<0.01-0.05)

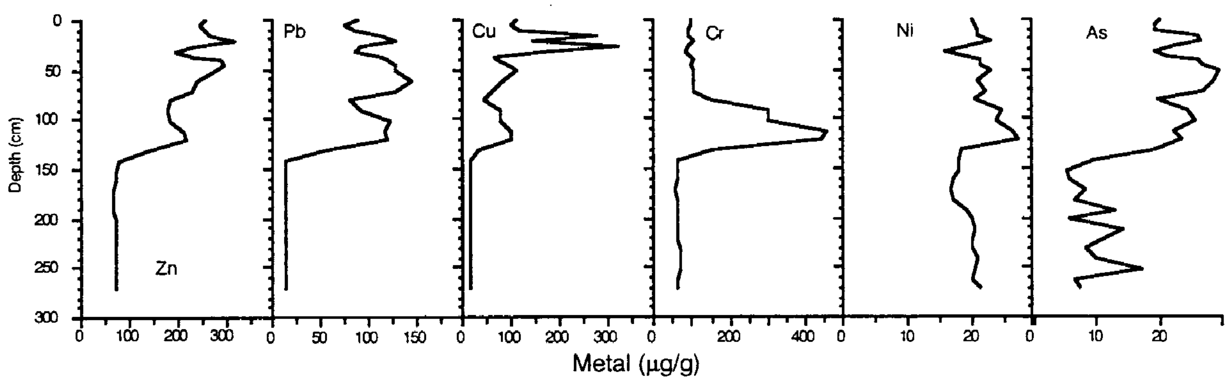

Fig. 4.4 Concentration profiles of Zn, Pb, Cu, Cr, Ni and As in a core taken in Mangere Inlet. Higher concentrations at depth of Pb, Zn, Cu and particularly Cr point to greater pollution in the past. Relatively little contamination by As and Ni has occurred.

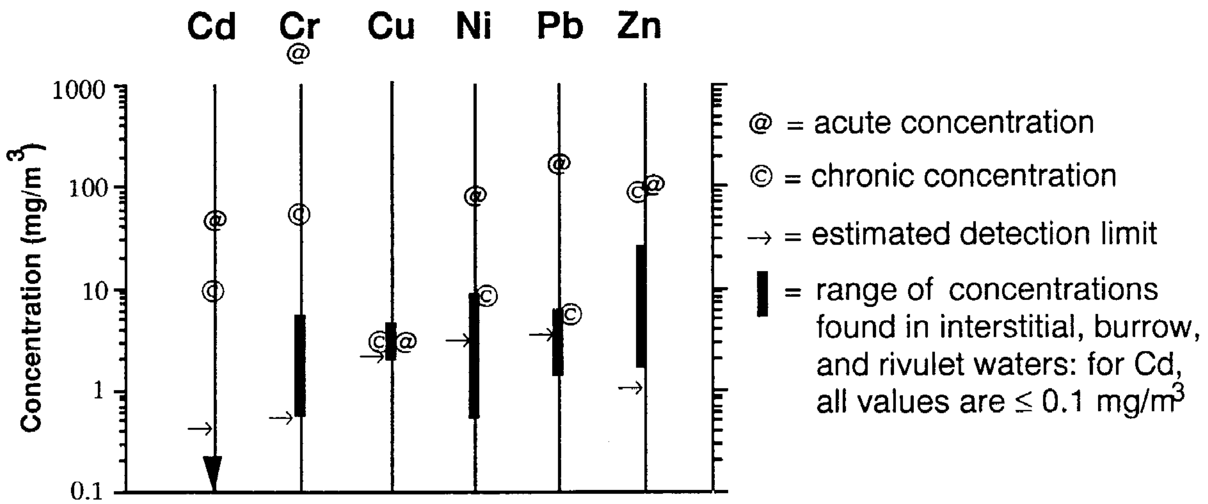

Fig. 4.5 The concentration range found for the six toxic metals analysed in interstitial, burrow and rivulet waters. US Environmental Protection Agency (1986) chronic and acute marine water criteria, and estimated detection limits, are also presented.

4.2 Natural concentrations

One of the commonest methods for evaluating trace element pollution is to compare concentrations found with the expected natural (sometimes termed background) concentrations for that site. Although conceptually simple, this method is difficult to apply because of the difficulty of defining natural concentrations. So far in Manukau Harbour studies, natural concentrations have been assumed to be similar to those found at an arbitrarily chosen remote site, or similar to world average shale composition as representative of an unpolluted fine-grained sediment. These approaches may result in choosing too high or too low concentrations as representative of natural sediments. Here we explain why and describe the factors affecting natural concentrations in the Manukau so that appropriate values can be chosen, for this or other estuaries. The most important factors are sediment texture, sediment provenance (i.e., their source) and analytical methods.

Sediment texture
The dominant sediments range from mud which contains a relatively high natural concentration of trace elements, to coarse sands with very low concentrations.

Sediment provenance
In the Manukau, sediments are predominantly sand originated from the Waikato River, and muds from catchment soil erosion. The sand source has presumably constant composition, but there are significant differences (up to 10 times) for Cu, Cr, Ni and Zn concentrations in catchment soils around the harbour. Examining the most comprehensive datasets for the Manukau (reviewed in Williamson et al 1992) does not indicate any strong provenance effects, although there may be some small effect obscured by other factors such as sediment texture and pollution.

Analytical method
Analytical methods (see Section 4.3) vary widely in the proportion of natural trace element detected.

Measured natural concentrations
Natural concentrations in the Manukau Harbour sediments are summarised in Table 4.3 along with the conditions under which they were measured. These samples were collected deep within the sediment below the level of contamination, with the exception of the samples from Wiroa Is near the airport, which are included to show the low concentrations found in very sandy sediments.

Table 4.3 Reported natural concentrations in Manukau Harbour sediments and in shale.

Study Location	1 Mangere	2 Mangere	1 Shale	3 Wiroa Is	4 Ellets	5 Waikowai
Sample	<20 µm	Total	Total	Total	Total	Total
Method	conc. HNO_3	XRF	XRF	conc. HNO_3	0.5M HCl	XRF
%mud	100	100	100	<2	15	?
As	-	9	-	-	0.3	12
Cd	-	-	-	-	<0.1	-
Cr	22	63	90	-	11	95
Cu	11	17	45	1.1	0.3	18
Hg	-	-	-	-	<0.01	-
Ni	17	19	68	-	4.4	22
Pb	18	14	20	0.45	1	22
Zn	46	71	95	7.8	20	66

Study 1 Williamson et al 1992; 2 Hume et al (in prep.); 3 Author's unpublished results; 4 Ports of Auckland 1989; 5 ARWB 1989.

HOW TO ESTABLISH NATURAL CONCENTRATIONS

Deep core method (preferred method)

1) Determine sediment depth with rods at sampling site.

2) Collect deep cores. In non-depositional environments, depth of core will need to be > bioturbation and physical mixing depths; ≥25 cm is a safe guess. In depositional environments, sedimentation rates up to 7 mm/year have been measured or estimated, so cores deeper than 70 cm should be collected (to allow for deposition + bioturbation). On the sides of channels, where sedimentation rates may be very high, cores as long as 3 m may need to be collected (e.g., see **Fig. 4.4**, Williamson et al 1991).

3) Identify a sediment layer that is likely to be uncontaminated (probably the deepest layer), that is also similar in sediment texture to the surface sediment.

4) Determine natural concentration using selected analytical method.

5) The most rapid method to check the level of contamination is acid extractable Pb, Zn. These two elements are almost always associated with pollution.

Remote sites method

If the collection of deep cores is not sensible (e.g., the study is in a strongly erosive environment where sediment accumulation is low), then samples collected at sites remote from pollution may be suitable.

1) Sites will have to be selected to match closely as possible sediment provenance (consult Soil Maps, Geological Maps and/or ARWB 1989 p72-75) and depositional environment. Check sediment texture is similar to study site by sieve analysis of the proportions of gravel, sand, fine sand and mud. The effects of provenance can be checked by comparing the concentrations of elements that are not pollutants (e.g., Co, V) between polluted and remote sites.

2) Determine natural concentration using selected analytical method.

3) It desired, check for contamination using acid extractable Pb, Zn.

4.3 Analytical methods. How different are they?

Manukau Harbour surveys of trace element concentrations have used X Ray Fluoresence (XRF); complete acid digestions using HF in combination with HNO_3, HCl, or $HClO_4$; concentrated acid digestions (using one or combinations of HNO_3, H_2SO_4, HCl, $HClO_4$,); and dilute acid (0.5M HCl). A review of these and other methods is given in ARWB (1989). It is inevitable that comparisons are made between different studies using different methods. This is generally regarded as inadvisable or invalid, and in some cases this is certainly true. However, managers and scientists need to make semi-quantitative comparisons, given the high costs of repeating studies and the value of historical information. Here we summarise what we know about the similarity of these methods.

Fig. 4.6 compares Zn concentrations found using different methods for a ‘muddy’ and a ‘sandy’ sediment. Similar results were found for Cu, Fe, Pb, and Mn. For the coarse sediment, even quite rigorous methods such as digestion with concentrated H_2SO_4 and HNO_3 only gets about 50% of that found with complete digestion, due to a high proportion of the trace elements bound within unreactive silicate minerals. Digestions with either HNO_3 and HNO_3/H_2SO_4 extract a similar proportion of the total element. HCl/HNO_3 or $HNO_3/HClO_4$ are reportedly better at extracting lithogenic trace elements (ARWB 1989). In muds, much higher proportions of the total trace element concentration is extracted by these concentrated acids.

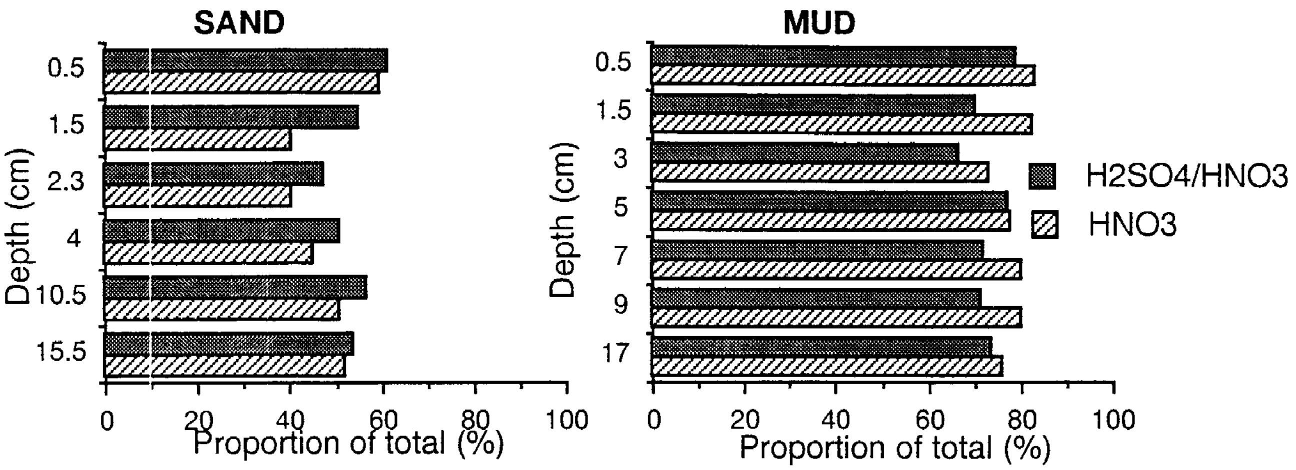

Fig. 4.6 The proportion of total Zn extracted by concentrated HNO_3 and H_2SO_4/HNO_3 digestions. Samples were sandy and muddy cores taken in Pukaki Creek. Total Zn was determined by $HF/HClO_4/HNO_3$ digestion.

Weaker extractants, like those used to obtain the non-residual fraction (trace elements bound to organic matter, sulphides and amorphous oxides) are particularly sensitive to texture, and to the degree of contamination. Fig. 4.7 compares the dilute acid extract (0.5M HCl) with the total element concentrations for 3 different sediments, of varying contamination and texture. The dilute acid extracts very little of the trace elements in sandy sediments (<20%) but about 65-90% in contaminated muds.

In summary, coarse sediments are very sensitive to the method used. Muddy sediments are much less sensitive, and with contaminated muds, it is valid to compare so-called 'total' methods on a semi-quantitative basis. Even moderate extractants such as dilute acids (>1M in strength- see later) are a good approximation to total concentrations in this case, as long as there is sufficient excess acid to react with sediment components that neutralise it (e.g., iron oxides, $CaCO_3$).

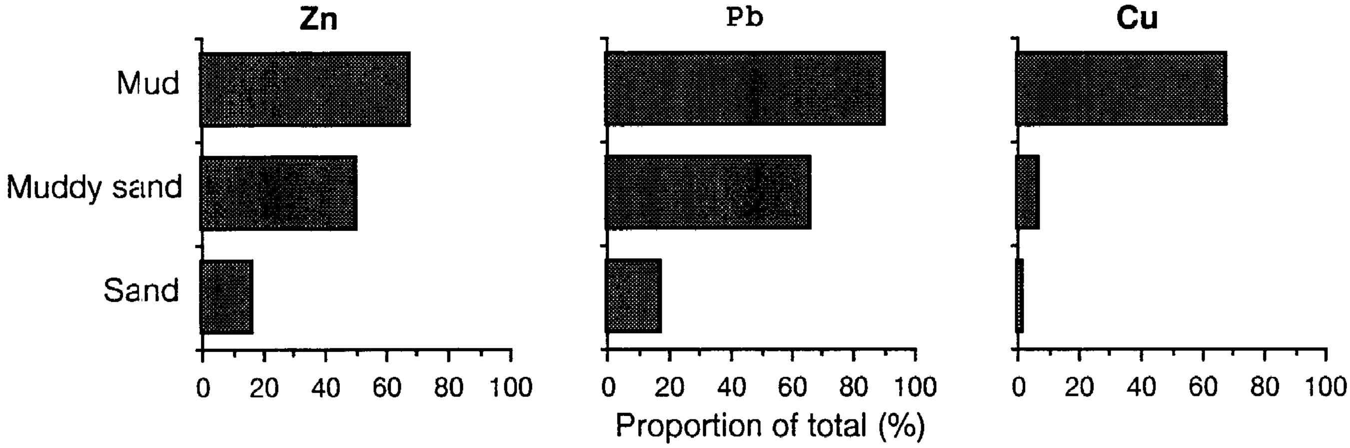

Fig. 4.7 The proportion of total Zn, Pb or Cu extracted with 0.5 M HCl in 3 different sediment types; unpolluted sand, muddy sand and polluted mud.

4.4 Marine sediment quality criteria

General sediment toxicity criteria are not available, but are currently the subject of much research overseas. Two sets of sediment criteria have been published for other specific purposes (Table 4.4): (i) A recent review of sediment toxicity data from a range of sites throughout the United States by Long & Morgan (1991) and (ii) criteria that have been derived for the Puget Sound Region of the USA (Barrick et al. 1988). The latter criteria are designed to control the deep water disposal of dredged polluted sediments in the Puget Sound region. There is uncertainty about their derivation and their applicability elsewhere, but they were recently adopted to control future dumping of dredge spoil from the Port of Auckland (Ports of Auckland 1990).

Long & Morgan (1991) list a range of concentrations at which there appear to be biological effects at different sites throughout the USA. From this they derive two statistics. The lower 10 percentile in the data was identified as an "Effects Range-Low" (ER-L) and the median was identified as an "Effects Range-Median" (ER-M). They also derive a subjective 'Apparent Effects Threshold' (AET) where their data summary suggested a value above which effects are consistently observed. For the Puget Sound data, two sets of criteria are available.
(i) AET which are the concentrations above which toxic effects were found for the tests: oyster larvae toxicity, toxicity to a luminescent bacterium, amphipod toxicity and benthic infauna presence/absence. The latter of these 4 tests are used by the Washington Department of Ecology (WDOE) as Sediment Quality Standards. The tests are not especially sensitive, so AET concentrations may still be chronically toxic.
(ii) "Screening Levels", which are guidelines used to monitor the quality of dredge spoil, so that if these are exceeded, then toxicity tests need to be conducted. They were arbitrarily chosen as one tenth of the highest of the four AET concentrations (T. Gries, WDOE, pers. comm.).

None of the criteria listed above are the result of a proven causal relationship between a particular toxicant and a biological effect. This is because they were derived from studies on sediments that contain a wide number of potential toxicants, where observed biological responses were consistent with variation in the concentration of the potential toxicant, i.e., there is correlation between concentration and response, but no causal relationship has been demonstrated. The observed effect may in fact be due to other toxicants whose concentrations also happen to correlate with those of the potential toxicant or to other environmental factors e.g., variation in sediment texture. In addition, we do not know if the sediment toxicity effects used to derive the criteria will be duplicated in the Auckland region. Therefore, we use the criteria in Table 4.4 cautiously, as indicators of potential problems, rather than of probable effects.

In summary, sediment quality criteria are based on a wide range of data collected in the USA. They are derived from correlative evidence and not a proven casual relationship. It is possible that some of the contaminants appear to be toxic only because their concentration correlates with the concentration of another contaminant which exerts the toxic effect. The criteria do not consider differences in sediment texture or sediment chemistry, so they may be insufficiently protective in some sediments (e.g., sands), but overly protective in others (e.g., enriched muds).

Table 4.4 Sediment quality criteria: ER-L, ER-M and overall AET (Long & Morgan 1991), Screening Levels for marine disposal (T. Gries, WDOE, pers. comm.), WDOE Sediment Quality Standards (Barrick et al. 1988).

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Effects Range-Low	33	5	80	70	0.15	30	35	120
Effects Range-Median	85	9	145	390	1.3	50	110	270
Apparent AET	50	5	-	300	1	-	300	260
Screening Levels	70	0.96	-	81	0.21	140	66	160
WDOE Standards	57	5.1	260	530	2.1	>140	450	410

- Data not available

4.5 The chemistry of trace elements in sediments

Introduction

In sediments, trace elements occur in a number different forms, both in the dissolved and in the solid state. The highest proportion is usually in the solid phase.

Forms of element in sediments
Dissolved
Free element ion
Complexed by inorganic ions (e.g., chloride, sulphide)
Complexed by dissolved organic matter
Solid state
Adsorbed onto surfaces of clays, element oxides, organic material
Co-precipitated with sediment phases
Incorporated into organic matter

The way an element is bound in a sediment determines the biologically active fraction and its fate and cycling. It is also a major factor controlling concentration of contaminants in sediments and dictating the method of analysis. Therefore, it is important to have a reasonable understanding of the way an element is bound in a sediment before designing a sampling programme.

In the Manukau, sediments are predominantly sand originated from the Waikato River. More recently this has been augmented by sands entering into the harbour after longshore drift up the North Island coastline, and by gravels, sands and muds from catchment soil erosion. These materials contain a certain amount of trace elements, and after the sediment is laid down, the trace elements remaining form the so-called natural concentrations. Once sediments are deposited, they undergo a wide range of physical, biological and chemical processes termed "diagenesis", which creates new chemical phases in the sediment. Diagenetic processes have a strong influence on the form of trace elements.

By far the most important factor in early diagenesis is the biological oxidation of metabolisable forms of organic carbon. This oxidation, together with the resulting anoxic conditions, produces large changes to the form of iron, manganese and sulphur; which play key roles in 'binding' trace elements in sediment and releasing them to the overlying water. The changes occur because the diffusion of oxygen from the air is too slow to keep up with metabolism, so micro-organisms use nitrate, Mn(IV) oxide, Fe(III) oxide, and sulphate to oxidize (metabolise) organic carbon (Froelich et al. 1979), and in the process produce reduced forms of these substances.

OXIDATION OF METABOLISABLE ORGANIC MATTER
Oxidizing agents
Oxygen O_2
Nitrate NO_3^-
Manganese (IV) oxide e.g., MnO_2
Iron (III) oxide e.g., Fe_2O_3
Sulphate SO_4^{2-}
Immediate products
Carbon dioxide CO_2
Nitrite NO_2^-, ammonia NH_4^+
Dissolved iron (Fe^{2+})
Dissolved manganese (Mn^{2+})
Sulphide, thiosulphate, sulphur
New sediment phases
Amorphous iron and manganese hydrous oxides MnOOH, FeOOH
Iron sulphide FeS, FeS_2

In sediments with high inputs of organic matter, such as those of the Manukau Harbour, these reactions are compressed close to the sediment-water interface (Shaw et al. 1990; Sorensen and Jorgensen 1987). Many of the oxidised and reduced forms of iron, manganese and sulphur, also react with one another abiotically. All these reactions produce a very complex sediment chemistry. A brief description of the most important phases is given below.

Iron hydrous oxides

In the anoxic region of sediments, the reductive dissolution of iron (III) oxides (e.g., goethite - Fe_2O_3) is slow and produces dissolved Fe^{2+}. If transported into an oxic region of the sediment by diffusion or advection, Fe^{2+} is very unstable in the presence of oxygen at the pH of estuarine sediments and is rapidly oxidized to Fe (III) and precipitates as amorphous iron hydrous oxides (FeOOH). If this newly formed FeOOH is mixed downwards into anoxic zones by bioturbation or wave action, it can undergo reduction to Fe^{2+} to initiate a new cycle.

Being amorphous, FeOOH has a large surface area per unit weight, and being abundant, it may be an important substrate for trace element adsorption. Our results indicate that a large proportion of Cd, Cr, Pb, Zn, Co and Ni appear to be associated with it. The amount of FeOOH varies by up to 50 fold in the Manukau depending on sediment texture (Fig. 4.8) and it would be reasonable to expect a similar order of magnitude variation in elements that are strongly associated with FeOOH. This is in fact observed in unpolluted sediments. FeOOH concentrations do not vary with depth in the near-surface sediments, so we would not expect strong concentration gradients of these elements with depth (Fig. 4.8). It is interesting to note (Fig. 4.8), that the total Fe does not differ greatly over the range of sediment types (about 2-5 fold), because it includes crystalline iron oxides and iron-bearing silicates, as well as iron sulphides. Total concentrations, then, do not yield useful information on the iron phases important in binding and cycling trace elements.

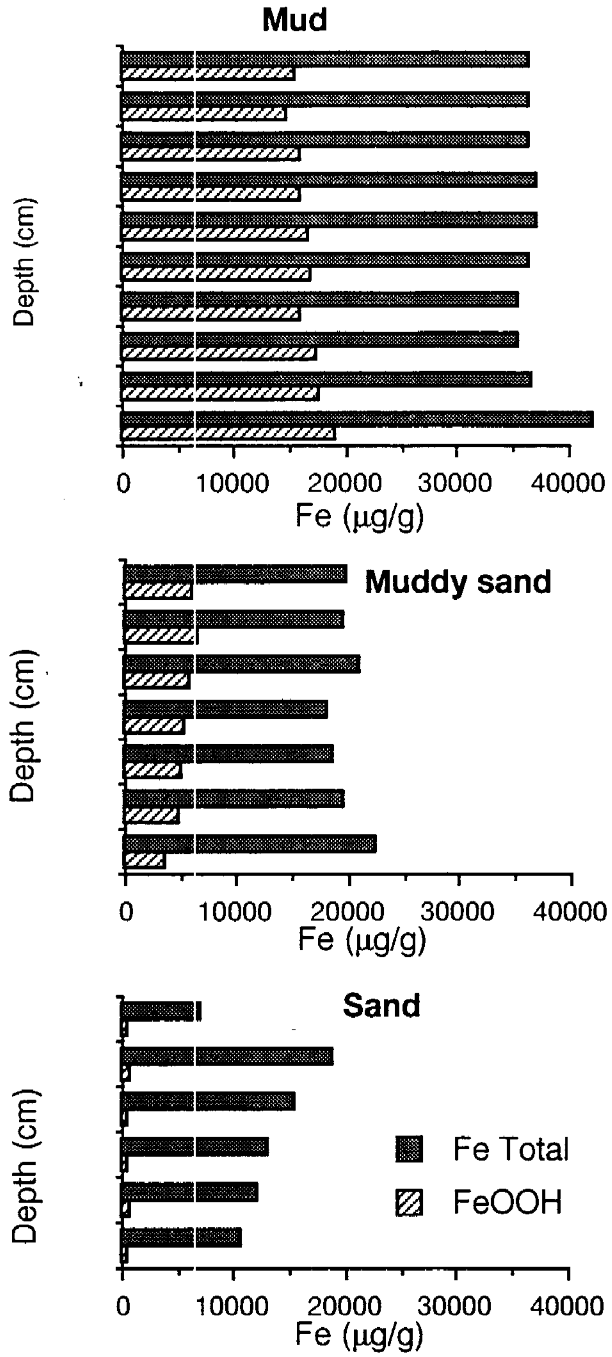

Fig. 4.8 Iron components in sand, muddy sand and muds.

Amorphous hydrous iron oxide is very abundant in sediments in the Manukau Harbour and elsewhere. It is reduced during sediment diagenesis. Concentrations do not change much with depth or redox conditions, but are strongly dependent on sediment texture. It is a major sediment phase which probably controls the concentrations, fate and cycling of Cd, Pb, Ni, and Zn (and other trace elements).

Manganese hydrous oxides

Manganese oxides (MnO_2) also undergo reductive dissolution (to Mn^{2+}) which in turn can undergo oxidative precipitation to reform amorphous manganese hydrous oxides. In contrast to iron oxides, the reductive dissolution of manganese (IV) oxides is rapid, while oxidative precipitation of Mn^{2+} is slow.

Small but significant concentrations of Cd, Ni, Pb and Zn appear to be associated with the MnOOH phase in sediments. Dissolved manganese is released from sediments and relatively high concentrations can be found in burrow waters or water draining over intertidal muds Table 4.5. The cycling between reduced and oxidised states appears to be more rapid than for iron and can lead to a build up in the top-most layer of surface sediments (Fig. 4.9). Although the concentration of manganese oxides is much lower than iron oxides, its more rapid reduction and mobility may mean it is an important substrate for trace element cycling.

Table 4.5 Manganese concentrations in the Manukau Harbour waters.

Location	Mn (µg/l)
Outer harbour	<10
Onehunga Wharf	20
Mangere Inlet low tide channels	210-410
Intertidal drainage	80-400
Burrow waters	115-400

Although amorphous manganese hydrous oxide is a relatively minor phase in estuarine sediments, its rapid cycling between reduced and oxidised forms, and between sediments and water, may mean it is important in trace element mobilisation from sediments.

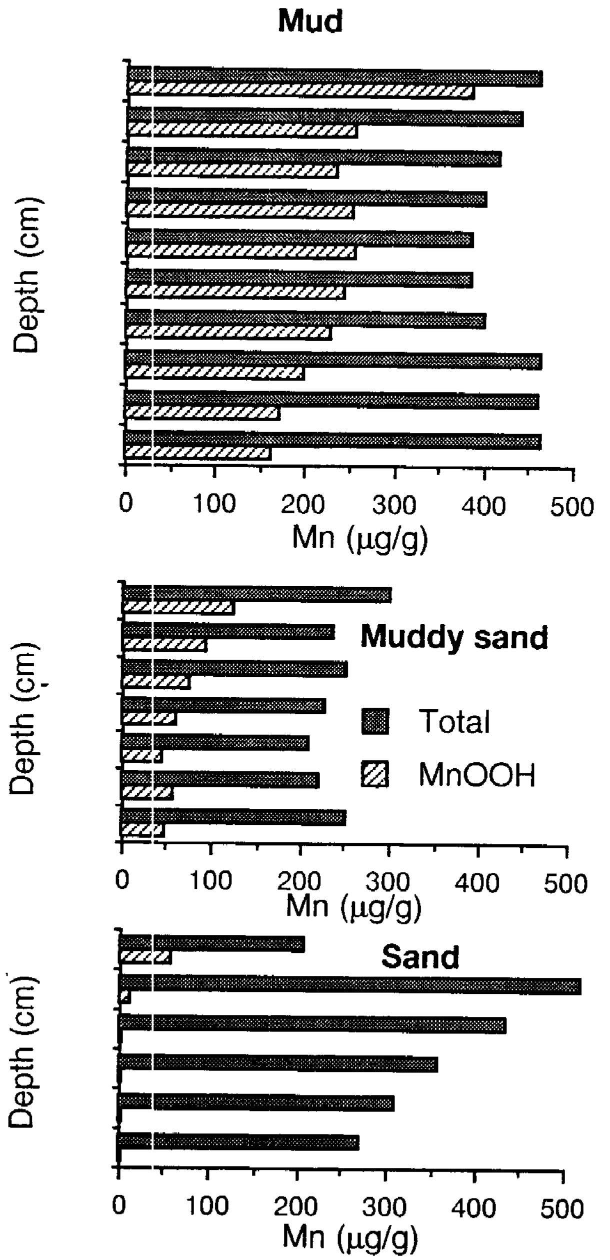

Fig. 4.9 Manganese components in sand, muddy sand and muds.

Ferrous sulphide (FeS)

FeS is formed by the combination of dissolved iron and sulphide in interstitial waters or the reaction of dissolved sulphide with FeOOH. It is precipitated as an amorphous material in the anoxic region of sediments. It is very unstable if subsequently exposed to oxygen, when it forms amorphous iron hydrous oxides and higher oxidation states of sulphur, such as sulphur itself. Some trace elements also precipitate as insoluble sulphides, probably coprecipitated with FeS, particularly the heavy metals Cd, Cu, Ni, Pb and Zn. Manukau sediments contain <10 - 3000 µg/g FeS (or more correctly Acid Volatile Sulphide, AVS) (Fig. 4.10). They sometimes show a strong concentration profile, with the maximum concentration often about 3-5 cm below the surface.

This variation in concentration has direct implications for heavy metal toxicity. AVS has recently been shown to buffer sediments against acute toxicity from toxic metals because it reacts with them to form insoluble metal sulphides (Di Toro et al 1992). They found that Cd and Ni in sediments do not become acutely toxic to amphipods until the sum of the concentration of heavy metals exceeds the stoichiometric concentration of AVS

In the Manukau sediments, this equates with an AVS concentration reported in Table 4.6. The muddy, polluted sediments in Mangere Inlet contain higher concentrations of acid volatile sulphide (AVS, chiefly FeS) than relatively unpolluted sandy sediments (about 100 times greater) or 'muds' (about 10 times greater). The sum of all the heavy metal concentrations (µmoles/g) is presently less than the AVS concentration at these sites (Table 4.6). It is also possible to calculate metal concentrations

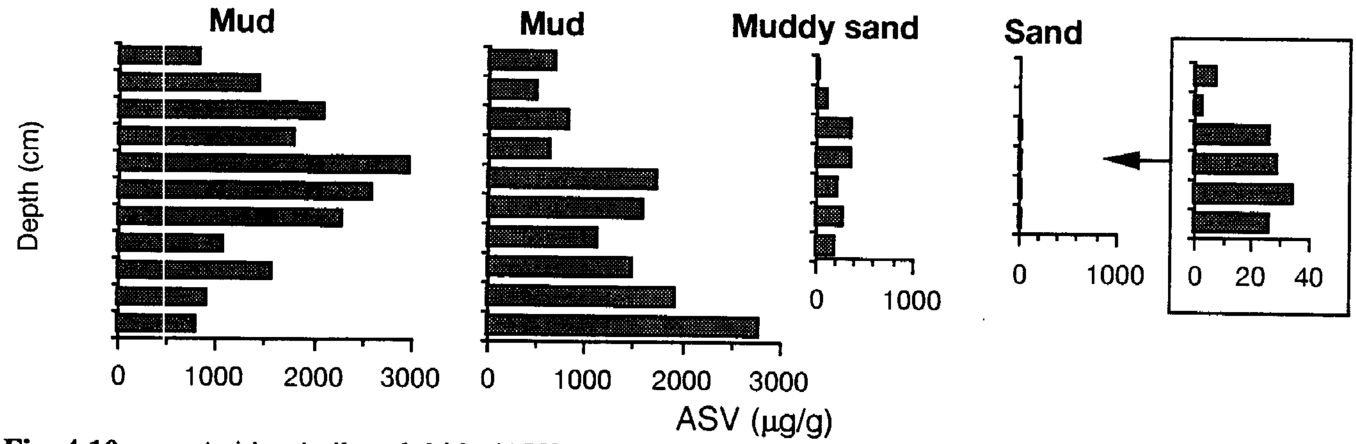

Fig. 4.10 Acid volatile sulphide (AVS) in sand, muddy sand and muds.

Table 4.6 Concentrations of AVS and heavy metals (µmoles/g) in Manukau Harbour sediments.

Sediment	Location	AVS 0-10 cm	Heavy metals (Cd+Co+Cu+Ni+Pb+Zn)
Sand	Wiroa Is	0.56	0.05–0.1
Muddy sand	Pukaki Creek	4.7	0.5–1
Mud	Mangere Inlet	35-59	5–12

which exceed these AVS concentrations, as an indication of the different sensitivity of these sediments to acute toxicity through this mechanism. Such a calculation may be relevant to estimating the sensitivity of animals like amphipods that live in anoxic environments and may be as sensitive as the amphipods used in overseas studies (Di Toro et al 1992). We do this in Table 4.7. Mangere muds are susceptible to this pollution mechanism at metal concentrations found only near some industrial stormwater outfalls. In contrast, in sands, quite low concentrations of metals are predicted to render these sediments susceptible to this pollution mechanism, but only over a short time period before the contaminants are flushed away (see Chapter 3). The concentrations of metals calculated for muddy sands are not particularly high, and these sediments are also susceptible to this pollution mechanism. The results should be interpreted cautiously. On one hand, metals are "bound" by other phases besides AVS so this calculation may overestimate the metal concentrations that are acutely toxic. On the other hand, the mechanism does not consider chronic toxicity, and so underestimates metal concentrations that are environmentally important. Furthermore, it does not consider other animals that live solely in an oxic environment, where AVS concentrations are low and may have little relevance to biotic interactions with heavy metals.

Overseas studies provide evidence that AVS (chiefly FeS) is directly implicated in the toxicity of trace elements that form strong sulphide compounds such as CdS and NiS (and most of the heavy metals). Calculations based on AVS concentrations found in the Manukau Harbour and overseas findings suggest that this mechanism is ameliorating acute toxicity in polluted sediments, but unpolluted parts of the harbour would be susceptible to heavy metal poisoning.

Iron pyrites (FeS_2)

Over time, amorphous FeS will crystallise (greigite and marcawasite) and react with polysulphides to form FeS_2. Pyrites is much more stable to oxidation than FeS, and can be found in oxic sediments. Manukau sediment contain about 100 - 13,000 µg/g FeS_2. Concentrations do not change much in surface layers but then tend to increase with depth (Fig. 4.11). Heavy metals associated with FeS_2 will be relatively immobile and unavailable to biota because of the relatively high stability of pyrites compared with FeS. Huerta-Diaz & Morse (1990) found that pyrites contained small, but significant proportions of Zn, Ni and Cd in unpolluted sediments in Texas. Our own studies in the Manukau do not distinguish the proportion associated with pyrites by itself, but the proportion associated with pyrites + organic matter is significant for all the heavy metals we examined.

Table 4.7 Hypothetical metal concentrations (µg/g) which exceed AVS concentrations given in Table 4.6. The ratio of metal concentrations is assumed to be similar to that found by Glasby et al (1988) for Mangere inlet.

Site	Wiroa Is	Pukaki Creek	Mangere Inlet Middle bank	Mangere Inlet Near north shore
Texture	Sand	Muddy sand	Mud	Mud
AVS (µmole/g)	0.56	4.7	35	59
Zinc	17	140	1050	1740
Lead	9	73	550	1020
Copper	10	83	620	1100
Chromium	4	35	260	360
Cadmium	0.2	1.4	11	20
Cobalt	0.6	5	13	13
Nickel	0.8	7	20	20

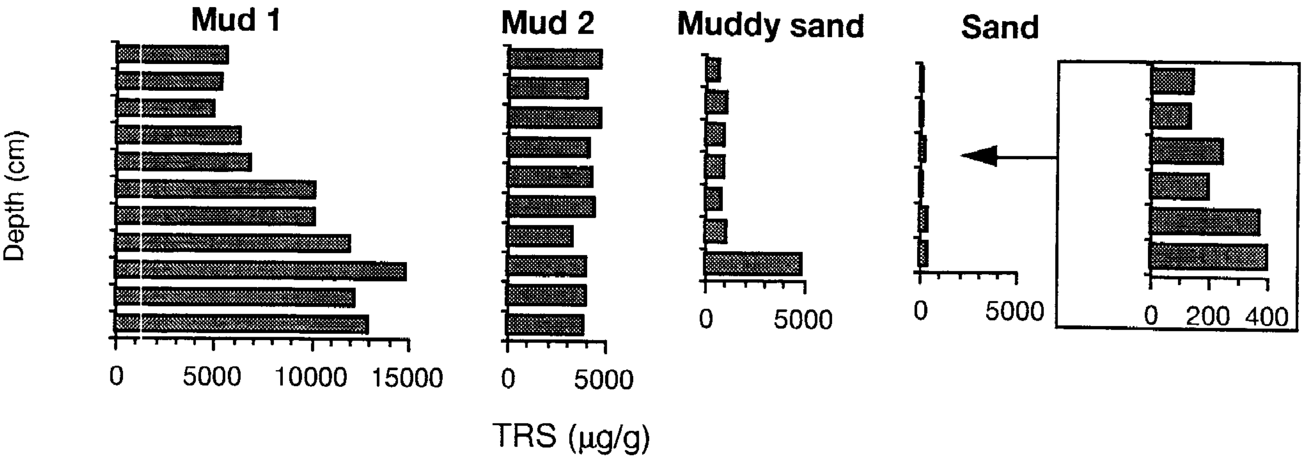

Fig. 4.11 Total reducible sulphur (TRS) (=S+FeS_2) in sand, muddy sand and muds.

FeS_2 is an important phase formed during sediment diagenesis, which probably effectively immobilises a proportion of trace elements that form stable sulphide phases (e.g., Cu). Future work will need to quantify the relative stability and trace element association.

Organic matter

The complex mixture of organic material found in sediments has many different 'sites' for adsorbing trace elements. Generally, the organic content of sediment increases as the sediment texture becomes finer. The organic content of muds in sheltered parts of the Manukau Harbour are typically of the order 1-2% organic carbon, while sandy sediments in the main part of the harbour are typically 0.2-0.5 % organic carbon (Fig. 4.12). Extreme values of 0.1% can be found in sandy areas, while concentrations as high as 3% are found near the MSPW oxidation pond outfall. This range of organic content in sediments is not large compared with other sediment phases that bind trace elements. The reasons for this is that although sediment texture will directly influences the amount of adsorbed organic matter and bacterial films, inputs of large organic particles (live and dead algae and animals, fecal pellets, plant detritus) will not necessarily vary with particle size in the same way.

Sediment profiles of organic matter show no systematic variation with the depth in sediments (Fig. 4.13) (Williamson & Jorgensen 1991), and concentrations can vary 3–4 fold. The classical situation in sediment diagenesis of decreasing organic carbon with depth is not found in the Manukau Harbour sediments, probably due to intense mixing by physical and biological processes.

Aluminosilicates

The basis of most muddy material are clays and amorphous aluminosilcates. These undergo slow diagenetic reactions in seawater and may also be important substrates for trace element adsorption. However, they and sand and silt particles also act as substrates for other

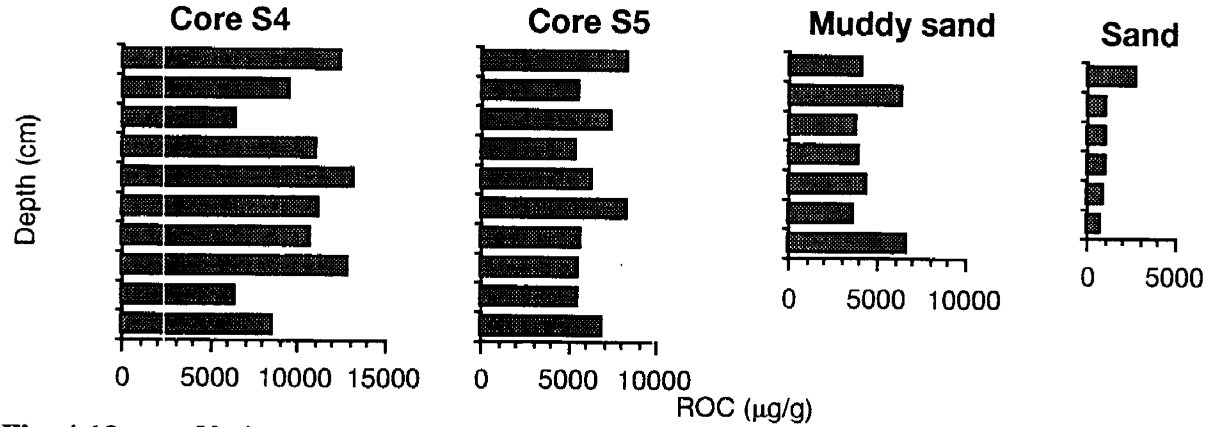

Fig. 4.13 Variation of organic matter with depth for a range of sediment textures.

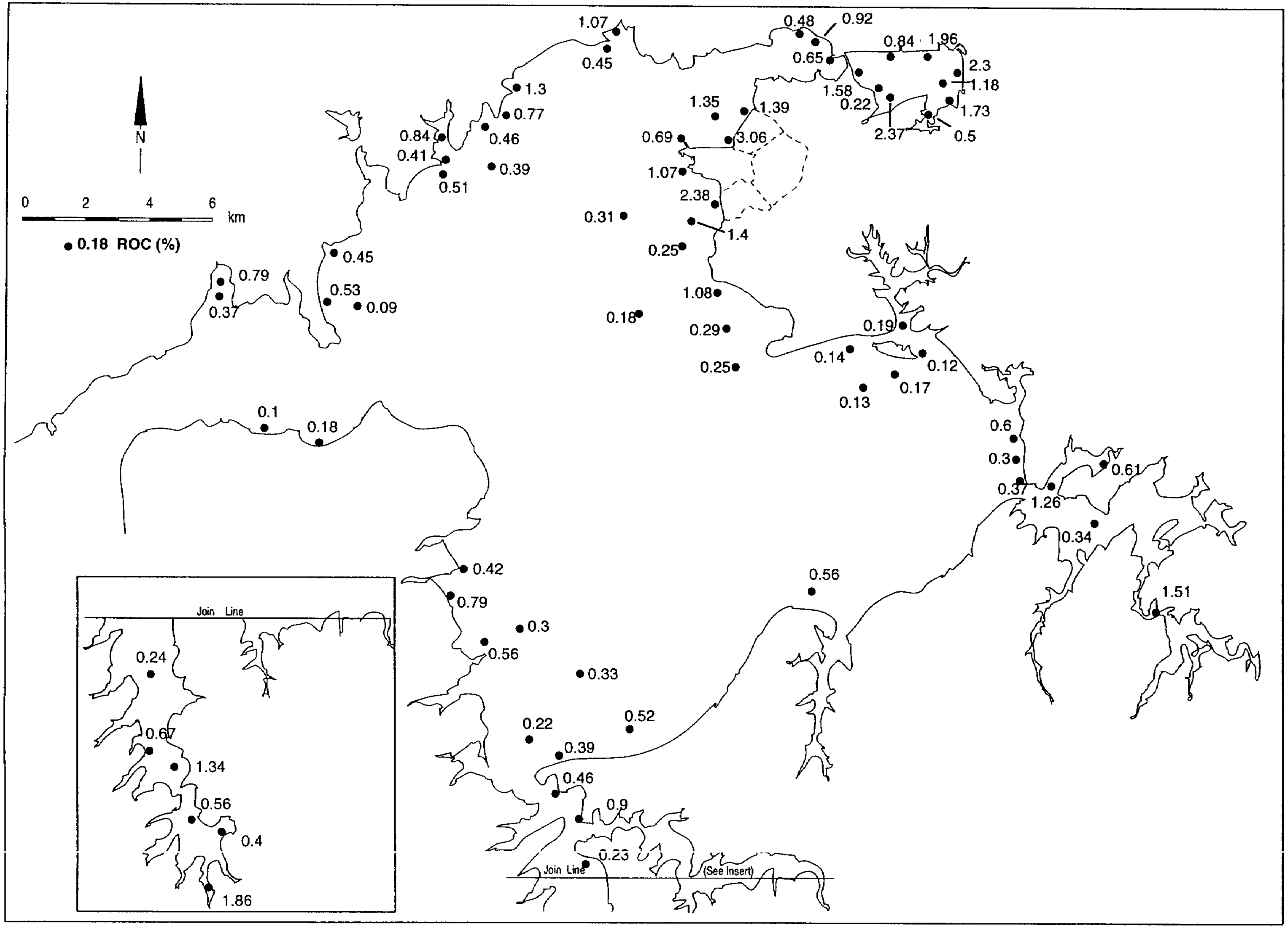

Fig. 4.12 Organic carbon content (%) of Manukau Harbour sediments (data from Taylor 1978, 1982, Henriques 1977).

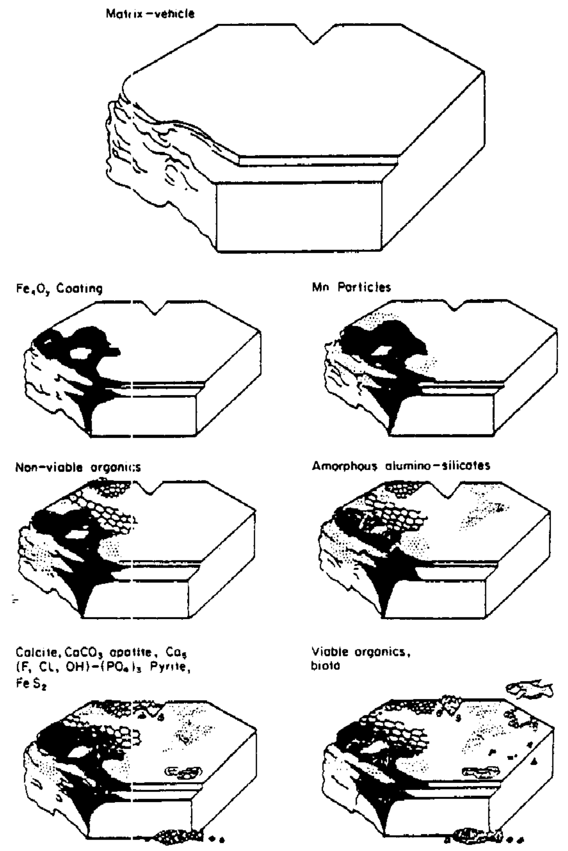

Fig. 4.14 Diagramatic representation of important trace element sinks on the surface of an idealised kaolinite crystal (from Martin et al 1987).

important sediment phases such as precipitated iron sulphides and oxides, and adsorbed organic matter (Fig. 4.14).

Minor phases

Minor, but important phases are often distinguished, in addition to the above. Trace element carbonate phases can be found, both those included at the time of deposition i.e., with $CaCO_3$ in shell material, and those coprecipitated during diagenesis (e.g., with $CaCO_3$, $FeCO_3$). They are regarded as very reactive phases because of their dissolution with a decrease in pH or their instability to oxidation ($FeCO_3$).

Adsorbed trace elements are distinguished by their release in the presence of low trace element/high ionic strength solutions. Adsorption sites include surfaces of all the phases described above.

Lithogenic fraction

In unpolluted sediments, early diagenesis leaves some trace elements still strongly bound inside the minerals which form the sediment, and some in the phases formed during diagenesis. For example, the trace element cobalt, which is not a pollutant in Manukau Harbour sediments, is well distributed amongst the different sediment phases (Fig. 4.15).

The lithogenic fraction is largely unreactive and unavailable, and is also termed the residual fraction. It consists of trace elements in lithogenic materials and stable phases formed during diagenesis (e.g., in crystalline aluminosilicates, minerals such as $FeTiO_2$, crystalline iron and manganese oxides or strongly bound to refractory organic matter). The non-lithogenic fraction described in the foregoing sections (FeOOH + MnOOH + FeS, FeS_2 + organic matter + minor phases) is much more available and reactive and takes active part in the diagenetic reactions in the sediments. Trace elements added through pollution are mostly incorporated into those phases formed during sediment diagenesis.

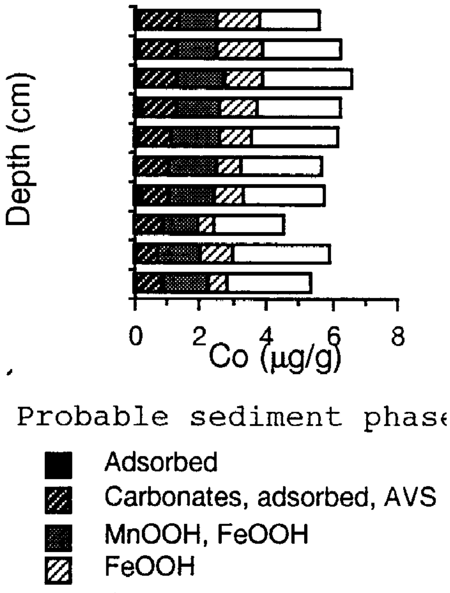

Fig. 4.15 The distribution of cobalt amongst sediment phases as determined by sequential extraction. This sample is from Mangere Inlet. Residual (lithogenic) cobalt was about 7 µg/g.

Implications for the fate of contaminants

Immobilisation

One of the potentially important mechanisms for the recovery (rehabilitation) of polluted sediments is that metals may become permanently immobilised with depth in the bioturbated layer. By this we mean they become tightly bound and are unlikely to become available to biota or be released by diagenetic processes over the medium term (decades). Our results to date suggest that this is not happening, because toxic metals do not show an increase in the residual fraction (crystalline Fe and Mn oxides, silicates etc) at the expense of a decrease in the non-residual fraction down the cores. Therefore, permanent immobilisation appears to be unimportant. However, Cd and Cu show marked changes with depth which indicate some degree of decreased mobility. Much of this is increase in the proportion strongly bound to organic matter and/or FeS_2. Other trace elements show smaller changes in their own unique fractionation, and in this sense, a small decrease in the degree of reactivity or mobility.

Contaminant cycling

We speculate trace elements that are;

- adsorbed onto or incorporated in FeS, diagenetically precipitated carbonates, FeOOH and MnOOH,
- or adsorbed onto clays and organic matter,

are cycled between these different phases because diagenesis can mobilise metals through the mechanisms identified in Table 4.8. These processes are not only fueled by metabolism of organic matter, but by the changing environmental conditions brought about by bioturbation (muds and sands) or waves (sands) changing the redox environment and pH, and irrigating the sediments. In contrast, FeS_2 and humic acid are relatively stable, and trace elements associated with these phases will be cycled more slowly. The turnover of the lithogenic fraction will be extremely slow.

Bioavailability

At the present time, there is no chemical method for distinguishing the bioavailable fraction, because this will vary with biota and sediment. We can, however, distinguish two measures of bioavailability.

1) Dissolved (interstitial water). Concentrations of trace elements in the interstitial water can be compared with water quality criteria designed to protect marine aquatic life. Exceedance of water quality criteria implies that sediments may be toxic, while concentrations much less than water quality criteria imply that sediments are not toxic to organisms. This is only an approximation. Solubility of trace elements is augmented by complexation with dissolved organic matter (DOM, often reported as dissolved organic carbon—DOC), S^{2-}, $S_2O_3^{2-}$, and this complexation probably ameliorates toxicity as well.

2 Reactive fraction. The sediment fraction that is most amenable to mobilisation probably contains the bioavailable fraction. This fraction is associated with phases that are actively involved in early diagenesis, i.e., adsorbed or coprecipitated with FeS, $FeCO_3$, $CaCO_3$, FeOOH, MnOOH, and degradable (metabolisable) organic matter.

Table 4.8. Rapid recycling mechanisms in sediments.

Diagenetic process	Affected sediment phase
pH change	adsorbed, carbonates
Salinity change	adsorbed
Reduction	MnOOH, FeOOH
Biological degradation of organic matter	adsorbed
Oxidation	FeS, $FeCO_3$

Sediment analysis

The complexity of sediments means that they are difficult to characterise through chemical analysis. Analytical methods measuring concentrations and forms of contaminants have had to treat sediments as "black boxes", and are entirely empirical in nature. The most common methods for measuring concentrations are the so-called total methods (e.g., strong acid digestion). These are favoured by some researchers because they are the most reproducible, are less affected by sediment properties such as texture, and have the largest database with which to make comparisons. However, in terms of fate, form, reactivity or bioavailability of contaminants, they are the least useful methods. Unfortunately, methods which purport to measure these latter characteristics are not soundly based scientifically, nor is there consensus about which is best. A major problem is that it is difficult to selectively target one or a group of phases without either partially extracting other phases or losing trace elements through readsorption.

4.6 Major factors influencing element concentration

Proximity to source

Element enrichment in the sediments is generally located close to past and present sources of pollution. 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 to the inlet. Moderately polluted areas are located immediately away from Mangere Inlet, in bays and sub-estuaries adjacent to urbanised catchments, 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.

The rate of decline in concentration with distance from sources of pollution is highly variable. Mangere Inlet is probably the source of much of the pollutants in the northern part of the harbour, and its influence extends at least 4 km from the mouth of the inlet (Fig 4.3). In contrast, the influence of the Glenbrook Steel Mill discharge is much less pronounced (Fig.4.16). High zinc concentrations fall rapidly with distance from the outfalls, although background levels are rather high (Williamson et al 1992). In this case, the concentration gradient near the discharge drain is very strong.

Sediment texture

Element concentrations in marine and estuarine sediments are determined not only by element 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 particle size. Contaminants concentrate in finer sediments due to the larger surface area/volume ratio. A second, and possibly more important factor, is that concentrations of reactive sediment phases (e.g., iron and manganese hydrous oxides, sulphides, humic acids) increase as sediment texture becomes finer.

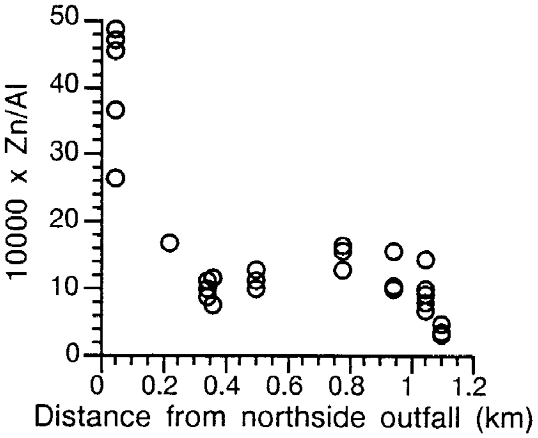

Fig. 4.16 Variation of Zn concentrations with distance from the Glenbrook Steel Mill outfall. Zn concentrations have been normalised to the Al content to minimise particle size effects.

Sediment textural gradients can be found in transport zones (see section 3.2), at different tidal heights in the intertidal profile, near physical features which produce rapid changes in texture, e.g., breakwaters, near drains or stream outlets, and in small scale morphological features such as ripples (crest/trough) and stingray pits.

Depth

Bioturbation not only mixes contaminants in the sediment profile but also ensures that some of the most important sediment phases, amorphous iron oxides, organic matter, and to some extent, sulphides ($FeS + FeS_2$) do not show strong concentration gradients. Consequently, concentrations of trace elements do not usually change rapidly with depth (with the exception of recent pollution events). One important consequence is that surveys of trace element concentrations do not need to rigorously control sampling depth. For example, in sampling the top 2 cm, it is adequate to use a surface scoop where depth is controlled by eye, even though

Table 4.9 Typical concentrations in major sediment phases (µg/g) in the Manukau Harbour.

Phase	Sand	Sandy mud	Mud
FeOOH	1000	5000	17000
MnOOH	50	100	400
FeS	30	400	2000
FeS_2	200	1000	5000
Organic matter (%)	0.1	0.4	1

the depth of sediment sampled in the process probably varies from 1.5-3 cm.

Sediment phases

The variation in major sediment phases that bind trace elements found in the Manukau Harbour is summarised in Table 4.9. A similar magnitude variation in trace elements is expected

Analytical method

See section 4.3

Sample Variance

Variability in concentrations at a site may need to be determined e.g., to carry out spatial or temporal comparisons. If sampling is carried out so as to minimise variation due to changes in distance to the source, or sediment texture and phases, then what residual variance can be expected? Some studies in the Manukau would suggest that the coefficient of variation could be kept within 10% (Table 4.10). In these studies, high coefficients of variance (>10%) were found when concentrations were near detection limits.

Table 4.10 Coefficients of variance (standard deviation expressed as a % of the mean) for some replicate samples collected in both muddy and sandy environments.

Site	%Mud	Pb	Cu	Zn	Ni	Cd
Muddy sites HNO_3 digestion n=5 28 m^2 plot						
Pukaki Ck	86	3	4	2	9	17
Big Muddy	70	5	3	2	6	90
Papakura	87	3	0	1	9	18
Mangere	84	2	2	2	7	26
Pahurehure	95	6	0	3	10	42
Waiuku	78	8	11	4	10	38
Sandy sites H_2SO_4/HNO_3 digestion n=3 ~0.5m^2 plots						
Inside stingray pits	0.5-1.3	8	7	5	-	-
Outside stingray pits	0.6-0.7	26	5	5	-	-
Sandy sites H_2SO_4/HNO_3 digestion n=10 ~200 m^2 plot						
Inside stingray pits	~1	8	5	8	-	-
Outside stingray pits	~1	2	2	4	-	-

4.7 Recommended analytical method for trace elements (As, Cd, Cr, Cu, Pb, Ni, Zn) in sediments.

Earlier (see section 4.3) we showed that coarse sediments are very sensitive to the analytical method used. Muddy sediments are much less sensitive, and with contaminated muds, it is valid to compare so-called 'total' methods on a semi-quantitative basis. Even moderate extractants such as dilute acids are a good approximation to total concentrations in this case.

Traditionally, analytical method have utilised strong acid digestion for metal analysis (see section 4.3). At present, these methods are unlikely to be totally replaced because many studies that have been used to derive sediment quality criteria (see section 4.4) are based on their use. For specific monitoring tasks that require reference to criteria, we recommend that these methods continue to be used. As pointed out earlier, these methods vary in their ability to extract all the trace element, roughly in the order $HF/HNO_3/HClO_4$) > $HNO_3/HClO_4$ > HNO_3/HCl > H_2SO_4/HNO_3 ~ HNO_3 (to mention the more common ones). Recovery also depends on other operating conditions, such as length of time for digestion. Digestions are time consuming, and require specialised facilities and safety precautions. We recommend aqua regia (HNO_3/HCl) as a good compromise between rigour and convenience.

In contrast to these total methods, many researchers have used less rigorous extractants, from the point of view of extracting a more meaningful fraction and for ease of analysis. The ARWB (1989) tentatively proposed 0.5 M HCl to target the 'anthropogenic' fraction (the fraction that has been added to the sediment from man's activities), as well as to simplify analyses. This method was originally recommended by Agemian & Chau (1977) for a measure of the nonlithogenic heavy metals in sediments. Their recommendation for this method (or for extraction with dilute ethylene diamine tetraacetic acid (EDTA)) was motivated by improved sensitivity to pollution over varying background concentrations.

From a fundamental point of view, what single method of analysis will provide sufficient information for surveys of trace element contamination? The most ideal would be the bioavailable fraction, but research has shown that there is no standard test available to do this (Luoma 1990). This is because of the different behaviour and physiology of animals, both across species and life stages and the difference in their modes of exposure.

In the absence of a single test that measures the bioavailable fraction, we recommend that the fraction targeted by analysis is that which is rapidly cycled in the sediment.

This fraction is associated with phases that are actively involved in early diagenesis, i.e., adsorbed or coprecipitated with FeS, $FeCO_3$, $CaCO_3$, FeOOH, MnOOH, degradable organic matter. It will include the bioavailable fraction, either that which is available at the time of sampling or after diagenetic changes in sediment characteristics (Table 4.8). We also suspect that much of the anthropogenic input will end up in this fraction. This fraction is of greatest interest in studying the fate of trace elements. Note that these considerations do not include Hg and Se, which require special analytical techniques.

There are a variety of extractants commonly used throughout the world which may fit the bill, notably solutions dilute acid, acidic hydroxylamine, oxalate and EDTA. We compared the first of these three on a range of

Table 4.11 Comparison of common extraction methods targeting reactive trace elements.

Extractant	Advantages	Disadvantages
Dilute acid 0.5 M HCl	Simplest We suspect it is the most effective at extracting trace elements from degradable organic matter.	Too weak to dissolve all FeOOH in muds. Increasing acid strength to dissolve FeOOH may partially extract metals strongly bound to organics and in lithogenic fraction
Hydroxylamine/ Acetic acid	Targets easily reduced FeOOH and MnOOH	Will not dissolve all FeOOH. Probably lose Cu (and other metals) via readsorption onto humic acid
Oxalate pH 3	Dissolves all reactive phases	Probably least efficient at extracting degradable organic matter. Probably lose Cu (and other metals) via readsorption onto humic acid

Manukau sediments (Table 4.11). We discounted a number of others that have been used to survey trace element pollution, as being inadequate in targeting the desired sediment fraction

We also evaluated dilute HCl at different acid strengths with other methods of analysis. We found that 0.5 M HCl is adequate for sandy or sandy mud sediments, but is inefficient at extracting polluted muddy sediments, probably because it does not dissolve all FeOOH. Increasing the acid strength overcomes these problems, but there is a small trade off, because the increased acid will probably extract more of the lithogenic fraction. The other widely utilised extractant, EDTA, was not tested. It has been recommended by Agemian & Chau 1977, as similar to 0.5M HCl.

There is no single cold, dilute extraction method that will target a unique fraction in all sediments, including the reactive fraction. This is because sediment characteristics change with sediment texture. The amount extracted depends on both kinetic and thermodynamic factors, so an extractant will underestimate the reactive fraction in some sediments and overestimate in others.

Of all methods used to survey trace element pollution, extraction with dilute HCl or EDTA are probably better than most others. On the basis of our work in polluted muddy sediments in Mangere Inlet, we recommend that 2 M HCl be used as a general extractant (using a sediment dry weight: solution volume of at least 1:50) and an extraction time of 24 hours.

There will be problems in comparing concentrations found in sandy sediments with the results from earlier studies which used different methods. However, we have seen that this problem is not peculiar to this relatively weak extractant and occurs with strong acid digestions as well, so this is not a compelling argument against its use.

Following ARWB 1989, we recommend that XRF be used for total metals should this be required. It provides total concentrations for a wide range of elements, including many that are not pollutants. It is insensitive to Cd, however. For a relatively small increase in cost, it has the advantage in providing information on sediment characteristics (Al, Si, Ti), which may be used for normalising concentrations.

Recommended supplementary analyses

Additional analyses are recommended to help interpret variations in trace element concentrations and their effects. As described above, trace element concentrations are partially controlled by different sediment phases. Some of the major phases such as FeOOH may be useful to normalise data, both to reduce the variability in concentrations and to explain biological uptake. In addition to particle size analysis (Chapter 3) we recommend that the important sediment phases be analysed, in particular:

- FeOOH
- AVS
- Organic matter

Fe extracted by 2M HCl is a good approximation to FeOOH. AVS can be analysed by literature methods, but a simple version of these is being developed at NIWA Ecosystems, and will be published in the near future. Organic matter should be analysed as ROC (Readily Oxidisable Carbon) or via a Total Organic Carbon (TOC) method.

5 ORGANIC POLLUTANTS

5.1 Historical Background

Prior to 1987 little was known about the levels of organic pollutants in marine sediments of the Auckland region. The analysis of sediment cores from Manukau Harbour (Fox et al. 1988) revealed some unexpectedly high concentrations of organic contaminants, notably chlordane and DDT. Surveys of shellfish from Manukau Harbour, initiated as part of the Manukau Harbour Action Plan, have been undertaken since 1987 and have shown the presence of many classes of organic contaminants (ARWB 1988, 1990, ARC 1993). Other studies, by consultants, have shown elevated concentrations of PAHs to be present in and adjacent to the MSPW, and near the Onehunga wharves (Ports of Auckland 1989). Cores (3 m) taken from two sites in Mangere Inlet (Williamson et al. 1991) have been analysed for anthropogenic PAHs in order to correlate the concentrations with other indicators of human activity that may be used to date sediments and quantify sedimentation rates (Hume et al. in prep.).

These discoveries have prompted questions about the ecological significance of organic contaminants and have stimulated research studies (carried out by NIWA). In one study, chlordane was applied to an intertidal sandflat in order to follow its fate, determine its effects on benthic fauna, and determine the extent of bioaccumulation by benthic shellfish (Smith et al. 1992, Pridmore et al. 1991, 1992, Wilcock et al. 1993). The effect of contaminant (chlordane) stratification in sediments on bioaccumulation by a bivalve has also been studied (Wilcock et al. 1994). Holland et al. (1993) have measured organic pollutant concentrations in surficial sediments along a "pollution gradient" of the northern Manukau Harbour. In a recent study, the fate of several PAH compounds (with a wide range of solubilities) has been observed in an intertidal sandflat near Wiroa Island, Manukau Harbour (Corban 1994). A summary of the major studies is given in Table 5.1 and shows that practically all of the work has focussed on Manukau Harbour, regarded as the most polluted of the Auckland harbours and estuaries.

The studies have verified the persistence and bioaccumulating characteristics of the organochlorine pollutants. DDT and PCBs are still being detected some time after their major uses have ceased (1970 and 1988, respectively). Patterns of bioaccumulation of chlordane in wedge shells and cockles of Manukau Harbour were similar, in relation to sediment levels, to other studies reported in the scientific literature. These results (along with other physical and chemical properties) indicate that the organochlorines can be treated as a single class with many common environmental properties, and that the PAHs comprise another distinct group of contaminants. Although the use of organochlorines has largely ceased, so that residues are (in the main) declining with time, the PAHs are products of our use of fossil fuels (as well as having natural origins) and will continue to enter the environment in the future.

5.2 Organochlorines

Sources

Organochlorines (OCs) are organic (carbon–based) chemicals which contain chlorine. Although a few OCs occur naturally, there have been some 60,000 different synthetic compounds produced over the past 50 years that are in use today.

The organochlorines that are found in marine sediments of Auckland originate from agriculture (DDT, dieldrin group, lindane), the electrical supply industry (PCBs), timber preservation (chlordane, PCP and associated chlorophenols), and as contaminants that were not intentionally manufactured but are now in the environment as a consequence of some other substances (HCB, dioxins).

Persistence and fate

The stable, nonionic structure of OC molecules is the basis for their persistence in the environment and their low water solubility. Persistence is usually expressed in terms of the half–life, or time taken for a substance to decline to 50% (half) of its original concentration. Some OCs, such as DDT, are converted to other compounds with similar properties (DDE and DDD) having longer half–lives than the parent compounds (up to 100 years in soils). NIWA studies involving the controlled addition of technical chlordane to an intertidal sandflat near Wiroa Island (Smith et al. 1992) showed that after an initial loss (probably related to the method of application), and some downward movement of soluble material, sediment concentrations at the surface remained constant for 21 days. After a storm caused some loss of surface material, the 0–2

Table 5.1 Organic contaminants in Manukau Harbour – a chronology of events.

Year	Event	Reference
1987	Significant concentrations of organochlorines first reported in Manukau sediments	Fox et al. 1988
1987	Use of historical DDT residues to measure sedimentation rate in Drury Creek	Hume et al. 1989
1987–1993	Shellfish surveys in Manukau harbour	ARWB 1988, 1990, ARC 1993
1989	In situ chlordane studies carried out at Wiroa Island – fate of chlordane in sediment – changes in benthic community – bioaccumulation	Smith et al. 1992, Pridmore et al. 1991, 1992, Wilcock et al. 1993
1989	Surface sediment surveys in Mangere Inlet, Onehunga Wharf, MSPW outfall, dredge spoil dump site	Ports of Auckland 1989
1989	Sediment and shellfish organic contaminants along a pollution gradient of the northern Manukau Harbour	Holland et al. 1993
1992	Cores from Mangere Inlet analysed for PAHs	Hume et al. in prep.
1993	Study of fate of PAHs in intertidal sandflats	Corban 1994

cm concentrations of chlordane were constant for a futher 41 days. Concentrations at depths of 2–10 cm declined very gradually throughout the experiment, showing that bioturbation had little effect on OC movement. This study showed that OCs, such as chlordane, are especially persistent in sandflats, and that sediment transport is the main process regulating their fate (and not chemical or biologically mediated processes). The persistence of OCs in sheltered, muddy sediments would, therefore, be expected to be much greater, and half–lives may be of the order of years.

Bioaccumulation

Practically all OCs are only slightly soluble in water, but are strongly soluble in fatty substances. They therefore tend to accumulate in the fatty tissues of living organisms – a process known as bioaccumulation. Organisms may bioaccumulate OCs directly from the soil or water in which they live, and concentrate them in their fatty tissue so that resulting "bioconcentrations" may be thousands of times greater than in the surrounding medium. Biomagnification, another bioaccumulation process, results when organisms at higher levels of the food chain feed selectively on biota that are already contaminated with OCs. Each step involves concentration of the contaminants so that there is overall an enormous magnification of the concentration of the OC pollutant. Most persistent chlorinated organic compounds are excreted slowly by vertebrates, compared to invertebrates and plants. Consequently, once these substances enter the bodies of vertebrates they tend to stay there, accumulating in the fatty tissue until an equilibrium is established between uptake and excretion.

A useful concept for quantifying bioconcentration from contaminated sediments is the accumulation factor, AF, (Lake et al. 1990). Equilibrium is assumed to exist between organisms and their environment/food sources. A further assumption is that this equilibrium exists between the principal reservoirs for OCs, in this case the biota lipid and the sediment organic carbon (TOC). AF values are high (typically 2–7) for OCs, and their use enables reasonably good predictions to be made about bioconcentrations in a variety of organisms feeding from, or near to, contaminated sediments.

The chlordane AF values for wedge shells and cockles of Manukau Harbour were about 3.5, in line with overseas studies (Colombo et al. 1990, Wilcock et al. 1993). Recent data (Holland et al. 1993, Hickey, pers. comm.) for five sites on the northern Manukau Harbour have yielded similar AF values to those of the chlordane study, for a range of organochlorines, but markedly smaller values for the PAHs.

Toxicity

Aquatic toxicities are expressed as LC50 values, which is the concentration of toxicant that is lethal to 50% of the test animals in a specified exposure period; most commonly 96 hours. **The values of LC50s for OCs to aquatic animals vary enormously from less than 1 µg/l to 10–100 mg/l.** A good example is provided by the PCBs. The acute toxicity data indicate that most of this group of compounds is not highly toxic to marine biota. However, some PCBs (the "coplanar" congeners) are markedly more toxic than the others and may be comparable in this regard with the most toxic of the dioxins (Safe 1990). **Furthermore, toxicity is increased by bioaccumulation and biomagnification.** Long–term (chronic) exposure to the relatively non-toxic PCBs lowers the lethality threshold in most marine biota by 2–3 orders of magnitude, depending upon the exposure period (Moore and Walker 1991). In a later section of this report it will be shown how aquatic toxicity data is used to derive sediment quality criteria.

In contrast to aquatic toxicity, little has been published about the toxic effects of contaminated sediments. The complex nature of interactions between sediment TOC and biota, and questions of bioavailability, have made it difficult to generalise about sediment toxicities in the same way that aquatic toxicities have been. Long and Morgan (1991) have summarised the available sediment toxicity data in the marine coastal environment for use in deriving sediment quality criteria. This will be discussed more fully elsewhere in this report.

Sub-lethal toxicity effects have been evaluated in New Zealand for chlordane. The effects of ecosystem disturbance as a result of low–level (in situ) OC contaminantion was observed in the NIWA chlordane study at Wiroa Island. An initial surface concentration of 7.5 ng/g (dry weight) caused a decline of 60–70% in the populations of juvenile shellfish after about 20 days. Juveniles gradually repopulated the site over the next 30–40 days, when surface chlordane concentrations had dropped to 3 ng/g (Pridmore et al. 1991).

This result shows that chlordane (and presumably other OCs) can reduce juvenile shellfish abundances at relatively low levels of exposure.

It is important to take into account the high bioaccumulation potential of OCs when assessing the significance of sediment concentrations. It may be possible for compounds at ostensibly non–toxic levels to attain tissue concentrations that are harmful to the host organisms, or to their predators.

5.3 Polycyclic aromatic hydrocarbons

Sources

Polycyclic aromatic hydrocarbons (PAHs, sometimes called polynuclear aromatic compounds, or PNAs) are a well–documented class of chemicals that have been found in marine, lacustrine, and riverine sediments throughout the world (Neff 1979). PAHs may enter the environment in spills and seepages of crude oil and refinery products, may be produced in situ through diagenetic transformations of plant materials, or may be a result of pyrolytic processes (natural and anthropogenic) (Lipiatou and Saliot 1991). Unsubstituted (non–alkylated) compounds are produced by high temperature combustion of fossil fuels and are typically the most abundant PAHs found in surficial sediments (Gschwend and Hites 1981, Bouloubassi and Saliot 1993). A number of studies are reported in the literature, in which variations in the distribution of pyrolytic PAH compounds have been used to examine changes in pollutant inputs over time in marine sediments (Gschwend and Hites 1981, Lipiatou and Saliot 1991, Bouloubassi and Saliot 1993). This technique has been used in conjunction with other core–dating methods to examine cores from Mangere Inlet. Here, the vertical profile of anthropogenic PAHs in each of the cores correlates strongly with profiles of other indicators of recent human activity; notably the heavy metals Cr, Cu, Pb and Zn.

It is probable that the major sources of PAHs entering New Zealand coastal and estuarine waters are fossil fuel combustion products (petroleum based) in urban stormwater.

It is common to define "total PAHs" as some combination (usually 10–20) of compounds typically found in environmental samples; especially those with molecular weight 178, 202, 228, 252, and 276 (Bouloubassi and Saliot 1993). A typical total PAH compilation might include: anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benz[a]anthracene, benzo[a]pyrene, benzo[a]fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, perylene, dibenz[a,h]anthracene, and benzo[g,h,i]perylene. All of these, with the exception of perylene, derive principally from the high temperature combustion of fossil fuels. Some are also present in lead–free petroleum. The relative abundances of individual compounds can sometimes indicate specific sources of pollution, and to distinguish natural inputs (diagenesis of plant material) from those resulting from human activities. For example, perylene concentrations in excess of 10% of total PAH are considered to derive from diagenetic processes (Tissier and Saliot 1981).

A lot of information about past and present pollutant loads to the marine environment can be obtained from the analysis of relatively few samples for PAHs. Total PAH data gives an overall picture of urban and industrial runoff inputs over time, while individual compound concentrations (either singly, or expressed as ratios) can be used to differentiate sources and specific events (such as forest fires, oil spills and certain chemical industry processes).

Persistence and fate

The structure of PAHs, comprising two or more fused benzene units, gives them great stability against biological and chemical breakdown and, thus, persistence in the environment. When considering the fate of organic compounds in the aquatic environment, a major factor is their solubility in water (McElroy et al. 1989) as this directly affects their distribution (partitioning) between the water, sediment, and biota. Low molecular weight PAHs, such as naphthalene, are water soluble and do not persist in the marine environment. The majority of PAHs, however, are virtually insoluble in water and will bind preferentially to sediments and suspended matter. A measure of this preference is given by the sediment–carbon partition coefficient, K_{OC}, which is the ratio of the concentration (of a given compound) bound to the sediment organic carbon phase to that in the surrounding water. K_{OC} values for most of the common PAHs are high, typically 10^5–10^6, and are similar to those of most OCs. PAHs, therefore, exert toxic effects primarily on sediment dwelling organisms (Varanasi 1989).

Persistence was evaluated in a student study supported by ARC (Corban 1994) on a sandflat in Manukau Harbour. Following an application of several PAHs, losses were mainly from the top 2 cm (surficial layer) and were greatest for the more soluble components. The less soluble, PAHs declined by only 50% over a period of 256 days following initial losses of the applied material.

Bioaccumulation

There is much less information available on the bioaccumulation of PAHs by comparison with that for OCs. Uptake of PAHs from sediment occurs largely via the sediment interstitial water and is controlled by the rate of desorption from sediment particles (Landrum 1989). Thus, the individual solubilities in water of PAH compounds are an important factor in determining how they are bioaccumulated by benthic organisms, as well as regulating their persistence in marine sediments. Sediment organic matter is the other major factor controlling the distribution of PAHs between the sediment and biota.

Bioaccumulation has been described for shellfish of Manukau Harbour in a student project within the sediment recovery programme (Williamson et al. 1992). Using the data collected by Holland et al (1993), a plot of percentage composition for various sample sites was obtained from which a pattern was found which characterised the sediments of the harbour. This showed that there was very little anthracene (three ring system), a predominance of fluoranthene and pyrene (four ring system), and moderate quantities of higher ring PAHs such as benzo[a]pyrene and benzo[g,h,i]perylene (see Fig. 5.1). When compared to percentage composition plots for oyster (ARWB 1990), wedge-shell and cockle taken from the same sites (Hickey et al. in prep.), it was noticed that there was an accumulation of fluoranthene and pyrene (up to 20% increase for the latter) and a corresponding loss in the higher ring PAHs in the shellfish compared to the sediment. An explanation was advanced which was based on the relative volatility, lipophilicity and solubility of the PAHs. Light PAHs are relatively more soluble and less lipophilic than heavier PAHs, and are more inclined to be washed out of sediments. Heavy PAH (≥5 rings) are insoluble and have a high affinity for sediment carbon and thus are less lipophilic than the intermediate size class (4 rings). Fluoranthene and pyrene are accumulated because they have little volatility (unlike anthracene) but also, they are not extremely insoluble. Therefore they are most bioavailable for shellfish.

The amounts of PAH bioaccumulated in selected species, relative to sediment concentrations (i.e. "sediment bioconcentration ratios"), for five locations along a notional pollution gradient of the northern Manukau Harbour were substantially less than for corresponding OCs (Hickey et al. in prep.). The values of the accumulation factor (AF), are much less than 1 (cf. an average of 3–4 for OCs in the shellfish). [Sediment bioaccumulation ratios may be converted to AF values by multiplying by the fractional carbon content of

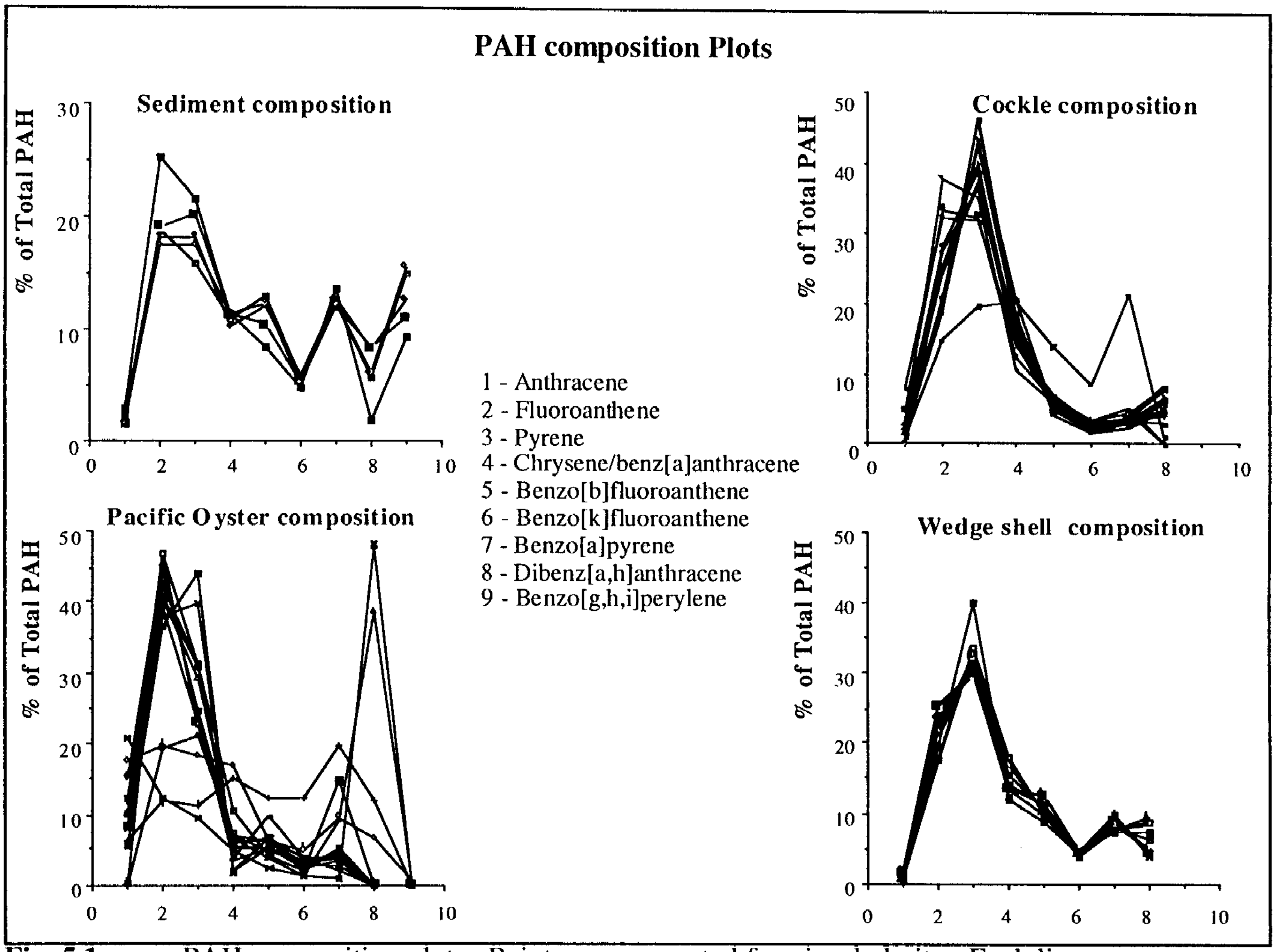

Fig. 5.1 PAH composition plots. Points are connected for visual clarity. Each line represents a different site.

the sediment (0.2–0.7%) and dividing by the fractional lipid content of the biota (3–5%)]. This data is summarised in Table 5.2.

The low accumulation factors (AF<1) are in line with what is observed overseas. "Excessive bioconcentration of PAH is rarely observed when comparing concentrations of PAH(s) in organisms to those in nearby sediments" (McElroy et al. 1989).

Toxicity

Several PAHs are reported to be strongly carcinogenic, and others are to lesser degrees (Nicholson 1984). Payne et al. (1988) have noted adverse effects in fish exposed to sediments contaminated with PAH derived from petroleum, with total concentrations (principally naphthalene, fluorene and phenanthrene) of 1 μg/g. Metcalf et al. (1988) reported the experimental induction of liver tumours in trout, using sediments contaminated with PAHs known to come primarily from combustion of fossil fuels (naphthalene, fluorene, phenanthrene, fluoranthene, pyrene et al.). All of these compounds have been identified in concentrations of 10-200 ng/g, each, in sediments near Onehunga Wharf (Ports of Auckland 1989) and at other sites in the northern Manukau Harbour, where total PAH values of up to 5.3 μg/g have been recorded (Holland et al. 1993).

In contrast to the sublethal effects, studies of acute toxicity found that high sediment concentrations – in the range of 100 μg/g dry sediment – were needed to produce mortality (e.g., Landrum et al. 1991). PAH action appears to be additive where there are several compounds present.

The overall biological impact of sediment–associated PAH compounds varies according to the molecular weight of each compound, or equivalently, according to the size–class as specified by the number of rings. Thus, 2– and 3–ring compounds (naphthalene, anthracene, and phenanthrene) are more toxic than compounds with 4 or more rings, but are often

Table 5.2 Sediment bioaccumulation ratios for PAH in Manukau Harbour (Hickey et al. pers. comm.). Approximate AF values are shown in brackets. See text for description of terms.

Site	wedge-shell	cockle	crab	whelk
Grannys Bay	0.94	3.4	0.10	0.07
Blockhouse Bay	1.21	0.58		
Armour Point	0.74	0.41		
Paturoa Bay	1.13	0.34	0.08	
Wesley Bay	0.054	0.013		
Average	0.81 (0.11)	0.95 (0.05)	0.09 (0.01)	0.07 (0.01)
cf PCB	34.7 (3.0)	27.3 (3.0)	56.5 (3.4)	70.7 (4.2)

less persistent because of their greater solubility in water. Compounds with more than 5 rings (e.g. benzo[g,h,i]perylene) seem to be so insoluble that they are probably not absorbed when ingested. A summary of how these properties vary with the number of rings is given in Table 5.3.

A comparison of the respective environmental properties of OCs and PAHs is given in Table 5.4

Concentrations of PAHs that are acutely toxic to marine organisms are about 100–1000 times higher than those for many OCs. Sublethal effects, however, are observed at sediment concentrations that are commonly found in urbanized estuaries and inlets.

5.4 Key pollutants in the Auckland Region

The location and magnitudes of organic pollutants in sediments and shellfish of the Auckland region has been documented (ARWB 1988, 1990, Fox et al. 1988, ARC 1993, Holland et al. 1993). It would be tempting to think that because terrestrial uses of OCs have largely ceased, residual concentrations in sediments are in decline. However, there has been no systematic sediment monitoring programme to confirm this and shellfish surveys indicate that this is not always the case (see Table 5.5 below).

Shellfish quality surveys, in which Pacific oysters *(Crassostrea gigas)* from selected sites have been analysed at various times since 1987, have given a semi-quantitative picture of changes in concentrations of water-borne pollutants.

Since sediments are a major sink for organic contaminants in the aquatic environment, and equilibrium partitioning of organic compounds is readily established between sediments, water and biota (Wilcock et al. 1993), the shellfish bioaccumulation data also qualitatively indicates how the Manukau sediments have changed over the monitoring period. An analysis of the Manukau shellfish survey data is shown in Table 5.5. Trends over the period 1987–1992 have been reported as being: major increases (in concentration), minor increases, no change, slight decreases, and major decreases. Very large (atypical) values recorded in the first year have been ignored, or regarded with suspicion. Sites for which insufficient trend data exists (Weymouth Point, Waiuku Yacht Club) are not included.

Table 5.3 Properties of sediment-associated PAHs for different ring-size classes. Values for examples of each class are given in brackets.

General trend	3-ring (phenan)	4-ring (fluor)	5-ring (BaP)
Water solubility[1]	————	decreasing ————	————>
in g/m^3 (25°C)	1.24	0.245	0.0034
Persistence[2]	————	increasing ————	————>
half-life in days	20	100	>100
Bioavailability[3]	negligible	maximum	low to negligible
Toxicity[4]	————	decreasing ————	————>
in ng/g	2040	3000	18,000

Key: phenan = phenanthrene, fluor = fluoranthene, BaP = benzo[a]pyrene.

[1]Pearlman et al. (1984), [2]Corban (1994), [3]See Fig. 5.1, [4]Sediment quality criteria for EqP method (1% organic carbon) (section 8.5)

Table 5.4 Environmental properties of OCs and PAHs – a comparison. See text for explanation of terms.

Property	**Organochlorines**	**PAHs**
Persistence (half–life in marine sediments)	years	years
Bioconcentration		
water: BCF	10^3–10^5	10^2–10^5
sediment: AF	2–7 (average 3–4)	much less than 1
Sediment toxicity	1–1,000 ng/g	1,000–10,000 ng/g
Typical sediment concentrations in Manukau Harbour	0–25 ng/g* (commonly <2 ng/g)	30–5,300 ng/g (commonly 300 ng/g for "total" PAH)

* For individual classes of compounds (e.g. ∑DDT)

Table 5.5 mostly gives information about the pollution status of the different sites. However, it also shows that chlorophenol concentrations have declined at most sites, PAHs have increased in two locations, and that DDTs and PCB levels have remained constant in many sites of the survey. Thus, OCs continue to "appear" in Manukau Harbour, long after their terrestrial uses have been banned.

5.5 Sediment quality criteria

A summary of two current approaches to setting sediment quality criteria is given in Section 4.4 of this report. These approaches use experimental sediment toxicity (i.e. dose–response) data to derive levels, below which no effect is observed (the Effects Range–Low value, or ER–L), or, above which an effect is nearly always observed (Effects Range–Median value, or ER–M). Another approach, that is of greater relevance to nonionic organic pollutants than to metals, is equilibrium partitioning (EqP).

It has frequently been observed that similar concentrations of a chemical can exhibit a range in toxicity in different sediments. Thus, in order to derive sediment quality standards it is important to account for the extent of bioavailability of sediment–associated chemicals.

> **"For example, if 1 µg/g of Kepone is the LC50 for an organism in one sediment and 35 µg/g is the LC50 in another sediment, then unless the cause of this difference can be associated with some explicit sediment properties it is not possible to decide what would be the LC50 of a third sediment without performing a toxicity test" (Di Toro et al. 1991).**

The EqP method assumes that the primary interaction of a sediment–associated contaminant with biota is via the pore water. EqP may be used to predict contaminant concentrations in sediment pore water (interstitial water) by assuming that a

Table 5.5 Summary of trends in Manukau shellfish data 1987–1992.

Site	**Total chlorophenols**	**Total DDTs**	**Total PCBs**	**Other OCs***	**Total PAHs****
Cornwallis	– –	0	0	–	–
Jenkins Bay	– –	–	–	–	– –
Granny's Bay	– –	–	0	–	+ +
Mangere Inlet	+	–	–	0	–
Pukaki Creek	–	–	–	–	– –
Puhinui Creek	– –	0	0	–	–
Pahurehure Inlet	– –	0	0	0	+ +
Hingaia Bridge	– –	0	0	–	0
Kahawai Point	– –	–	–	– –	–
The Needles	–	–	– –	–	–
Awhitu Park	–	–	0	–	–

*Sum of lindane, heptachlor, heptachlor epoxide, dieldrin group, chlordanes

**Sum of 10 anthropogenic PAHs

Key: + + major increase, + minor increase, 0 no change, – minor decrease, – – major decrease thermodynamic equilibrium is established between the sediment and pore–water concentrations of nonionic organic compounds (such as PAHs). The calculated pore–water concentration is then compared with water–only toxicity values published in the literature, or with tabulated data for the protection of aquatic life (Cowan and Zarba 1987). The predicted pore–water concentrations are based on the concept that organic contaminants are associated with sediment organic carbon, so that the fractional organic carbon content of the sediment (f_{oc}) controls the bioavailability of the contaminants. Thus, the bulk sediment concentration (C_s) is related to the pore water concentration (C_p) by

$$C_s = f_{oc} K_{oc} C_p \qquad (1)$$

where K_{oc} = the organic carbon/water partition coefficient for the chemical of concern. Values of K_{oc} are given in compilations of environmental constants (e.g. Schnoor et al, 1987, Montgomery 1993), or may be calculated from other physicochemical parameters (Di Toro et al. 1991). An indication of sediment carbon percentages (f_{oc} x 100) to be found in Manukau Harbour is shown in Fig. 4.12. Sediment Quality Criteria (SQC) are then calculated from

$$SQC = f_{oc} K_{oc} FCV \qquad (2)$$

where FCV are the final chronic values (for given compounds) from the U.S. Environmental Protection Agency water quality criteria (USEPA 1986, Di Toro et al. 1991).

The EqP method derives criteria (SQC) for the assessment of significant adverse effects – not only mortality.

The important point to note about Eq.2 is that the SQC value is dependent upon the organic carbon fraction (f_{oc}), which regulates the bioavailability of the contaminant in question.

There is an uncertainty of approximately a factor of two between predicted and measured mortalities using Eq 2. This reflects the inherent variability in the experimental data, as well as phenomena that have not been accounted for in the EqP model, and appears to be the limit of the accuracy and precision to be expected (Di Toro et al. 1991).

The EqP method was selected by the U.S. EPA because it seemed to be the most practical, scientifically defensible, and effective regulatory tool for addressing individual chemicals associated with contaminated sediments.

The rationale behind the EPA preference for the EqP method is discussed by Di Toro et al. (1991), and in a recent EPA publication (USEPA 1993a).

A comparison of different SQC values for some commonly reported contaminants is given in Table 5.6. In this comparison organic carbon contents of 0.2% (i.e. f_{oc}=0.002) and 1% (f_{oc}=0.01) have been chosen as being representative of sandy and muddy sediments, respectively, within Manukau Harbour. Clearly, there is substantial scatter of values for the various criteria. This reflects the enormous range of toxic responses of different organisms and test procedures, and the different objectives of the respective SQCs.

ER–L and ER–M

The ER–M values are especially influenced by the range of sensitivities of different organisms

Table 5.6 Sediment Quality Criteria (SQC), in ng/g, for some commonly reported contaminants: a comparison between the Equilibrium Partitioning (EqP, for 0.2% and 1% organic carbon contents), Effects Range–Low (ER–L), Effects Range–Median (ER–M), Apparent Effects Threshold (AET) and Screening Level (SL) methods. Data (Long and Morgan 1991) for most sensitive species listed have been chosen.

SQC	**Organic contaminant**					
	chlordane	ΣDDT	ΣPCBs	phenanthrene**	fluoranthene***	BaP
EqP 0.2%	0.3	1.7	59*	480	600	1000
EqP 1%	1.5	8.3	295*	2400	3000	5000
ER–L	0.5	3	50	225	600	400
ER–M	6	350	368	1390	3600	2500
AET	2	3.9	54	88	1700	> 1300
SL	10	6.9	130	320	630	680

Key: ΣDDT = total DDTs, ΣPCBs = total PCBs, BaP = benzo[a]pyrene

* Calculated values, ** USEPA (1993b), *** USEPA (1993c)

to any given contaminant and, thus, are not suitable for the protection of sensitive species. The ER–L values confer a much greater degree of protection for marine organisms and can be thought to approximate a transition between the "no effect" range and the "possible effect" range, of concentrations having a biological impact. Overall, the degree of confidence in the accuracy of the ER–L and ER–M values is considered to be low for pesticides and PAHs (Long and Morgan 1991).

AET and SL
The Apparent Effects Threshold (AET) is defined as the sediment concentration of a contaminant above which statistically significant ($p<0.05$) effects for a particular biological indicator are always expected, relative to certain reference conditions. AET values from Puget Sound were used to derive screening level (SL) guidelines, for use in Puget Sound only, which are defined as the concentrations below which dredging material may be suitable for marine disposal without the need for biological testing. SLs are calculated to be 10% of the greatest AET value measured (for a variety of test animals).

EqP
The EqP criteria are dependent upon the reliability of available toxicity (FCV) data and accurate measurements of K_{OC}, the carbon–normalised sediment/water partition coefficient. Values of FCV are tabulated by USEPA (1986), but are not available for all compounds of interest. Notably absent are values for PAHs. Partition coefficients, when not available, are probably best calculated from K_{OW} values using published empirical correlations between K_{OC} and K_{OW} (Kenega and Goring 1980, Di Toro et al. 1991). In many cases the two constants are approximately equal in value and can be interchanged. Ready access to all of this data, and uncertainties about some published values for parameters, are major limitations to the practical use of the EqP method.

The two levels of organic carbon in Table 5.6 correspond roughly to those of sandflats and mudflats, respectively, in Manukau Harbour. Thus, comparison between the EqP 1% criteria and the sediment concentrations found in five mudflats of Manukau Harbour (Fox et al. 1988) shows that two sites (Pukaki Creek and Mangere Inlet) exceeded the chlordane and DDT SQC values. No sites came close to the SQC for total PCBs. PAH compounds measured by Holland et al. (1993) in northern Manukau sites were generally well below SQC values.

Which SQC?
Choosing appropriate values for SQC is not straightforward. The ER–L and ER–M values should be used as rough indicators for concentrations having "little or no effect" to "almost always an effect". AET data relates to individual species and habitats (mostly foreign) and should be assessed accordingly. The EqP is probably the best way of assessing potential toxicity for sediments, provided reliable input data (f_{OC}, K_{OC}, FCV) is available. There is a need for better data for PAHs and for many "modern" pesticides.

5.6 Which pollutants? What detection limits?

Since 1987 a number of studies conducted in Manukua Harbour have detected, or sought to detect, various organic contaminants in shellfish and in sediments (Table 5.1). In early studies organic contaminants were identified and quantified according to the standards that were available (often mixtures representative of different groups of compounds; e.g. the tetrachloro PCBs are represented by the compounds with IUPAC Nos 40–81), rather than whether they were priority pollutants.

Table 5.7 lists the compounds specified (but not always found) in shellfish (ARWB 1988, 1990, ARC 1993) and in sediments (Fox et al. 1988, Holland et al. 1993) of Manukau Harbour.

Chlorophenols
The frequent detection of low levels of total chlorophenols in shellfish is indicative of the persistence and the ubiquity of these chemicals. If an AF value of 3.5 is assumed (see section 5.2.3) it is possible to calculate the corresponding sediment concentrations "in equilibrium" with the shellfish. Thus, for a muddy sediment (1% organic carbon), a shellfish lipid content of 5% (dry weight), and total chlorophenol concentrations up to 46 ng/g (median 11 ng/g), the equivalent sediment concentrations are 0–2 ng/g (median 0.5 ng/g). A corresponding SQC value (Eq 2) can be calculated using an FCV of 7.9 µg/l for PCP (USEPA 1986) and a K_{OC} value of 35,800 ml/g (Montgomery 1993). The resulting SQC for chlorophenols in mudflats is 2830 ng/g (compared with the estimated sediment concentrations of 0–2 ng/g). Similar reasoning for sandflats (organic carbon content 0.2%) gives a SQC of 570 ng/g, compared with estimated total chlorophenol sediment concentrations of 0–0.5 ng/g. Concentrations of chlorophenols in shellfish have declined over

the period 1987–1992 at all sites except Mangere Inlet (Table 5.5).

Analysts do not always report whether they have included the methoxy derivatives (anisoles) of chlorophenols in their results. These are often more persistent than their precursors and of comparable toxicity. Also, some sediment–associated chlorophenol may be bound to the mineral lattice and require more rigorous digestion than for freely associated material. These additional complications should be considered when determining chlorophenols in sediments.

Chlorophenol concentrations found in shellfish from Manukau Harbour indicate a very low level of contamination that is about 10^{-3} times the value considered to have adverse effects on aquatic organisms. Sediment concentrations of free chlorophenols appear to be low, in general. Concentrations of anisoles and bound chlorophenols in sediments are largely unknown. For these reasons, chlorophenols should only be monitored in sediments from areas where there is a liklihood of their occurrence or in new surveys.

DDT

DDT and its co–occurring compounds have been found in most samples; not surprising in view of the widespread past use of DDT. Concentrations of total DDT in muddy and sandy sediments recorded by Holland et al. (1993) are comparable with the relevant SQC for biological effects (Table 5.6). The same is true of the data collected by Fox et al.(1988) in muddy sites within Manukau Harbour. Shellfish surveys of Manukau Harbour have yielded total DDT flesh concentrations of 9–93 ng/g, corresponding to equilibrium sediment concentrations of 0.1 ng/g for sandy locations (SQC=1.7 ng/g), and 5.3 ng/g for muddy sites (SQC=8.3 ng/g). Trends in the shellfish data for the period 1987–1992 (Table 5.5) indicate that little change has occurred in measured concentrations.

DDT residues are continuing to be found in sediments and shellfish of the Auckland region in concentrations likely to have some effect on marine organisms. Thus, DDT compounds should continue to be monitored, especially in muddy locations, until concentrations decline by at least 10–fold. Sensible detection limits for monitoring would be 0.05 ng/g for sediments, and 1 ng/g for shellfish – both dry weight basis.

PCBs

Examination of Table 5.7 shows that only a few PCBs are regularly found in sediments and shellfish of Manukau Harbour. PCBs were used almost exclusively in transformers and capacitors in the electrical supply industry, and waste oils have largely been confined to specific sites. Thus, it seems likely that little material containing PCBs has entered the marine environment of New Zealand. Of the compounds listed in Table 5.7 only PCBs 31, 49, 118, 138, 141, 151, 153 and 180 have been detected in at least 30% of the samples. Interestingly, two PCBs (126, 169) identified as being highly toxic (comparable with the dioxin, 2,3,7,8–TCDD) have not been selected for analysis of samples from Manukau Harbour.

A large proportion of PCB toxicity is due to the presence of the coplanar PCBs: 77, 126 and 169 (Safe et al. 1985), and it is usual for surveys to include these compounds (e.g. Daelmans et al. 1992). We would <u>not</u> recommend that these be routinely analysed at the same detection levels as dioxins, because of prohibitive costs and the uncertainty about the significance of very low levels (parts per trillion). Detection levels used for other PCBs should be employed.

Total PCBs reported by Fox et al. (1988), 0.5–14.2 ng/g, were well below the relevant (1% organic carbon) SQC value (295 ng/g), and the "effects range low" (ER–L) value of 50 ng/g. Similarly, total PCBs in shellfish equate to surrounding sediment concentrations that are generally well below the most stringent SQC; even for shellfish from Mangere Inlet and Granny's Bay, which had the highest body burdens. PCBs seem to be declining slowly in most parts of Manukau Harbour (Table 5.5).

We suggest that the following revised list of PCBs be analysed in sediment and shellfish samples of the Auckland region: #s 31, 49, 77, 118, 126, 138, 141, 151, 153, 169, 180. Sensible detection limits for monitoring would be 0.05 ng/g for sediments, and 1 ng/g for shellfish – both dry weight basis.

This list includes the most toxic (coplanar) PCBs, and representative members of tri–, tetra–penta–, hexa–, and hepta–chlorinated compounds. It excludes compounds that have never been found (and possibly never introduced to New Zealand) or have only been detected at extremely low concentrations, so that savings can be made on analytical costs.

Table 5.7 Toxic organic compounds specified, or found, in samples analysed from Manukau Harbour. The number of significant results in samples for the reports cited are given (maximum possible is 63).

Compound	Significant results	Reference	Priority Pollutant USEPA	Priority Pollutant EEC
2,4,5 trichlorophenol	16	2,3	√	x
2,4,6 trichlorophenol	25	1,2,3	√	√
2,3,4,6 tetrachlorophenol	33	1,2,3	√	x
pentachlorophenol	31	1,2,3,4	√	√
p,p–DDT	52	1,2,3,4,5	√	√
o,p–DDT	30	1,2,3,5	√	x
p,p–DDD	56	1,2,3,4,5	√	√
o,p–DDD	41	1,2,3,4,5	√	x
p,p–DDE	57	1,2,3,4,5	√	√
o,p–DDE	30	1,2,3,4	√	x
PCB 15	ND	3,4	*	*
PCB 18	3	4	*	*
PCB 28	ND	2	*	*
PCB 31	20	1,2,4	*	*
PCB 40	2	1,2,3,4	*	*
PCB 44	11	1,3,4	*	*
PCB 47	3	3	*	*
PCB 49	21	1,2,3,4	*	*
PCB 52	2	2,4	*	*
PCB 54	ND	1,2,3,4	*	*
PCB 60	ND	4	*	*
PCB 77	11	1,2,3,4	*	*
PCB 86	13	1,2,4	*	*
PCB 87	ND	4	*	*
PCB 101	4	3,4	*	*
PCB 103	ND	4	*	*
PCB 105	4	3,4	*	*
PCB 110	3	3	*	*
PCB 114	ND	4	*	*
PCB 118	39	1,2,3,4,5	*	*
PCB 121	3	1,2,3,4	*	*
PCB 128	3	4	*	*
PCB 129	2	4	*	*
PCB 137	ND	4	*	*
PCB 138	56	1,2,3,4,5	*	*
PCB 141	24	1,2,3,4,5	*	*
PCB 143	ND	4	*	*
PCB 151	27	1,2,3,4,5	*	*
PCB 153	57	1,2,3,4,5	*	*
PCB 154	ND	4	*	*
PCB 156	1	1,2,3,4	*	*
PCB 159	3	4	*	*
PCB 170	9	1,2,3,4,5	*	*
PCB 171	ND	4	*	*
PCB 173	ND	4	*	*
PCB 180	26	1,2,34,5	*	*
PCB 182	4	4	*	*
PCB 185	2	3,4	*	*
PCB 187	ND	4	*	*
PCB 189	ND	4	*	*
PCB 191	ND	4	*	*
PCB 194	1	1,2,3,4	*	*
PCB 195	ND	1,2,3,4	*	*
PCB 196	3	1,2,4	*	*
PCB 200	ND	4	*	*
PCB 201	1	1,2,4	*	*

Table 5.7 continued

Compound	Significant results	Reference	Priority Pollutant USEPA	Priority Pollutant EEC
PCB 202	ND	4	*	*
PCB 203	2	4	*	*
PCB 205	ND	4	*	*
PCB 206	2	2,3,4	*	*
PCB 207	2	4	*	*
PCB 208	2	4	*	*
PCB 209	2	1,2,3,4	*	*
lindane	45	1,2,3,4,5	√	√
heptachlor	17	1,2,3,4	√	√
heptachlor epoxide	26	1,2,3,4,5	√	√
aldrin	ND	4	√	√
dieldrin	57	1,2,3,4,5	√	√
endrin	25	1,2,3,4	√	√
cis–chlordane	54	1,2,3,4,5	√	√
trans–chlordane	55	1,2,3,4,5	√	√
anthracene	46	1,2,3,5	√	x
fluoranthacene	52	1,2,3,5	*	√
pyrene	52	1,2,3,5	*	√
chrysene/benz[a]anthracene	52	1,2,3,5	*	√
benzo[b]fluoranthene	52	1,2,3,5	*	√
benzo[k]fluoranthene	52	1,2,3,5	*	√
benzo[a]pyrene	49	1,2,3,5	*	√
benzo[g,h,i]perylene	19	1,2,3,5	*	√
dibenzo[a,h]anthracene	25	1,2,3,5	*	√

Key: (1) ARWB (1988), (2) ARWB (1990), (3) ARC (1993), (4) Fox et al. (1988), (5) Holland et al. (1993), * indicates classes (PCBs and PAHs) that are regarded as priority pollutants, without specifying individual compounds. Priority pollutant lists for EEC (List 1) and USEPA, cited by Anthony and Breimhurst (1981), Bingham (undated) and USEPA (1986).

Miscellaneous organochlorines

These include lindane, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, *cis*– and *trans*–chlordane. Aldrin has not been detected in the New Zealand environment and can be removed from further consideration, here. All of the others occur frequently in samples, as would be expected from their histories of use in the region. It is doubtful that cited values of heptachlor and heptachlor epoxide are entirely credible. Research studies on chlordane persistence and bioaccumulation have failed to detect heptachlor epoxide, and have established that the parent compound (heptachlor) does not persist in the marine environment as long as other chlordane compounds (Smith et al. 1992, Wilcock et al. 1993, 1994). Heptachlor and heptachlor epoxide should only be routinely monitored where there is a likelihood of detection (e.g. near a timber treatment yard).

Lindane appears in the most contaminated sediments of Manukau Harbour at concentrations of about 1 ng/g and is usually substantially less than that. The shellfish data has a median of about 2 ng/g, consistent with a sediment concentration of about 0.1 ng/g. The absence of suitable toxicity data (and, as a result, SQC) makes it difficult to assess the impact that these low lindane concentrations will have on aquatic organisms.

Dieldrin levels range up to 0.5 ng/g in sediments, and up to 30 ng/g in shellfish (sediment equivalent=1.0 ng/g). The published SQC values for dieldrin, using the EqP method (USEPA 1993d) are 40 ng/g for sandflats and 200 ng/g for mudflats. The ER–L value for dieldrin is 0.02 ng/g, whereas the ER–M value is 8 ng/g (Long and Morgan 1991). Thus, dieldrin levels are below those thought to have measurable impacts on aquatic organisms. Endrin levels are generally much lower than dieldrin values and, consequently, are not as significant. A better approach in assessing these two compounds would be to sum concentrations and compare them with one SQC.

The two chlordane compounds listed in Table 5.7 have been found in most of the samples analysed. Total chlordane comprises over 140 compounds, but is mostly comprised of 9 chlorinated compounds (Smith et al. 1992). It is common in environmental studies to refer to "chlordane" or "total chlordane" as the sum of *cis*– and *trans*–chlordane, and occasionally include other compounds (e.g. *trans*–nonachlor and heptachlor). The sum of *cis*– and *trans*–chlordane can be taken as an underestimate, or can be divided by 0.42 to provide an approximate value, of total chlordane (Shigenaka 1990, Smith et al 1992). Total chlordane values reported by Fox et al. (1988) were 0.9–5.3 ng/g, in 5 muddy sites, whereas concentrations in sandy sites recorded by Holland et al. (1993) ranged up to 0.41 (median 0.2) ng/g. The shellfish survey chlordanes (*cis*– + *trans*–chlordane) ranged up to 270 (median 6) ng/g and equate to equilibrium sediment values of 0–9 (median 0.2) ng/g. Comparison of these values with the SQC in Table 5.6 shows that chlordane concentrations are commonly close to those thought to have measurable effects on aquatic organisms.

***Cis*– and *trans*–chlordane are still being detected in environmentally significant concentrations and should continue to be monitored in areas receiving industrial and urban inputs. Recommended detection limits (dry weight basis) are 0.1 ng/g for sediments and 1 ng/g for shellfish samples. Lindane, dieldrin, endrin and heptachlor (and heptachlor epoxide) should not be determined routinely unless there is good reason for doing so. It would sensible, however, to include them in new surveys.**

PAHs

All of the PAHs in Table 5.7 are priority PAHs (USEPA undated) and should continue to be monitored. Other priority pollutants are naphthalene, acenaphthalene, acenaphthylene, fluorene, phenanthrene and indeno[1,2,3–c,d]pyrene. Studies of PAH persistence in sandflats of Manukau Harbour (Corban et al. 1994) have shown that most low molecular weight PAHs, such as naphthalene, fluorene and phenanthrene, are unlikely to persist in marine sediments because of their solubility in water (≥ 1 mg/l). To date there is a lack of reliable data for setting sediment quality criteria for most PAHs. It is common practice to choose a group of PAHs, such as those in Table 5.7, that are representative of the major classes (see section 8.3.1). Difficulties arise when comparing "total PAHs" compiled by different analysts, because of the large number of compounds to choose from. Methods used by analysts should enable resolution of individual compounds. Some older methods, based on HPLC, do not achieve good compound resolution.

Because of the sensitivity and selectivity of contemporary GC/MS methods practically all PAHs of environmental interest, for which standards are available, are amenable to analysis. Thus, it may be desirable in some situations to look for PAHs with methyl and ethyl substituents, as being indicative of uncombusted petroleum products (spills and seepages). Likewise, the presence of perylene and retene may be useful to delineate natural inputs (deriving from vegetation and forest fires) from anthropogenic sources (Lipiatou and Saliot 1991).

A recommended list of PAHs for analysis from samples from the Auckland region should take into account the likely sources of pollution (urban runoff, steel mill/coke wastes, creosote spills). The distribution of PAHs in sediments and shellfish of Manukau Harbour is shown in Fig. 5.1 and, clearly, the major compounds should be included in any monitoring programme. Below (Table 5.8) is a list of PAHs routinely determined in marine sediment samples at NIWA Ecosystems, with the relevance of each compound given. The NIWA list is by no means exhaustive, nor should it be considered a minimum set. Instead, it might be used as an aid to defining which PAHs should be determined for specific samples.

Other compounds

Other organic contaminants that may warrant closer scrutiny in future are: modern pesticides (e.g. organophosphates and pyrethroids), surfactants (e.g. linear alkyl sulphonates), and high production volume chemicals (e.g. chlorinated solvents and hydrocarbons).

5.7 Sampling procedures

Before mounting an expensive investigation of sediment organic contaminant status, it is important to ask the question, "what is the purpose of sampling?" If the purpose is to identify hot spots (e.g. near urban stormwater outfalls, or specific industries) then it may be necessary to conduct an initial (scoping) survey that defines the extent and variablity of the problem. Sufficient results should be acquired to enable subsequent sampling to be optimised in terms of the minimum number of samples (i.e.lowest cost) for the maximum amount of useful information. The preliminary survey should establish the depth of contamination.

Recently, guidelines on sediment sampling procedures have been published for: toxicological testing (ASTM 1992), evaluation of dredged material for ocean disposal (USEPA 1991), and assessment of sediment physicochemical and biological status

Table 5.8 Suggested PAHs for analysis in sediments.

	Rationale			
PAHs routinely analysed by NIWA Ecosystems	Manukau shellfish[1]	Mangere Inlet cores[2]	USEPA priority PAH[3]	NOAA NSTP[4]
naphthalene			√	√
2–methylnaphthalene				√
1–methylnaphthalene				√
biphenyl				√
acenaphthene			√	√
fluorene		√	√	√
phenanthrene		√	√	√
anthracene	√	√	√	√
1–methylphenanthrene		√		√
fluoranthene	√	√	√	√
pyrene	√	√	√	√
benz[a]anthracene	√	√	√	√
chrysene	√	√	√	√
benzo[b]fluoranthene	√	√	√	
benzo[k]fluoranthene	√	√	√	
benzo[e]pyrene		√		√
benzo[a]pyrene	√	√	√	√
perylene		√		√
indeno[1,2,3–c,d]pyrene		√	√	
dibenz[a,h]anthracene	√	√	√	√
benzo[g,h,i]perylene	√	√	√	

[1] ARWB (1988, 1990), ARC (1993), Fig. 5.1; [2] Hume et al. (in prep); [3] USEPA (undated); [4] NOAA (1993)

(Environment Canada 1993). The most comprehensive of these is the Canadian publication, which recommends a study plan (before field work commences) that takes into account the following points:

- potential sources of contamination
- location of fine–grained materials, usually associated with low energy zones in water
- selection of appropriate sampling sites
- consideration of sample size (weight or volume) required to satisfy the analytical methods and QA/QC programme for all intended tests
- determination of the level of confidence and the acceptable size of effect from the sample data
- determination of the sampling frequency required to meet the study goals and objectives and take into account seasonality, when relevant
- a minimum of three replicate samples (preferably five) from each sampling station – the need for replicates (and the number) may be determined *a priori* from a preliminary survey
- statistical evaluation of the programme before sampling begins

Methods for addressing all of the above points are listed in the Canadian guidelines (Environment Canada 1993). Some of these are included in the Guidelines section of this report.

5.8 Sample analysis

A number of methods for the analysis of trace level organic compounds in sediments have been published in the scientific literature. The NOAA (1993) protocol is used by NIWA Ecosystems for analysing sediments and shellfish, and is broadly similar to other well–established methods. We do not wish to endorse any one particular method for all occasions; methods for trace organic analysis are constantly being reassessed and new ones being developed. What is important is ensuring that the method delivers the appropriate detection levels and that adequate quality assurance/quality control (QA/QC) procedures are in place to give credibility to the results. A checklist should include the following items:

- recovery of surrogate standards for each class of compounds (should be 50–120%), at levels similar to those found in samples.
- blanks, duplicate analyses, and spike recoveries should be carried out and documented with every group of (as a minimum) 20 samples.

- operational detection limits based on low-level spike recoveries of real samples should be derived and be available on request. These are more relevant than instrument detection levels based on recoveries of spiked blanks.
- standard reference materials should be used to allow analytical performance checks to be made over long periods (decades).
- where possible an indication of participation and performance in accredited interlaboratory comparisons should be given.
- precision, bias and sensitivity at different concentration levels should be available on request.

5.9 Recapitulation

This chapter has sought to provide a framework for targetting specific organic pollutants in sediment monitoring programmes. The choice of compounds has been based on what has been found in past surveys, and published sediment quality criteria. A list of recommended organic compounds for inclusion in sediment surveys in the Auckland region is given in Table 5.9. Sediment criteria (ER-L, ER-M and EqP) values are given where data is available. SQC values calculated using the EqP method, for a sediment organic carbon content of 0.5%, are given in *italics*. **NB**: Sediment criteria are subject to change as better concentration-effect data become available.

Table 5.9 Recommended organic pollutants for analysis. Sediment quality criteria cited are: ER–L, ER–M, and EqP (derived from the EqP method for an organic carbon level of 0.5%).

Compound	Sediments quality criteria (ng/g)			Recommendation for analysis
	ER–L	ER–M	EqP	
2,4,5–trichlorophenol				sometimes
2,4,6–trichlorophenol				sometimes
2,3,4,6–tetrachlorophenol				always
pentachlorophenol			1400	always
p,p–DDT	1	7	0.8	always
o,p–DDT				optional
p,p–DDD	2	20	3	always
o,p–DDD				optional
p,p–DDE	2	15	13	always
o,p–DDE				optional
Total DDTs	3	350	4	always
PCB 31				always
PCB 49				always
PCB 77				always
PCB 118				always
PCB 126				always
PCB 138				always
PCB 141				always
PCB 151				always
PCB 153				always
PCB 169				always
PCB 180				always
Total PCBs	50	400	150	always
lindane				optional
heptachlor				sometimes
heptachlor epoxide				sometimes
dieldrin	0.02	8	100	always
endrin	0.02	45	3.8	optional
cis–chlordane	0.5	6	0.75	always
trans–chlordane	0.5	6	0.75	always
naphthalene	340	2100	250	always
2–methylnaphthalene	65	670		always
1–methylnaphthalene				always
acenaphthene	150	650	1150	always
fluorene	35	640	30	always
phenanthrene	225	1380	200	always
anthracene	85	960		always
1–methylphenanthrene				always
fluoranthene	600	3600	1500	always
pyrene	350	2200	425	always
benz[a]anthracene	230	1600	800	always
chrysene	400	2800		always
benzo[b]fluoranthene				always
benzo[k]fluoranthene				always
benzo[e]pyrene	400	2500		always
benzo[a]pyrene	400	2500	5000	always
perylene				always
indeno[1,2,3–c,d]pyrene				always
dibenz[a,h]anthracene	60	260		always
benzo[g,h,i]perylene				always

6 RECOVERY (SELF-CLEANSING) OF SEDIMENTS FROM CONTAMINATION

6.1 Introduction

This chapter describes physical, biological and chemical processes that lead to the recovery (self-cleansing) of estuaries. Contaminants in estuaries are trapped, buried and unburied, immobilised, broken down, diluted and dispersed by physical, biological and chemical processes. The principal mechanisms for self cleansing in the Manukau Harbour have been identified (Williamson and Hume 1990) as:

- resuspension and dispersal of fine sediments
- sediment mixing and dilution
- sedimentation and burial
- immobilisation of contaminants as unreactive sediment phases
- solubilisation and dispersal of contaminants
- decomposition of toxic organic compounds

Most of the mechanisms which control these processes have been described in the foregoing discussion. Here we summarise and briefly describe these processes (Table 6.1).

6.2 Sediment resuspension and dispersal

Our studies have shown that the resuspension of fine sediments (along with any associated contaminants) is a major process in Manukau Harbour. This process could result in

- a nett loss of polluted suspended sediments from the harbour,
- dispersal of polluted suspended sediments to other parts of the harbour,
- or the dilution of polluted sediments by incoming unpolluted sediments.

It is important from microscale (mm) to large scales (km). A model is presently being developed by NIWA which will predict the resuspension and dispersal of fine suspended sediment.

6.3 Sediment mixing and dilution

The constant reworking of sediment by physical forces and bioturbation mixes sediments vertically. Bioturbation is the principal mixing agent in muddy sediments, while physical mixing is also important in sandy sediments. Wave action typically affects 1-2 cm in sands

Table 6.1 Key mechanisms of sediment recovery.

Process	**Mechanism**
Resuspension of fine sediments	Wave action on all sediment textures Intertidal bank erosion in muds, sandy mud or muddy sand Currents in channels
Dispersal	Currents
Sediment mixing and dilution	Wave action on all sediment textures Bioturbation
Burial	Sedimentation
Solubilisation	Metabolism of organic material containing trace elements Sediment phase changes (FeS to FeOOH) Complexation (e.g., dissolved organic matter, S^{2-}, $S_2O_3^{2-}$) Exchange of organic compounds between sediment organic carbon and pore water phases
Exchange with overlying waters	Tidal pumping Diffusion Wave mixing Bioturbation Burrow irrigation
Dispersal	Currents
Degradation	Physical, microbial and chemical processes

and a few mm in muds, but can affect depths to 25 cm along the eastern shore where bars form (see Section 3.3). Bioturbation is typically intense in the top 10-20 cm, but some animals live deeper, albeit at low densities, and will have relatively small effect. Consequently, contaminated sediments are subject to very intense mixing in the surface layers (~2 mm to 2 cm), fairly intense mixing to 10-20 cm, then a drop off below this level. Contamination tends to be spread vertically in these surface layers, and as such is diluted by less contaminated sediments.

6.4 Sediment burial

Polluted sediments can be removed from the system through burial if the input sediments are 'clean'. The incoming sediments bury contaminated surface sediments, effectively reducing the toxicity of surface sediments. Sediment mixing attenuates this process by mixing the deeper contaminated sediments upward to the surface. Once sediments are moved to below the bioturbated layer, they are effectively removed from cycling processes in the harbour, at least over the short term.

For example, in one part of Mangere Inlet, coring has revealed that Cr is buried at depth in the sediments (Fig. 4.4). The 70 cm thick Cr enriched (450 µg/g, or a factor of 9 times above background) layer some 70 cm below the sediment surface presumably derives originally from tanneries and electroplating industries operating since the early 1900's which discharged untreated waste directly into Mangere Inlet. The discharges would have ceased when the factories closed or when all industrial sewage was diverted to the Mangere Sewage Works in 1962. The layer is overlain by sediments relatively low in Cr. Burial has resulted from high accumulation rates in this part of the inlet (radiocarbon dating suggests 26 mm/yr) of Cr-poor sediment once the industrial inputs of Cr ceased. The accumulation has apparently been high enough to override physical and biological processes that could mix incoming cleaner sediment with Cr-enriched sediment, and hence a layer is preserved. Because the Cr-enriched layer is buried at depth and out of the way of mixing by waves and currents and bioturbation, it is therefore trapped and unavailable to present day processes.

6.5 Immobilisation

As sediments age, they undergo diagenetic changes, which include a wide variety of reducing, oxidising, solubilisation, diffusion and crystallisation processes. These affect the manner in which pollutants, especially trace metals, are bound and the transformations they undergo. It is possible that trace metals could become immobilised in the sediment phase. For example, amorphous hydrous oxides and FeS strongly adsorb dissolved trace metals. Over time the adsorbed trace metals become incorporated in the mineral lattice as the substrates grow or slowly re-crystallise to Fe_2O_3 and FeS_2. Any tendency for trace metals to become less available and less reactive with time is a form of recovery.

Our studies (see section 4.5) have shown that this is a relatively minor effect. Cd, Cr, Cu, Ni, Pb and Zn show a slight decrease in reactivity with depth.

6.6 Solubilisation and dispersal of contaminants

Recently researchers have found that release of metals from sediments into the water column is important, leading to readsorption and deposition at less polluted sites or flushing from the system. Measured fluxes of metals at the sediment/water interface are usually positive (i.e. from the sediments to the water). This is not a contradiction of the well-known tendency of trace metals to be strongly adsorbed by particulate material, but seems to be a natural consequence of early diagenetic reactions. It is probably associated with the microbiological decomposition of organic substrates containing metals, and complexing by soluble organic material. Solubilisation may also be an important recovery process for some of the more soluble toxic organics. These are also strongly associated with particulate material, although in this case their association is regarded as dissolution in particulate or sorbed organic matter rather than adsorption *per se*.

Relatively high concentrations of some trace elements are found in water draining over intertidal areas in Mangere Inlet, which are much higher than concentrations found entering or leaving the inlet. Therefore mobilisation is undoubtedly occurring. These mobilisation processes will be attenuated by the subsequent processes of readsorption (onto suspended sediment, algae, surface sediments) and deposition (settling, biological uptake and excretion). Therefore, if there is a nett loss from the harbour through mobilisation, it will possibly be through progressive cycles of solubilsation, readsorption and settling. This is currently the subject of research at NIWA.

Soluble contaminants are dispersed via exchange processes between the sediment and overlying waters and then tidal currents.

6.7 Decomposition of toxic organics

Toxic organics and other undesirable organic material undergo a variety of transformations such as oxidation, UV photolysis, reduction, hydrolysis and microbial breakdown. Individually, these reactions lead to the formation of less or more toxic forms, but collectively and ultimately, they lead to recovery. This will be an important recovery route for the less stable toxic organics (e.g. organophosphates) but less important for others such as the stable PAH and organochlorines (DDT, DDE, PCB) (see Table 5.3 and 5.4). It also depends on the source and manner in which pollutants are incorporated in sediments. For example, PAHs derived from urban runoff and atmospheric fallout appear to be highly stable (Readman et al 1987), whereas those derived from oil or creosote spills decompose in aerobic sediments (McElroy et al. 1989).

7 GUIDELINES FOR SEDIMENT SAMPLING

7.1 Introduction

Why sample?

Any study must have clear aims and clear objectives to meet these aims. The aim is the overall goal and should include the proposed action in response to the results. The objectives are the means to by which the aims are achieved. It may help to formulate objectives as hypotheses that can be tested. Hypotheses demand attention to the steps necessary to achieve the aims and objectives. Even in a general survey to obtain baseline data from a previously unstudied area, it pays to formulate an hypothesis such as: "the concentration (of a given pollutant) in area A is less than or equal to that in area B", or, "the concentration in area A is less than the sediment criterion". Such hypotheses require careful attention to sampling and analytical methodology, detection limits, and confidence intervals, as well as asking whether the comparisons being made are sensible. In contrast, a more general aim such as, "to study the metal concentrations in area A", may provide limited information and unclear conclusions (e.g., the methods used may not be comparable with those used previously in Area B).

Any study must have clear aims and clear objectives to meet these aims. The aims should include the proposed action in response to the results. Without these, the sampling programme may turn out to be inadequate.

Previous studies

So far in the Auckland Region, sampling exercises have addressed:

- General surveys: What are the contaminant concentrations in surface sediments over a wide area?
- Specific impacts: What is the extent of impact (magnitude and areal extent) of a specific input on the contaminant concentrations in surface sediments in a given area?
- Time variation: How do concentrations of contaminant change with time in the vicinity of a specific input?
- Baseline surveys during Environmental Impact Assessments.

These exercises have had mixed success. One outcome has been a considerable improvement of our understanding of the significance of metals and organic contaminants in sediments of Manukau Harbour. In particular, we have improved our understanding of:

- The natural variability in metal concentrations, especially the effect of sediment texture.
- Methods for minimising variance from factors outside the scope of interest of a particular study
- The range and average contaminant concentrations in sediments in the Auckland region.
- The impacts of a number of specific and non-point discharges on contaminant concentrations.
- The persistence of organic contaminants in sandy and muddy locations.

Future studies will build on these findings and are likely to involve further work on general surveys, impacts of specific discharges, and changes in sediment quality over time at specific locations. In addition, there is an increasing interest in the response of sediments to management practices and in biological effects of trace elements and organic pollutants.

Problems experienced in the past have resulted from:

- Lack of clear aims and objectives.
- The difficulty of comparing results from different analytical methods.
- High variability in comparative studies.
- Difficulty in interpreting results in terms of impact on the environment.
- Lack of quality control in analytical methods.

The following guidelines address these problems, based on the discussion in the preceding chapters. The problem of quality control has been extensively discussed in ARWB (1989) and is not further discussed here.

Philosophy behind the guidelines

1) Questions being addressed through sediment analysis can be formulated in a more sophisticated way than in the past.

Improvements in our understanding of contaminants in sediments means that these sophisticated approaches are available. Their use will yield a higher level of understanding.

2) There is no universal method suitable for all questions.

Applying a standard protocol to all studies would result in a comprehensive database which would allow confident comparisons on sediment chemistry across the Auckland region. This approach is taken by major overseas agencies for specific programmes (e.g., NOAA 1993,). While laudable in some respects, this approach fails to address the complexity of sediments and their interactions with the ecosystem. We advise against "wholesale", uncritical adoption of protocols and methodologies developed by overseas agencies.

3) All methods are empirical and each has advantages and disadvantages. In choosing a method one must be aware of these.

4) Methodology should be based on a reasoned course of action rather than trying to adopt studies to a particular protocol.

In particular, choices need to be made on:

- Sampling depth
- Particle size separation
- Rigour of extraction
- Supplementary analyses
- Obtaining natural trace element concentrations

If protocols are too rigorous they will constrain and limit aims and objectives.

5) It is likely that methodology will continue to change in the foreseeable future.

While there has been a considerable improvement in our understanding of sediments, there remain many unknowns. We anticipate rapid developments in methodology, particularly because of continued research into the biological effects of contaminants and the strong push for sediment criteria.

7.2 Analytical Requirements

Sampling methods are well reviewed in ARWB (1989). Additional useful information can be obtained in USEPA (1991), ASTM (1992), Environment Canada (1993), NOAA (1993). Some of the more common and simple methods are listed in Table 7.1.

For general analysis sampling and preservation conditions are given in Table 7.2. Amounts are given as ideal (a sufficiently large amount that allows duplicate or repeat analysis while minimising the amount that needs to be collected) and as a minimum. Of course, smaller quantities can be processed under special circumstances. Sampling for acid volatile sulphide requires special precautions. The actual analysis only requires 5 g (wet weight), but any handling of anoxic sediment in the air results in surface oxidation. If a large amount is collected (e.g., >100 g wet weight) then this oxidised sediment can be scraped off or avoided when subsampling under oxygen-free N_2 during analysis. Smaller quantities will need to be bagged under oxygen-free N_2.

Table 7.1 Common sampling methods.

Situation	**Intertidal**	**Subtidal**
Surface	Plastic shovel made from clear polyethylene for metals. Stainless steel spatula (e.g., wide putty knife) for organics.	Box core and shovel, spatula or perspex corer as above. Capped perspex cores as above deployed by diver.
Cores	Hand held perspex corers with plastic coated rubber stoppers, or plastic screw caps.	Capped perspex cores as above deployed by diver. Pneumatic perspex corer for deep cores.

Table 7.2 Sampling and preservation conditions (PE=polyethylene).

Determinand	**Amount required** (g wet weight)		**Container**	**Comments**
	Ideal	Minimum		
Particle size	100	50	PE Bag	Chill, dry on return to lab (40-60°C)
Trace elements	20	10	PE Bag	Chill, freeze on return to lab
Organics	200	50	Glass (acetone rinsed) PE Bag	Chill, freeze on return to lab
TOC	5	2	PE Bag	Part of trace elements or organics sample
AVS	100	10	Plastic petri dishes in double PE Bag	Chill, freeze on return to lab. If <50g then must bag or cap under oxygen-free N_2.

7.3 GENERAL SEDIMENT SURVEYS

Version 1: 30 April 1994

To establish levels of contamination in a location not previously examined, or to obtain baseline data on an area that is likely to be impacted some time in the future.

Method

1) Formulate aim and objectives. Some ideas that can be included in aims and objectives are given in Table 7.3.

2) Formulate action that will be taken in response to the results. The aim and the action will define the information requirements.

3) Map the sediment dynamic environment (see section 3.5).

4) Decide on what sedimentary environments will be analysed. Generally, it is better to study accumulation zones. Sampling transportation or erosion zones may be desired, but one must be clear of the implications for interpreting the results (see Chapter 3).

5) Choose a sampling method (see p25 ARWB 1989). For general surveys, it is probably better to analyse whole sediments, minus the shell fragments, animal, large plant detritus and gravel. Therefore pass through 2mm plastic (trace elements) or stainless steel (organics) sieves.

6) Decide on the sampling depth. Generally, use the top 2-3 cm, which provides an integration of inputs over a reasonable length of time (e.g., it will an approximate sample of 5-10 years deposition in accumulation zones - ARWB 1989). Other choices are listed in Table 7.4). For trace elements, take cores to establish background concentrations (see Section 4.2).

Table 7.4 Sampling depths.

Depth	Rationale
Surface (2-3 mm)	Surface feeders Recent pollution
10-20 cm	Bioturbated layer for most organisms
Specific depth range	Specific animal habitat Specific time interval of deposition

6) Analyse samples following a recognised procedure (see Sections 4.6 and 5.8). We recommend 2 M HCl extraction as a general method for most trace elements. For Hg, Se or toxic organics use procedures such as those recommended by USEPA and NOAA, and incorporate adequate QA/QC checks.

7) Analyse particle size, TOC, and reactive iron to aid interpretation of the measured distribution and to calculate sediment quality criteria (see Section 5.5).

Table 7.3 Examples of aims and actions.

Aims	Actions
Conduct survey in accumulation zones Conduct survey in a range of sediment environments Carry out a baseline study	Compare with natural concentrations Compare with sediment criteria (see Tables 4.4 and 5.9). Compare with specific surveys conducted elsewhere.

7.4 EVALUATION OF SEDIMENT CONCENTRATIONS BY CRITERIA

Version 1: 30 April 1994

To assess the potential toxicity of sediments to biota.

Method

1) Formulate aim and objectives.

2) Formulate action that will be taken in response to the results. The aim and the action will define the information requirements.

3) Choose 1 or more of the following approaches

Approach	Applicable to
Calculate ratio of AVS to heavy metals	Heavy metals (Pb, Ni, Zn, Cu, Cd)
Compare sediment concentrations to published sediment quality criteria	Trace elements and organic pollutants
Compare sediment concentrations to calculated sediment quality criteria	Organic pollutants

i) Acid volatile sulphide. Compare AVS concentrations with reactive metal concentrations. Choose sampling depth (Table 7.2). Analyse AVS and reactive metals using 2M HCl. Compare the ratio of the sum of the molar concentrations of heavy metals, with the molar concentration of AVS. If ratio is < 1, then the metals are potentially acutely toxic.

ii) Sediment quality criteria. Compare contaminant concentrations with published sediment quality criteria. For trace elements refer to Table 4.3. For organic pollutants, normalise concentrations with total organic carbon concentration. Use published USEPA criteria, based on Equilibrium Partitioning method (EqP) method, where available (Table 5.9). Alternatively use ER–L and ER–M values (Long and Morgan 1991 – Table 5.6).

Sediment analytical procedures are given in the Guideline for General Sediment Surveys. Strictly speaking, trace elements should be analysed as totals.

iii) Calculated sediment quality criteria. Estimate appropriate criteria values for organic pollutants from calculated EqP values using published K_{ow}, FCV data (see Section 5.5).

4) Map the sediment dynamic environment (see section 3.5).

5) Decide on what sedimentary environments will be analysed. Generally, it is better to study accumulation zones. Sampling transportation or erosion zones may be desired, but one must be clear of the implications for interpreting the results (see Chapter 3).

6) Choose a sampling method (see p25 ARWB 1989). Analyse whole sediments, minus the shell fragments, animal, large plant detritus and gravel. Therefore pass through 2mm plastic (trace elements) or stainless steel (organics) sieves. For AVS analysis, miss the sieving step.

6) Decide on the sampling depth, based on aims and objectives (see Table 7.4). For trace elements, take cores to establish background concentrations (see Section 4.2).

Qualifying remarks

Sediment quality criteria development is in its infancy, and a number of techniques have recently become available. The techniques listed above represent the state-of-the-art, but all have major shortcomings. It is likely that these techniques will be refined or superseded in the near future. At present, these techniques can only be used to indicate whether sediments might, or might not, be toxic to benthic organisms. This may allow setting of priorities or suggest areas of future study, but use in a legalistic or policing matter would need a great deal of caution. Improved assessments on likely toxic effects can only come from toxicity testing and *in situ* population surveys of the animals themselves.

The advantages and limitations of the above guidelines are:

1) AVS has been shown to be a factor determining acute toxicity of heavy metals to some animals (see Section 4.6). The widespread application of these findings has received justifiable criticism (Luoma & Carter 1993), and calls for further research. We therefore do not recommend its use by itself, but as an adjunct to sediment concentration criteria .

2) The status of sediment concentration criteria was reviewed in Sections 4.4 and 5.5.

3) The EqP method is based on widely accepted principles which are generally endorsed by the USEPA (see Section 5.5). The lack of specific, officially-endorsed USEPA criteria for most compounds, means that most EqP values have to be calculated. Disagreement between some published data for equilibrium constants and toxicities can lead to large uncertainty in calculated criteria. Long and Morgan's (1991) review should be used as a convenient check on calculated concentrations.

7.5 SPATIAL OR TEMPORAL COMPARISONS

Version 1: 30 April 1994

To make valid comparisons of contaminant concentrations repeatedly measured over time, or in different locations.

Method

1) Define aims and how these will be achieved. When comparing sediments from one location with another, or at one site at different times, it is important to address the following questions:

i) What is being compared? Usually the aim is to compare different situations or conditions (e.g., compare sediment pollution in one part of a harbour with another). To meet this aim, the objective may then compare sediment concentrations that represent those situations or conditions (e.g., compare sediment concentrations in one part of a harbour with another). In some studies, the aims have been confused with objectives, resulting in an inability to meet the (unstated) aims.

ii) What magnitude of difference between two (or more) samples is important (e.g., from a pollution, ecological, or environmental perspective)? To help in this decision, consider such things as the range of concentrations found in the Manukau Harbour, background concentrations and the differences between sediment criteria such as the ER-L and ER-M (Long & Morgan 1991) summarised in Tables 4.4 and 5.6

iii) Is it a valid comparison in terms of methodology, sediment environment etc?

iv) What type of statistical test will be used and what is the desired power of the test. In most studies, particular attention is paid to the statistical significance rather than whether the comparison is valid, or what is the environmental or management significance.

2) Establish sample design. When designing the sampling programme, it is important to recognise that the potential for spatial or temporal patchiness always exists.

i) Ensure samples are representative of the situation or condition being compared. In practical terms, this means choosing the appropriately sized and positioned plot from which replicates are to be taken. For example, to compare site A with site B may only require a small number of replicates from a small plot at each site. However, to compare one part of an estuary with another may require replication over a wider area to ensure that the samples are truly representative of the parts of the estuary being compared. At the present time, we have a very poor understanding of patchiness in sediment contaminant concentrations, (this is currently under research), and so cannot give prescriptive guidance for choosing plot size. The key factor is to make a sensible choice based on the aims and objectives, and the constraints of the immediate environment. The plot should be as homogeneous as possible in respect to factors not under investigation, e.g., sediment texture, hydrology, biota, flora. It is a mistake to assume a plot is homogeneous in an area of strong environmental gradients (e.g., near a drain or in a transportation zone) and in such cases the plot would need to be small compared with the environmental gradient.

ii) It is critical to choose the appropriate sediment zone from which the samples are to be taken, which requires an understanding of the sediment environment the study is taking place in. It would be usual to choose accumulation zones when monitoring the change in contaminant concentration through time or space. When monitoring in transportation or erosion zones, the object may be to monitor concentration changes in the fine sediment fraction, which is being transported through the zone.

iii) The ability to detect changes in concentrations is limited by the amount of unexplained variance. Minimise sample variance by one of the following techniques. Choice of technique will depend on the nature of the work and aims.

a) Analyse the <20 µm fraction (Forstner & Wittman 1979). This technique has been used by Glasby et al (1988) for trace elements in sediments in the Manukau and Waitemata Harbour and is excellent for reducing concentration variations caused by sediment texture. It has been used in a number of overseas studies (Forstner & Wittman 1979). It needs to be applied cautiously to sediments with a low mud content (<10%), because the larger particles may be more important in binding trace elements and the fine fraction may have substantially different sediment phases. We do not know if this method is suitable for organic pollutants.

b) Analyse the <63 µm fraction, using wet sieving through nylon mesh. Although not as efficient in reducing sample variance as the <20 µm techniques, it is much more widely used. As with the <20 µm techniques, it needs to be applied cautiously to sediments with a low mud content (<10%). We do not know if this method is suitable for organic pollutants.

c) Use normalisation techniques. This involves dividing concentrations by a factor which reflects the sediment composition. There are a number of possibilities depending on the ancillary information collected. For **trace elements**, if using XRF or concentrated acid digestions, then the most common technique is to use Al_2O_3 content, which largely reflects clay content. If using 2M HCl extraction, then reactive iron content could be used. Failing these, the proportion of mud can be used, although it is probably the least preferable. **Organic** contaminant variance is usually reduced by expressing data as masses (ng) per unit mass (g) of organic carbon, viz by dividing sediment dry weight concentrations by the sediment organic carbon fraction (concentrations are sometimes referred to as being organic carbon normalised).

iv) Choose the number of replicates using procedures described in ARWB (1989) or based on the statistical method chosen. It must be emphasised that the aims establish the magnitude of the difference to be confidently detected, as well as the degree of confidence.

v) As well as replicate sampling of the environment, it is important to differentiate the variance generated during the analyses from the environmental variance. This not only helps explain any differences between sites but is essential quality control. At least one sample replicate should be analysed in 3 times.

3) Permanently identify plot position for time series surveys. Near shore sites (<30m can be triangulated using tapes from permanent markers on the shore. Further off-shore (< 1 km), Electronic Distance Meters are good to ± 0.01m.

4) Sampling depth. Generally, use top 2–3 cm which provides an integration of inputs over a reasonable length of time in muddy sediments. In addition, collect long cores to establish background concentrations of trace elements (see Section 4.2).

5) Choose a sampling method (see p25 ARWB 1989). For general surveys, it is probably better to analyse whole sediments, minus the shell fragments, animal, large plant detritus and gravel. Therefore pass through 2mm plastic (trace elements) or stainless steel (organics) sieves.

6) Analyse samples following a recognised procedure (see Sections 4.7 and 5.8). We recommend 2 M HCl extraction as a general method for most trace element. For Hg, Se or toxic organics use procedures such as those recommended by NOAA (1993).

7) Analyse reactive iron (metals), particle size, TOC (organics or metals) to aid interpretation of measured distribution or reduce contaminant concentration variance.

7.6 RECENT POLLUTION EVENTS

Version 1: 30 April 1994

To establish the extent of a recent pollution event.

Method

1) Identify contaminants of concern.
2) Map sediment environment based on bathymetry, and sediment texture (see section 3.5).
3) Choose sampling locations, based on reasoned guess as to where impact might be. In a survey such as this, single samples at each sampling point are normally collected. Replication should be taken to ensure samples are representative of locations.
4) Choose sampling depth. The deeper the sediment, the less sensitive the survey. The top few mm offers the best compromise between sensitivity and practicality.
5) Choose sampling method (refer p25 ARWB 1989).

   i) Intertidal sediments: Shallow samples can be collected using a polyethylene or stainless steel spatula to remove the top layer. In accumulation zones, the top 2 mm should be collected. For 500 g of wet sediment this will necessitate collecting the surface sediment from a 0.25 m^2 plot. In sandy sediments, contaminants are mixed downwards quite rapidly, so the top 1 cm could be collected.

   ii) Sub-tidal sediments are best collected from a box core (ARWB 1989). This provides the best control in choosing sample depth and size. It may be difficult to obtain sufficient sample for analysis, in which case it may be better to compromise on sampling depth for all samples collected in the survey (e.g., 1 cm deep x 0.04 m^2 is needed to give 500 g of wet sediment).

6) Consider the need for depth profile in a likely highly impacted area. This will establish depth of impact at one site.

7) Analyse samples following a recognised procedure (see Sections 4.6 and 5.8). We recommend 2 M HCl extraction as a general method for most trace element. For Hg, Se or toxic organics use procedures such as those recommended by NOAA (1993).

8) Include at least one other contaminant of a similar chemical nature to those, but not implicated, in the pollution event, to act as a check that any contaminant gradient is the result of the pollution event and not some other environmental factor.

9) Analyse reactive iron (metals), particle size, TOC (organics or metals) to aid interpretation of measured distribution.

7.7 BIOLOGICAL STUDIES

Version 1: 30 March 1994

To measure contaminant concentrations in sediment from which biota samples are collected.

Method

1) Formulate aim and objectives.

2) Describe the sediment dynamic environment at the sampling sites.

3) Choose sample design. The chemical sampling design should be based on the biological sampling design. The latter require expert design and execution. The plots need to be of sufficient size for replicates for biological, chemical and physical analysis to be taken. It is advantageous that plots are as homogeneous as possible in respect to factors not under investigation, e.g., sediment texture, hydrology, flora.

4) Decide on the sampling depth, based on aims and objectives of biological sampling (see Table 7.4). For trace elements, take cores to establish background concentrations (see Section 4.2).

5) Choose a sampling method for required depth and size (see p25 ARWB 1989). Analyse whole sediments, minus the shell fragments, animal, large plant detritus and gravel.

6) Analyse samples following a recognised procedure (see Sections 4.6 and 5.8). We recommend 2 M HCl extraction as a general method for most trace element. For Hg, Se or toxic organics use procedures such as those recommended by NOAA (1993).

7) Analyse particle size, TOC, and reactive iron to aid interpretation of the measured distribution and to calculate sediment quality criteria (see Section 5.5).

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