

## Chemical fractionation of lead in intertidal sediments from Manukau Harbour, Auckland, New Zealand

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**Abstract** Four cores were collected from intertidal sites in the Manukau Harbour, Auckland, New Zealand. Cores were sub-sectioned under nitrogen; total lead was determined following an acid digestion. Pb was also determined in each of six chemical phases resolved by differential extraction procedures. Total Pb concentrations in surficial sediments varied in the range 3.5–98 mg kg<sup>-1</sup>, with the highest level observed at Little Huia. Although background Pb concentrations are difficult to define, it is apparent that discharges from the northern effluent outfall at the New Zealand Steel Works, Glenbrook, have approximately doubled sedimentary Pb concentrations in the immediate vicinity. Analyses of Pb partitioning indicate that no diagenetic processes are operating to remove Pb from the sediments. At Little Huia, Pb preservation within the sedimentary record is accompanied by transformations from iron/manganese oxide to organic/sulfide phases.

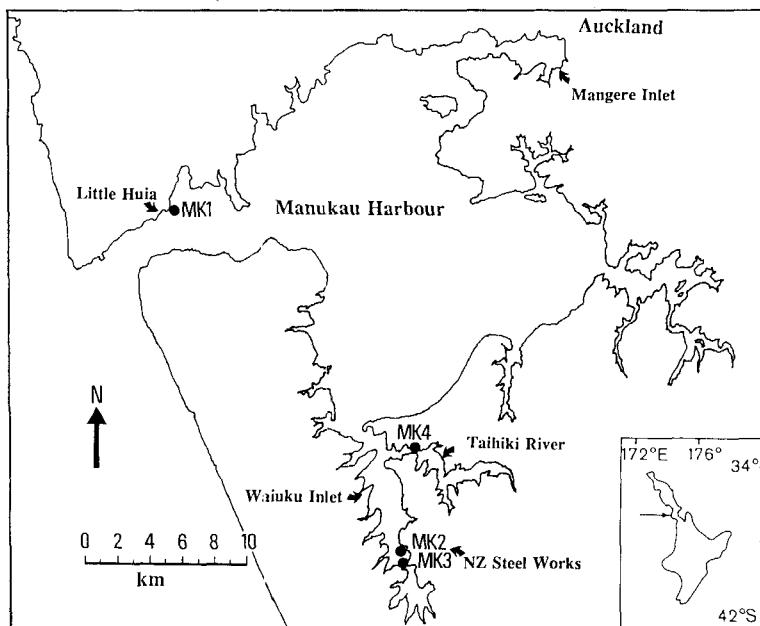
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### INTRODUCTION

Determination of the total concentration of an element in a sediment core may provide a record of pollution history. Typically, lead (Pb) profiles in sediments are considered to exemplify anthropogenic influences, manifest as high surficial Pb burdens with concentrations diminishing to background levels at depth (Vernon et al. 1987). However, such an interpretation is feasible only in the absence of diagenetic remobilisation of an element within the sediment. The depth distribution of total manganese in a core often mimics that described for Pb, but reflects markedly different processes; namely reductive remobilisation at depth, followed by diffusion upwards into oxygenated surficial sediments via the interstitial waters and subsequent oxidative precipitation (Robbins & Callender 1975).

Increasingly the role of chemical speciation is being considered to aid the interpretation of geochemical processes (de Mora & Harrison 1984). For sediments, this generally means the determination of elements within fractions resolved by sequential extraction techniques. The scheme of Tessier et al. (1979) has gained widespread acceptance and has been utilised for investigations of atmospheric aerosols and fly ash (Wadge & Hutton 1987), street dusts and soils (Harrison et al. 1981; Fergusson & Ryan 1984), riverine suspended particulate material (Tessier et al. 1980) and various other sediments (Dominik et al. 1983; Rapin et al. 1983). Although few such investigations have been conducted, down core studies enable an assessment to be made of the environmental mobility of an element. This is important in defining the ability of the sediments to act as a sink for contaminant discharges and establishing a local pollution record. But also, elucidating Pb diagenesis has implications with respect to the application of Pb-210 dating techniques.

The present study investigates the partitioning of Pb in four cores collected at intertidal sites within the Manukau Harbour. These cores are used to seek post-depositional variations in Pb behaviour and the local effect of the New Zealand Steel Works with respect to Pb.



**Fig. 1** Map of Manukau Harbour showing location of four sampling sites.

## METHODS

Cores, up to 50 cm in length, were collected from four intertidal sites in the Manukau Harbour (Fig. 1). Two sampling locations in the Waiuku Inlet were c. 10 m downstream of the northern (MK2) and southern (MK3) effluent outfalls from the New Zealand Steel Works at Glenbrook. The other locations at Little Huia (MK1) and in the Taihiki River (MK4) were meant to represent control sites. The site at MK1 was c. 20 m from the coastal road.

Upon collection, cores were immediately subsectioned into 2 cm layers under nitrogen in order to prevent aerial oxidation. Separate aliquots of sediments were removed for the determination of total Pb content following an acid digestion using an  $\text{HNO}_3/\text{HClO}_4/\text{HF}$  mixture, Pb fractionation utilising a differential extraction procedure (based on Tessier et al. 1979 and Hong & Förstner 1983) as shown in Table 1, and moisture content by drying to constant weight at 105°C (Jeffrey 1970). Thus, all analyses utilised wet sediment and results were subsequently corrected to be expressed on a dry weight basis.

Pb analyses were carried out by graphite furnace atomic absorption spectroscopy using a Perkin Elmer 5000 spectrometer with an HGA-500 graphite furnace and AS-40 autosampler unit. Absorbances were measured at 283.3 nm and the background corrected using a deuterium lamp. Quantification was by the method of standard addition. Ten replicate analyses

of NBS 1646 Estuarine Sediment gave a concentration of  $28 \pm 4 \text{ mg kg}^{-1}$ , in good agreement with the certified value of  $28 \pm 1.8 \text{ mg kg}^{-1}$ . Using the paired *t*-test, there was no significant difference between the Pb determined by total acid digestion and that calculated by summation of the six phases.

## RESULTS

Geological description of the cores and major element chemical data have been presented elsewhere (Demeke 1987). Only the Pb chemistry is considered here.

### Total lead

Sediment profiles for total Pb at all study sites are presented in Fig. 2. The greatest Pb burden was found in the core collected at Little Huia (MK1). The maximum concentration,  $98 \text{ mg kg}^{-1}$ , occurred in the surficial sediments and Pb levels decreased gradually with depth to a minimum of  $65 \text{ mg kg}^{-1}$  at 18–20 cm. In contrast, the lowest Pb content in the cores was observed at the Taihiki River location (MK4). Concentrations were  $3.5\text{--}5 \text{ mg kg}^{-1}$  throughout the upper 28 cm. This location is utilised by New Zealand Steel Works as a control site for evaluating the impact of effluent discharge in the Waiuku Inlet.

Intermediate Pb burdens were observed in the cores obtained in the vicinity of both outfalls from

the New Zealand Steel Works. Higher concentrations were found at the northern outfall (MK2), consistent with the higher discharge rate and longer history of effluent emission at this point. For this core, the upper 8 cm contained 34–39 mg kg<sup>-1</sup> Pb but below 8 cm the concentration was 15–27 mg kg<sup>-1</sup>. Pb concentrations at the southern outfall (MK3) were relatively uniform throughout the 24 cm length, being in the range 9–16 mg kg<sup>-1</sup>. Although dates are not available to provide confirmatory evidence, the sediment characteristics in the lowest layer (22–24 cm) were markedly different to those of overlying sediments and so it is likely that the complete pollution record at this site was obtained (Demeke 1987).

### Chemical fractionation of lead

The partitioning of Pb within sediments for the four cores is illustrated in Fig. 2. In all cases, the data are expressed in terms of relative composition to highlight possible down-core variations.

For the Little Huia location (MK1), about half of the Pb at all depths was present in the residual fraction. This was the only site at which neither exchangeable nor carbonate phase Pb was observed. Surficial sediments contained equal proportions of reducible and organic/sulfide associated Pb but with depth, the relative amount of Pb associated with reducible phases decreased. Also at the Taihiki River site (MK4), the dominant phase was the residual fraction which comprised about 35–55% of the total Pb. There were no marked changes in partitioning down the length of the 28 cm core. In contrast to other sites, very little organic/sulfide Pb was present. Below 22 cm the sediment was light brown in colour. Such observations suggest that the sediments did not become anoxic.

The Pb fractionation in sediments near both the northern (MK2) and the southern outfalls (MK3) was uniform throughout their length. However, the two adjacent sites exhibited quite distinct differences. The residual fraction constituted a minor portion (only

10–20%) of the total Pb at MK3, but this was the dominant phase at the northern outfall (MK2). The easily and moderately reducible phases comprised the majority of the Pb burden for MK3. Finally, exchangeable Pb was detected only at the northern discharge site in this study.

### DISCUSSION

The Pb content of surficial sediments is variable within the Manukau Harbour, being 98 mg kg<sup>-1</sup> at Little Huia, 18–34 mg kg<sup>-1</sup> in Waiuku Inlet, and <5 mg kg<sup>-1</sup> in Taihiki River. Relatively few data are available here, but results do agree well with those of Glasby et al. (1988). In an extensive sampling programme, they found that surficial Pb concentrations in the main body of the Manukau Harbour were in the range 27–108 mg kg<sup>-1</sup> in the < 20 µm size fraction. Lower levels (20–46 mg kg<sup>-1</sup>) were observed in Waiuku Inlet. They noted that subsurface Pb concentrations were less than surficial levels, probably as a result of anthropogenic inputs; they do not discount diagenetic influences. Similarly here, the Pb profile for the Little Huia core exemplifies recent contamination, possibly resulting from localised contamination from moored boats, road run-off, or from the nearby city of Auckland. Roper et al. (1988) reported slightly lower Pb concentrations in surficial sediments from mudflats at six intertidal sites around the Manukau Harbour. Concentrations generally ranged between 10 and 20 mg kg<sup>-1</sup>, although a level near 60 mg kg<sup>-1</sup> was observed in the Mangere Inlet.

The marked inter-site differences in total Pb content ensures that background Pb levels are rather difficult to define. However, on the basis of the cores from Waiuku Inlet, a reasonable estimate for the background Pb concentration is 20 mg kg<sup>-1</sup>. This level is relatively low but is consistent with values observed elsewhere in New Zealand (Smith 1986; Kennedy in press). The concentration of Pb in the Taihiki River

**Table 1** Six chemical fractions characterised by sequential extraction procedures.

Fraction	Extractant	Time	Temp.
Exchangeable	1 mol l <sup>-1</sup> Na <sup>+</sup> CH <sub>3</sub> COO <sup>-</sup> (pH 8.2)	1 h	Ambient
Carbonate	1 mol l <sup>-1</sup> Na <sup>+</sup> CH <sub>3</sub> COO <sup>-</sup> (pH 5)	5 h	Ambient
Easily reduced	0.04 mol l <sup>-1</sup> NH <sub>2</sub> OH.HCl in 25% CH <sub>3</sub> COOH	6 h	96°C
Moderately reduced	0.2 mol l <sup>-1</sup> (COONH <sub>4</sub> ) <sub>2</sub> .2H <sub>2</sub> O and 0.2 mol l <sup>-1</sup> (COOH) <sub>2</sub> .2H <sub>2</sub> O (pH 3)	24 h	Ambient
Organic and sulfide	30% H <sub>2</sub> O <sub>2</sub> / 0.2 mol l <sup>-1</sup> HNO <sub>3</sub>	24 h	Ambient
Residual	HNO <sub>3</sub> / HClO <sub>4</sub> / HF; Evaporate to dryness; Residue dissolved in concentrated HCl		

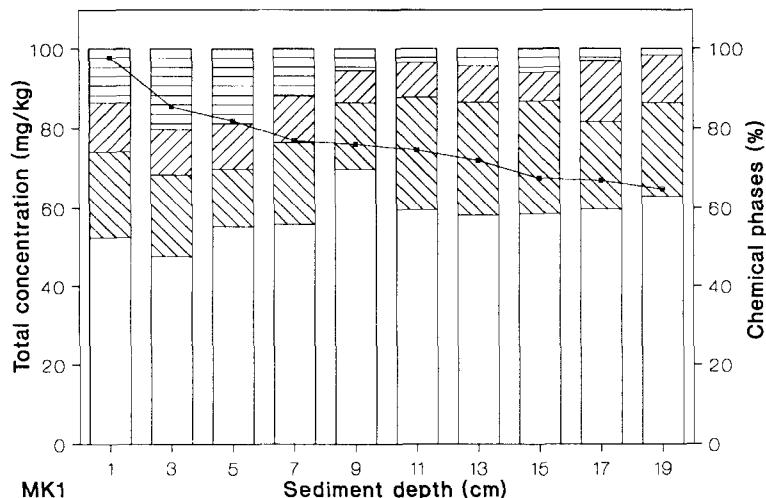
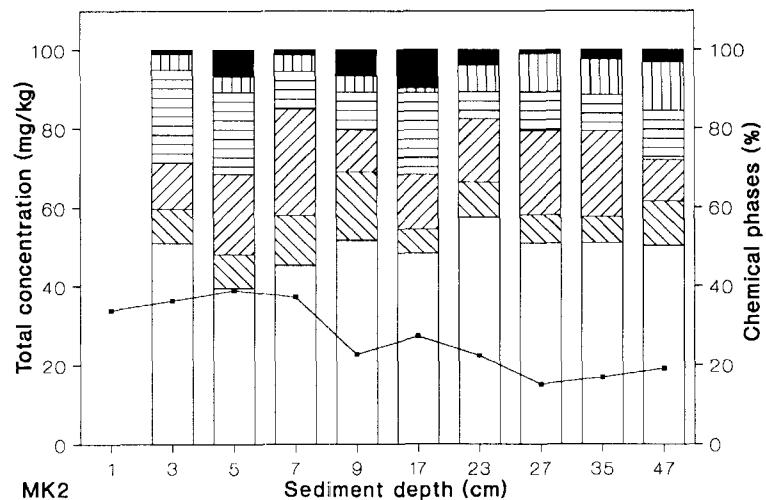


Fig. 2 Sediment profiles of total Pb concentration ( $\text{mg kg}^{-1}$ ) and distribution of Pb in different chemical fractions (%).

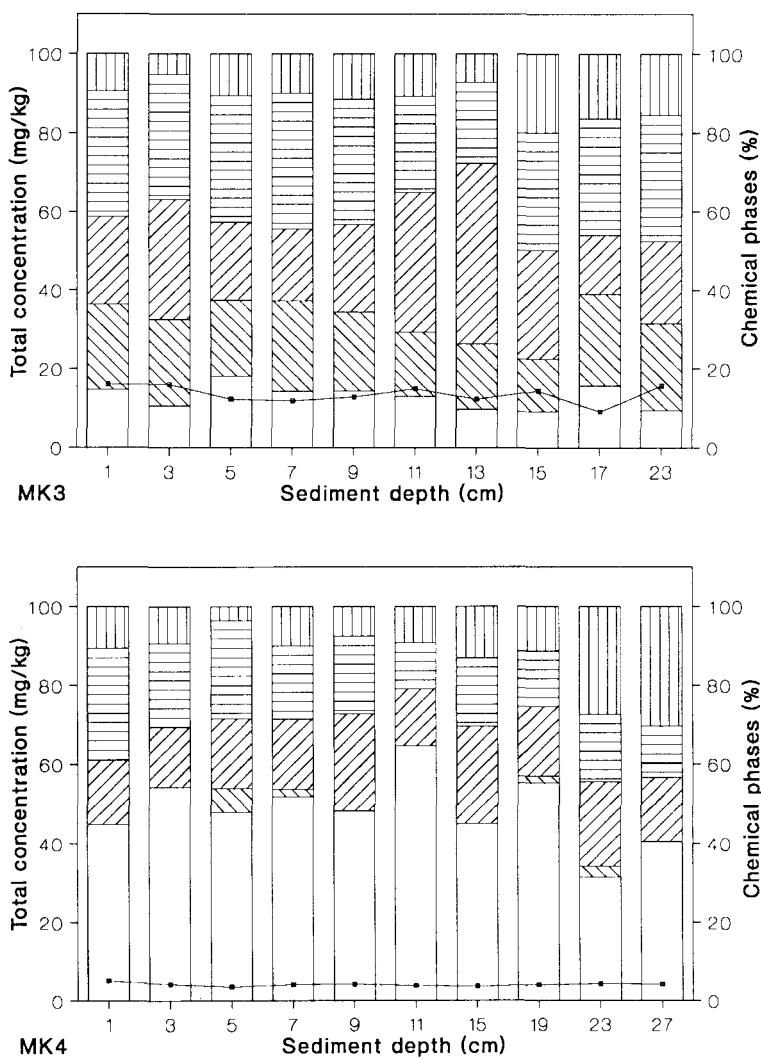


sediment is appreciably lower,  $<5 \text{ mg kg}^{-1}$ , suggesting that this is perhaps not a good control site for considering possible impacts of the steelworks with respect to Pb. It is worth noting that the mineralogy at this site was distinctly different from the other three locations, being silica-enriched but depleted with respect to Fe and Al (Demeke 1987). Assuming a background of  $20 \text{ mg kg}^{-1}$ , effluent discharge from the New Zealand Steel Works has caused a Pb enrichment of c.  $20 \text{ mg kg}^{-1}$  in sediments near the northern outfall. No impacts near the southern discharge could be discerned.

Considering Pb partitioning, the widespread usage of the scheme of Tessier et al. (1979) allows inter-site

comparisons to be made. Although the relative proportions of the Pb species in the four cores examined here varied considerably, the residual fraction generally constituted a substantial fraction of the total Pb burden. This contrasts with the dominance of iron/manganese oxide phase association in fresh waters (Tessier et al. 1980; Dominik et al. 1983; Viel et al. 1983). Carbonate phases predominate in marine sediments (Dominik et al. 1983; Rapin et al. 1983). It should be noted that Förstner (1982) observed that residual Pb comprised 54% of that present in a surficial sediment from the lower Rhine River which he ascribed to aerial deposition of PbO. The results in the Manukau Harbour suggest that the mineralogy of

Fig. 2 (continued) Key on p. 572



the sediments may pose a significant control on the Pb content of the sediments. This would in part explain the differences in the background Pb levels observed within the harbour.

Although problems such as a lack of selectivity (Kheboian & Bauer 1987) and re-adsorption (Rendell et al. 1980) may limit the rigour with which sequential extraction data can be interpreted, such operationally defined fractions can provide valuable indicators of environmental mobility and possibly bioavailability (de Mora & Harrison 1984). Anthropogenic metal discharges comprise relatively reactive phases and so recent inputs should be manifest as surficial enrichment of exchangeable, carbonate, and easily-

reduced phases. Subsequent loss from the sediment would tend to reinforce this profile in that the relative importance of the residual component would increase with depth. Such behaviour has been observed in Lake Geneva (Dominik et al. 1983). Containment within the sediments should be evident by either the preservation of the chemical fractionation of the surficial sediments or, more likely, by the transformation of the reactive phases into moderately reducible and organic/sulfide fractions at depth.

With the exception of the Little Huia sample (MK1), there is little down-core variation in Pb partitioning at any one location. As discussed above, this observation indicates that Pb is not being removed

from the sediments. Similar findings have been noted for coastal sites in the Mediterranean Sea (Rapin et al. 1983; Dominik et al. 1983). Although it is surprising that the Little Huia core alone contains no carbonate-associated Pb, a distinct trend is evident in the Pb profile. The residual fraction constitutes about 50% of the Pb at all depths, but the proportion associated with the easily reducible iron/manganese oxides decreases with depth. A concurrent increase in the organic/sulfide phase is evident. Using X-ray diffraction techniques, Purchase & Fergusson (1986) identified the dominant Pb phases as  $PbCO_3$  at the surface and PbS at depth in a riverine sediment profile. Pb that may be released following the reduction of iron and manganese oxides is retained in the sediments, probably as PbS. Hence in this investigation, there is no evidence to suggest that diagenetic processes are remobilising Pb from the sediments in the Manukau Harbour but, rather, the Pb is apparently being retained in association with organic/sulfide phases.

## CONCLUSION

Although background concentrations are difficult to define, it is apparent that discharges from the northern effluent outfall at the New Zealand Steel Works have approximately doubled sedimentary Pb concentrations in the immediate vicinity. The Pb burden is greater still at Little Huia, an intertidal site in the main body of the Manukau Harbour, possibly being influenced by urban pollutants or local contamination from roads or moored boats.

Analyses of chemical fractionation indicate that no diagenetic processes are operating to remove Pb from the sediments. The high proportion of Pb in residual phases suggests that the major influence controlling Pb may be the mineralogy of the sediments.

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