

Copper, chromium, and lead in Manukau Harbour sediments

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Abstract A limited survey was undertaken to determine the concentrations of copper, lead, and chromium in sediments of the upper Manukau Harbour, New Zealand. The concentrations of copper and chromium (33–70 and 70–107 $\mu\text{g g}^{-1}$ respectively) were of the same order of magnitude as those reported for other New Zealand harbours. However, lead concentrations (98–247 $\mu\text{g g}^{-1}$) were higher than those found for the other harbours. This may be a consequence of higher traffic densities in the surrounding area.

Keywords copper; chromium; lead; Manukau Harbour; sediments; trace elements; pollution; heavy metals

INTRODUCTION

Little is known about the concentrations of trace elements and their mode of accumulation in near-shore sediments around New Zealand. Although a recent reconnaissance survey by Stoffers et al. (1983) included some information on three North Island harbours (Wellington, Whangarei, and Ohiwa), there appear to be no data available on harbours such as the Manukau and Waitemata which are probably affected to considerable extents by human activities.

Manukau Harbour is one of the most extensive inlets on the west coast of New Zealand, covering an area of about 340 km², much of which (145 km²) is exposed mudflat at low spring tide. The harbour receives a heavy metal pollution load from a number of sources, by far the most important of which

is the Auckland Regional Authority Waste Purification Works at Mangere. This system treats waters from domestic, commercial, and industrial sources together with storm water, and discharges some 250 000 m³ of treated water per day from a single point on the southern shore of the harbour. Before the inception of this scheme, numerous independent trade waste and storm water outfalls existed on the harbour shores so that the harbour received wastes containing unknown concentrations of heavy metals for a considerable period.

The shallowness of the harbour and the fact that a very large proportion of its area is emptied at every low tide would appear to indicate that the degree of tidal flushing is very high. However, this is not so as the volume of the deep entrance channel is relatively large, and Heath et al. (1976) have concluded that the mean residence time is probably about 22 days. Thus there is the possibility that heavy metals could interact with sediment matter and become incorporated into the body of the sediment.

To determine the status of this problem, a limited survey was undertaken on the extent to which three elements likely to originate from human sources have accumulated in sediments in the upper Manukau Harbour. The elements chosen were copper, chromium and lead (to indicate possible inputs from electroplating industries, tanneries and motoring respectively).

METHODS

Sampling sites are shown in Fig. 1. Sites 1, 2, and 5 were c. 50 m from the northern shore near the long established Onehunga industrial area. The main difference between these three sites was their distance from Mangere Bridge, a major traffic artery. Sites 3 and 4 which were c. 200 m offshore were chosen to provide an indication of the extent to which the contaminant metals were confined to the old shoreline outfalls.

Sediment samples (c. 500 g) were collected in perspex tubes (50 mm inside diameter). They were dried at 70°C and, after removal of shells, were ground and homogenised. Subsamples (c. 300 mg) were digested with nitric-sulphuric acid for 1 h. The supernatant was diluted to 50 ml and analysed for copper, chromium, and lead by atomic absorption spectroscopy.

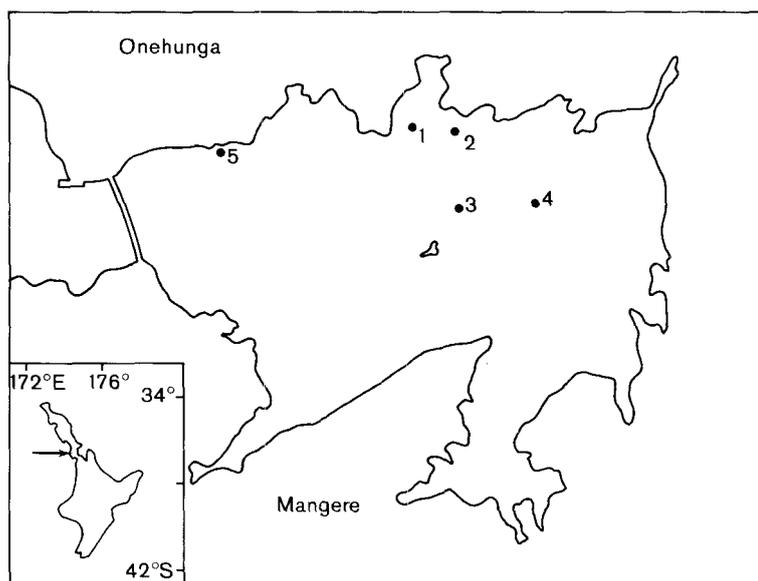


Fig. 1 Sampling sites in inner Manukau Harbour, North Island, New Zealand.

Water samples were collected from three sites in 1-litre clear polyethylene bottles. The sampling sites were chosen to provide information on the concentration of copper and lead in water from the Sewage Treatment Plant effluent, from near the sediment sampling sites (Mangere Bridge), and from the outer region of the harbour (Little Huia). These samples were filtered through 0.45 μm membrane filters and analysed as soon as possible after collection. The method of standard additions was used for all analyses. Total element concentration was determined by photolysing the samples for 4 h with a 25 W Hanovia UV lamp and then extracting into oxine/toluene at pH 6.5 using either 1:1 or 1:10 phase ratio. Free element concentration was determined by extracting into oxine/toluene without photolysis. The toluene extracts were then analysed by atomic absorption with a tantalum strip atomiser (Aggett 1983).

RESULTS AND DISCUSSION

The best estimates (means of 5 determinations) for the concentrations of copper, chromium, and lead in the sediment samples are listed in Table 1. Uncertainties in these estimates, of the order of 4–6%, are largely a consequence of incomplete sample homogeneity.

The copper and chromium concentrations in Samples 1, 2, and 5 are very similar and are significantly higher than those in Samples 3 and 4, which suggests that these elements have entered the harbour through shore outlets within the harbour

Table 1 Concentrations of copper, chromium, and lead in sediments of Manukau Harbour. All concentrations in $\mu\text{g g}^{-1}$ dry weight.

Sample	Copper	Chromium	Lead
1	69	104	159
2	64	101	160
3	33	70	98
4	43	74	111
5	56	107	247

basin. The same pattern exists for the lead concentrations, except that Sample 5, from near Mangere Bridge, contains a considerably higher concentration of lead than the other close-to-shore samples. This indicates the extent to which motor-ing activities based on leaded fuels can contaminate sediments in the vicinity of motorways. Although all the sites are contaminated by water-borne lead, Site 5 is subject to air-borne contamination to a much greater extent than the others. Several studies have shown that the concentration of particulate lead near motorways decreases quite rapidly over a relatively short distance from the motorway, e.g., Ward et al. (1975a, b) found that the bulk of the emission was within 100 m of the road.

If the major source of the lead is automobile exhaust then two different forms of lead are likely to be found in the sediments. Much of the lead halides and oxy-halides from automobile exhausts is converted quite rapidly into lead oxides and under some conditions into lead sulphate. These

Table 2 Concentrations of copper and lead in waters of Manukau Harbour. Concentrations in $\mu\text{g l}^{-1}$.

Site	Copper (II)		Lead (II)	
	Total	Free	Total	Free
Little Huia	5.0±0.3	4.7±0.3	1.2±0.3	0.9±0.3
Mangere Bridge	8.5	4.7	2.0	2.0
No. 4 pond effluent	43.8	30.0	72.5	60.0

are insoluble species and would appear most likely to be transported in storm water as small particles which probably remain unaltered in the sediments unless their residence times are very long. Exhaust particles not converted to oxide or sulphate by the time they are initially removed by bulk water may dissolve to form soluble lead(II) species. In a combined sewage-storm water system, such as that operated at Mangere, these soluble lead(II) species may interact with organic matter, and eventually they may adsorb, with or without organic matter, on mineralised material in the sediments. The relative amounts of these lead(II) species should be determinable by selective dissolution.

Copper is most likely to enter the water purification system in soluble form and since copper(II) has greater complexing ability than lead(II) it is more likely to interact with organic materials and be adsorbed on mineralised matter. The former point appears to be borne out by the data in Table 2. Comparison of copper(II) concentrations in waters from the Manukau Bridge area and Treatment Plant effluent with and without photolysis suggests that 30–45% of the copper(II) in the water is associated with decomposable organic matter.

Comparison of the sediment copper concentrations reported here with those reported by Stoffers et al. (1983) shows that levels in the Manukau Harbour sediments are higher than those from Whangarei and Waitara Harbours, and are also higher than most of those from the Wellington Harbour. However, they are all very much lower than the single value ($> 150 \mu\text{g g}^{-1}$) reported for Ohiwa Harbour. Little credence can, however, be given to results from this single sample from Ohiwa since the degree to which it is representative of the harbour sediments cannot be estimated.

Chromium concentrations are of the same order of magnitude as those from the other harbours. However, as with copper, they lie at the upper end of the range observed.

Of the three elements studied, only lead appears to have accumulated to a significantly greater extent in Manukau Harbour sediments than in the other harbours, with three of the five samples containing more than double the concentration of lead in the most contaminated sample from any of the other harbours. Whether the higher lead concentrations in Manukau Harbour are a consequence of higher traffic densities or greater absorptivity of the sediments has yet to be determined.

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