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To cite this article: Jenny G. Webster (1995) Chemical processes affecting trace metal transport in the Waihou River and estuary, New Zealand, New Zealand Journal of Marine and Freshwater Research, 29:4, 539-553, DOI: [10.1080/00288330.1995.9516686](https://doi.org/10.1080/00288330.1995.9516686)

To link to this article: <http://dx.doi.org/10.1080/00288330.1995.9516686>



Published online: 29 Mar 2010.



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## Chemical processes affecting trace metal transport in the Waihou River and estuary, New Zealand

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**Abstract** The Waihou River, North Island, New Zealand, receives trace metals from two contaminated drainage systems: Ohinemuri River and Tui Stream. In the upper Waihou River and its tributaries, trace metals are transported in bed sediments and in the water column—the latter providing a low-level but continuous flux of dissolved metals (particularly Cu, Zn, Mn, and As) and/or metals bound to suspended sediments (particularly As, Fe, and Pb). As the river water becomes saline, suspended sediment flocculates and settles, increasing the trace metal concentration of estuarine sediments relative to those of the upper river. Fe, Mn, Pb, and Zn are fully adsorbed onto the suspended sediment in the estuary, and should be effectively removed from the water column by this process. Cu and As are only partially adsorbed and are unlikely to be completely removed from the water column in the estuary region. Trace metal partitioning between dissolved and particulate phases appears to be generally consistent with regulation by adsorption onto hydrous iron-oxide in the sediments.

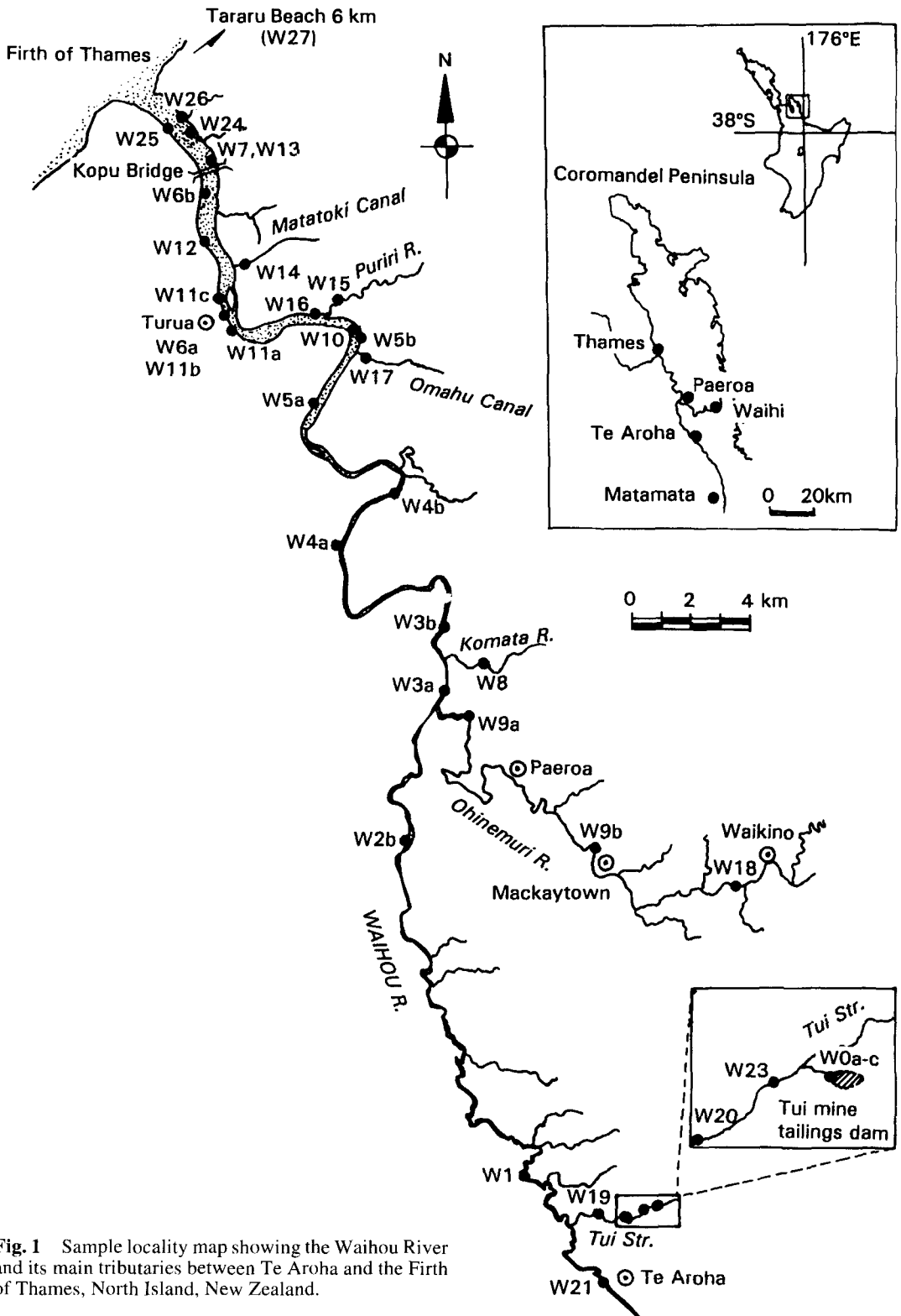
**Keywords** Waihou River; trace metals; transport; iron-oxide

### INTRODUCTION

The Waihou River, at the base of the Coromandel Peninsula, North Island, New Zealand, receives water and sediments from two drainage systems known to be contaminated with trace metals: the Ohinemuri River and the Tui Stream near Te Aroha (Fig. 1). The Ohinemuri River is the largest tributary of the Waihou River, entering at Paeroa (Fig. 1). Trace metal contamination of the Ohinemuri River is the result of natural erosion and previous mining activity in a highly mineralised catchment. Gold was mined between 1890 and 1940 from epithermal quartz vein deposits containing minor (< 3%) base metal sulphides, and is presently mined at the Martha Hill mine near Waihi and at the Golden Cross mine near Waikino.

Tui Stream is a minor tributary of the Waihou River, entering near Te Aroha, and is also contaminated as a result of previous mining activity. The Tui mine was opened in 1884 to mine a base-metal sulphide vein deposit, but operated for only a short period as the zinc-rich lead ore was unsuitable as a flux for local gold smelting (Williams 1974). The mine was reopened in the late 1960s and shipped Pb-Zn-Cu ore to Japan for smelting until 1973, when mercury levels in the ore were considered too high for the Japanese market. It is the tailings dam of this recent mining episode, lying within the Tui Stream catchment (Fig. 1), that has adversely affected stream water quality and caused a multitude of environmental problems for local authorities and the town of Te Aroha (e.g., Weissberg & Wodzicki 1968; Tay 1980; Hendy 1981; Fyson 1991).

In a general survey of the trace metal content of stream waters and sediments of the southern Coromandel region, Livingston (1987) identified Tui Stream and two tributaries of the Ohinemuri River as drainages with elevated trace metal concentrations in the water. However, the fate of these metals in the Waihou River and estuary is largely unknown. The purpose of the present study was to identify the principal chemical processes



**Fig. 1** Sample locality map showing the Waihou River and its main tributaries between Te Aroha and the Firth of Thames, North Island, New Zealand.

affecting trace metal transport in the Waihou River, its tributaries, and estuary.

### Waihou River and estuary

The Waihou River is the largest river in the Coromandel region, flowing from near Matamata to the Firth of Thames and entering a wide, shallow, mud estuary near the coast. Tidal influence on the river is extensive, both in terms of river level and chemistry. Tides typically affect river level as far up stream as Paeroa and a short distance up the Ohinemuri River, but may extend to Te Aroha under conditions of low river flow. As an indication of typical river flows, the annual mean flow for the Waihou River at Te Aroha in 1993 was  $31.8 \text{ m}^3 \text{ s}^{-1}$ , ranging from  $25.7$  to  $91.8 \text{ m}^3 \text{ s}^{-1}$  (Waikato Regional Council unpubl. data). The largest tributary, the Ohinemuri River, averaged  $7.5 \text{ m}^3 \text{ s}^{-1}$  in the lower reaches over the same period. Of the remaining tributaries, the Komata River is one of the largest (estimated flow =  $0.5 \text{ m}^3 \text{ s}^{-1}$ ), whereas Tui Stream makes a considerably smaller contribution (estimated flow  $< 0.1 \text{ m}^3 \text{ s}^{-1}$ ).

In the estuary region, the suspended sediment load of the Waihou River is high and the water takes on an extremely muddy appearance. However, there is little evidence for rapid accretion of sediment in the estuary (Henshaw 1989; Jim Dahm, Waikato Regional Council pers. comm.). Typically sediment accretion rates in the Coromandel region are in the vicinity of  $0.5\text{--}1 \text{ mm yr}^{-1}$ ; before human habitation, rates of  $\leq 0.1\text{--}0.2 \text{ mm yr}^{-1}$  appear to have been more typical (Jim Dahm pers. comm.).

## SAMPLING AND ANALYTICAL TECHNIQUES

### Waters

Water samples were collected from selected sites on the Waihou River and its tributaries (Fig. 1). For the lower river, samples were collected at both high and low tide to establish the extent of tidal incursion. Conductivity and pH were measured on-site in the river, calibrated against standard KCl solutions and phosphate buffers, respectively. Water samples were analysed by high-pressure ion chromatography (HPIC) for all major ions except  $\text{HCO}_3^-$ .  $\text{HCO}_3^-$  concentrations were determined by titration with HCl, followed by further acidification to  $\text{pH} = 3.2$  and purging with  $\text{N}_2$  to remove  $\text{CO}_2$ , and then by back titration with NaOH to correct for other ions affecting alkalinity. Although not

reported here,  $\text{HCO}_3^-$  concentrations, along with those of the other major ions, were required as input data for the modelling program MINTEQA2 (see Discussion).

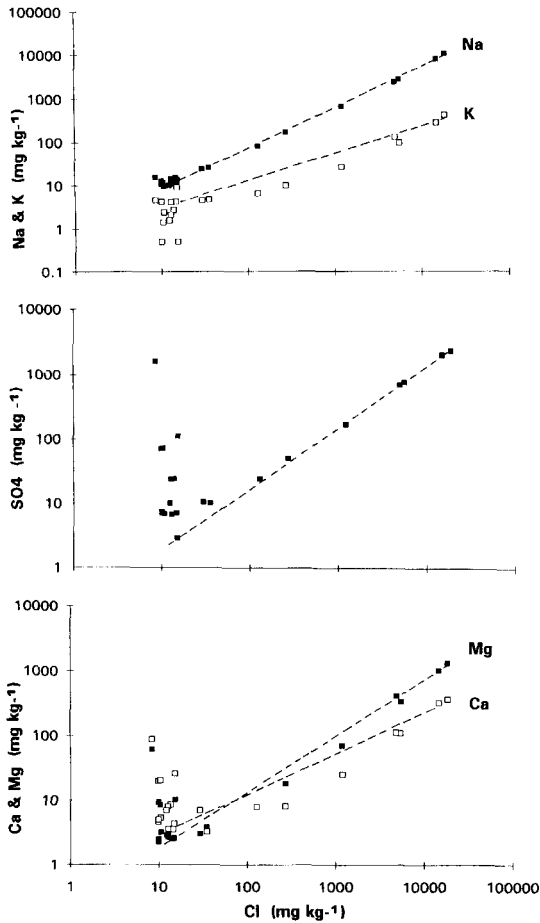
From selected sites, two 250 ml water samples for trace metal analysis were collected into acid-washed polyethylene sampling bottles. Care was taken to avoid sample contamination both during and after collection. To determine dissolved metal concentrations, one sample from each site was filtered through  $0.45 \mu\text{m}$  Millipore filters before acidification to  $\text{pH} \approx 2.0$  with redistilled  $8N \text{ HNO}_3$ . For "acid-soluble" metal analysis, the second sample was acidified without filtration. This sample was used to determine the concentration of metals bound to readily dissolved particulate phases such as amorphous oxides. Two blanks of distilled, deionised water, one of which was carried and opened during field sampling, were also filtered and acidified in this way.

The samples were analysed for Cu, Pb, Zn, Fe, Mn, and Cr by ICP-mass spectrometry at the ESR analytical laboratory in Wellington, New Zealand. Concentrations of As were determined by hydride generation atomic adsorption spectrophotometry (HGAAS) at ESR in Auckland, New Zealand. The two deionised water blanks each registered metal concentrations below the detection limit ( $0.1 \mu\text{g kg}^{-1}$ ).

### Sediments

Two sediment sampling programmes were undertaken on the Waihou River and its tributaries (Fig. 1). At each site a volume of 300–350 ml of wet surface sediment ( $< 8 \text{ cm}$  deep) was collected from the river or stream bank, as close as possible to low-tide river level. Four sediment cores, each 20 cm deep, were also taken at Sites 4b, 10, 11b, and 13. The sediments were dried at  $60^\circ\text{C}$  before aggregates were broken down using a ceramic mortar and pestle, and the sediment was dry-sieved through  $85 \mu\text{m}$  nylon mesh.

Analyses were conducted on the  $< 85 \mu\text{m}$  fraction. For each sample, 0.5 g of sieved sediment was digested in 10 ml concentrated  $\text{HNO}_3$  in a teflon beaker. The sample digestion was evaporated almost to dryness twice on a hot plate, refilling with  $1N \text{ HNO}_3$ , then diluted to 50 ml with distilled water. Digests were analysed for Cu, Pb, Zn, Cr, Mn, and Cd by atomic absorption spectrophotometry (AAS), and for Fe by UV/Vis spectrometry (as the red Fe-thiocyanate complex). HGAAS was again used to determine As concentrations.



**Fig. 2** Major ion concentrations in the waters of the Waihou River and its tributaries, plotted against Cl concentration. A theoretical fresh water/sea water mixing line is drawn between the upper Waihou River water at Site W21 and sea water at Tararu beach at Site W27.

The < 85  $\mu\text{m}$  fraction of sediments from the main channel of the Waihou River were also analysed for total organic carbon by the National Institute of Water & Atmospheric Research in Hamilton, New Zealand. To remove inorganic carbonates, all samples were fumed over HCl in a desiccator for 6 h and then dried at 60°C before analysis. The analyses were performed using a PE 2400 CHN analyser which combusts the sample at 925°C in pure oxygen.

## RESULTS: WATER CHEMISTRY

### Major ions

Near-surface water chemistry of the Waihou River reflects sea water incursion between the coast and Site W5a at high tide, and between the coast and Site W6a at low tide. Major ion concentrations were individually plotted against Cl concentrations to determine the source of the ions. A straight line drawn between the major ion concentrations at Site W21 (the upper Waihou River) and Site W27 (sea water at Tararu beach in the Firth of Thames) provides a theoretical sea water/freshwater mixing line (Fig. 2). Concentrations of Na and K plotted on or near this line, indicating that these ions were derived from the upper Waihou River and/or from sea water. However, Mg, Ca, and SO<sub>4</sub> concentrations in some, mainly fresh, waters plotted significantly above the theoretical mixing line, indicating that these ions have a source other than the upper Waihou River or sea water. The relatively high concentrations of these ions in waters of Tui Stream and, to a lesser extent, the Ohinemuri River, reflected the mineralised nature of these catchments. Finely ground ore tailings containing sulphides and carbonates are rapidly weathered, and will raise the Mg, Ca, and SO<sub>4</sub> content of receiving drainage systems. HCO<sub>3</sub> concentrations did not show a strong relationship with Cl as they may be regulated by a variety of processes other than sea water mixing: for example by atmospheric CO<sub>2</sub> interaction, biological activity, and carbonate mineral weathering.

Because the more dense saline waters move in beneath the river water on an incoming tide, an estuary will often have some degree of salinity stratification, together with variations in temperature and dissolved oxygen. However, the Waihou estuary is shallow and wide, ranging from 2.5 to 3.5 m deep between Site W4b and the coast, and there is little opportunity for significant stratification to be preserved. Profiles of conductivity, dissolved oxygen (dO<sub>2</sub>), and temperatures were taken in the centre of the Waihou River channel, near Sites W17, W10, W16, W11a, W14, W7, and W24. Surface water conductivities ranged from 62 to 89% of the conductivity at the base of the estuary, but there were only minor variations in temperature and dO<sub>2</sub>. The profile measured just up stream from the junction of the Waihou River with the Omaha canal is a typical example: from the surface to 3.5 m depth, the conductivity increased from 1470  $\mu\text{S}$  to 2090  $\mu\text{S}$ , dO<sub>2</sub> decreased from 7.1 to

6.5 mg kg<sup>-1</sup>, and the temperature from 19.2 to 18.9°C.

The suspended sediment content of Waihou River increased from 10 mg kg<sup>-1</sup> in the upper river (W21) to 280 mg kg<sup>-1</sup> in the estuary (W24), and 490 mg kg<sup>-1</sup> outside the estuary on the coast at Tararu Beach (W27). The suspended sediment loads of the Ohinemuri River and Tui Stream were low, at <1 mg kg<sup>-1</sup>.

## Trace metals

### *Tui Stream*

The seepage from the Tui tailings dam (WOa) mixes with diverted drainage water (Woc) before joining Tui Stream approximately 0.5 km up stream from Site W23 (Fig. 1). The seepage below Tui dam was acidic, and contained high concentrations of dissolved Fe, Mn, Cu, Pb, Zn, and As (Table 1). Acid-soluble particulate metal concentrations were below detectable limits for all except As. Further down stream at Site W23, below the confluence of the dam seepage and Tui Stream, stream waters were of neutral pH and Fe had become entirely bound in the "acid-soluble" suspended particulate fraction. Because only amorphous oxides and carbonates are likely to be fully dissolved during

acidification of the water samples, it is reasonable to assume that this Fe has precipitated as an oxide. Hydrous oxides of ferric Fe readily precipitate at pH > 3.5.

Cu, Pb, and As were also mainly bound to the suspended particulates at Site W23, whereas Zn and Mn remained predominantly dissolved in the stream water. In the lower, slow-flowing, region of Tui Stream (Site W19), particulate Fe has been removed from the water column as the suspended sediment has settled out. Other metals bound to the suspended sediments such as Cu and As have also been removed in this way, increasing the relative proportions of dissolved metals.

When sampled in 1994, the seepage from the Tui tailings dam was more acidic (pH = 2.80) than had previously been measured by Tay (1980: pH = 4.34). In Tui Stream pH had increased, however: pH = 7.03 (Site W23) and 7.05 (Site W19) measured in 1994 compared to pH = 4.4 (near Site W19) in 1980 (Tay 1980). This suggests that the volume of acidic dam seepage added to Tui Stream was considerably greater in 1980 than under summer flow conditions in 1994: a premise which is supported by a brief survey of past and present trace metal concentrations in this drainage. With the exception of Fe, trace metal levels were higher

**Table 1** Dissolved and acid-soluble particulate (in italics) trace metal concentrations ( $\mu\text{g kg}^{-1}$ ) in waters of the Waihou River catchment and at Tararu beach. The acid-soluble particulate metal concentrations shown have been calculated from differences between filtered and unfiltered water analyses.

	pH	Fe	Mn	Cu	Pb	Zn	As
<b>Tui Stm</b>							
WOa	2.80	18 300 <i>&lt;1</i>	11 400 <i>&lt;0.1</i>	2670 <i>&lt;0.1</i>	1240 <i>&lt;0.1</i>	44 100 <i>&lt;0.1</i>	33 <i>6</i>
W23	7.03	<1 <i>140</i>	360 <i>&lt;0.1</i>	6.7 <i>16</i>	0.7 <i>16</i>	1460 <i>50</i>	0.13 <i>0.85</i>
W19	7.05	<1 <i>&lt;1</i>	150 <i>&lt;0.1</i>	1.7 <i>0.5</i>	<0.1 <i>&lt;0.1</i>	590 <i>&lt;0.1</i>	0.24 <i>0.15</i>
<b>Ohinemuri R.</b>							
W9b	7.85	15 <i>40</i>	22 <i>&lt;0.1</i>	0.7 <i>&lt;0.1</i>	<0.1 <i>&lt;0.1</i>	2.2 <i>&lt;0.1</i>	0.5 <i>0.8</i>
<b>Waihou R.</b>							
W21	7.75	39 <i>71</i>	8.8 <i>7.2</i>	<0.1 <i>&lt;0.1</i>	<0.1 <i>&lt;0.1</i>	<0.1 <i>&lt;0.1</i>	0.33 <i>0.54</i>
W24	7.37	<0.1 <i>1260</i>	3.1 <i>157</i>	0.1 <i>0.7</i>	<0.1 <i>5.5</i>	<0.1 <i>6.0</i>	4.0 <i>2.1</i>
W27	7.93	<0.1 <i>1130</i>	1.4 <i>149</i>	0.7 <i>0.6</i>	<0.1 <i>5.3</i>	<0.1 <i>3.3</i>	3.5 <i>4.1</i>

in the Tui dam seepage in 1994, than when measured by Tay (1980) and Livingston (1987), but were lower in Tui Stream. Dissolved Zn concentrations in the lower Tui Stream, for example, were less (590–1460 ppb) than those measured by Tay (1980: 4200–5000 ppb).

#### *Ohinemuri River*

In terms of flow and sediment load, the Ohinemuri River is the largest tributary contributing to the Waihou River. Trace metal concentrations in the Ohinemuri River water were considerably lower than those in Tui Stream owing to a higher ratio of surface water to mineralised ground or metal sources such as the fine ground tailings of the Tui tailings dam. The river waters were of neutral pH (6.96–7.85), and Fe was again predominantly bound in the suspended acid-soluble particulates under these conditions. Cu, Mn, and Zn were mainly in dissolved form in river water, whereas As occurred both in dissolved form and bound to suspended particulates (Pb concentrations were below the detection limit).

Comparison with previous trace metal concentrations in the Ohinemuri River is complicated by lack of data and the use of incompatible analytical and sampling techniques. Livingston (1987) did not include analyses for the Ohinemuri River, although two tributaries of the Ohinemuri containing elevated metals concentrations were identified: the Comstock and Jubilee Streams. The concentrations of Fe, Cu, Pb, and Zn measured in the Ohinemuri River in 1994 appeared to be lower than those reported for “low flow” conditions in the environmental impact report for the Martha Hill mine developments in 1985 (Waihi Gold Co. 1985).

#### *Waihou River*

At Site W21 in the Upper Waihou River water, measurable metal concentrations existed only for As, Fe, and Mn, which were present in both dissolved and particulate form. Down stream from Te Aroha, Waihou River water metal levels increased with the assimilation of waters and suspended sediments from Tui Stream and the Ohinemuri River, and of municipal waste waters from Te Aroha, Paeroa, and Turua. In the lower estuary at Site W24, metal concentrations were relatively high. Fe, Mn, Pb, Cu, and Zn were predominantly bound to suspended particulate in the flocculate-laden estuary waters, whereas a

significant proportion of the As remained dissolved. Similar dissolved/particulate metal distributions were evident in the sea water sample collected from Site W27 (Tararu Beach) just outside the mouth of the estuary, although dissolved Cu concentrations were relatively high at this site.

No previous data were available for trace metal concentrations in the Waihou River. However, As, Cu, Pb, and Zn concentrations in the upper Waihou River at Site W21 were similar to those determined as “background” concentrations in streams of the Coromandel region (Livingston 1987).

## SEDIMENT CHEMISTRY

### **Mineralogy**

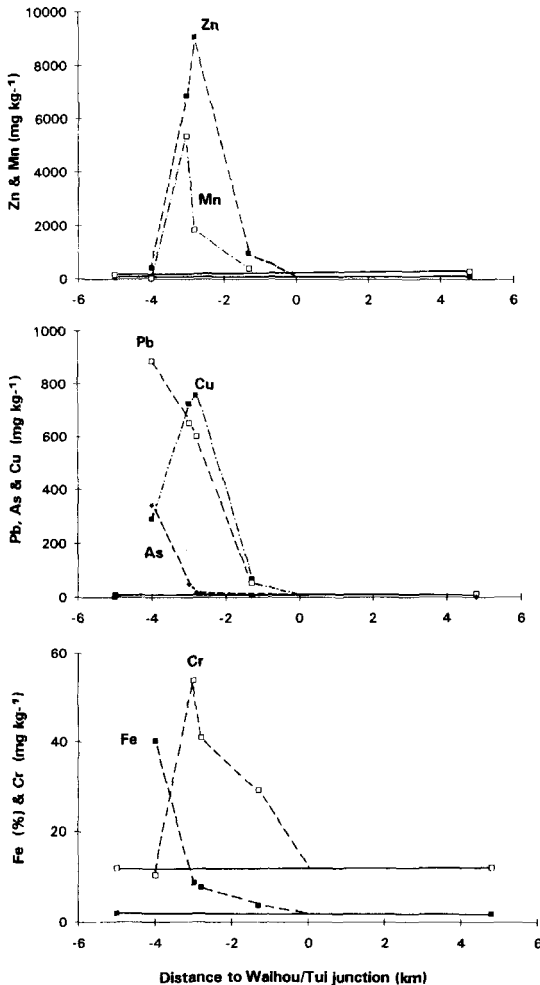
Representative sediments from Tui Stream and the Waihou and Ohinemuri Rivers, including suspended sediment from the Waihou River at Site W24, were analysed by X-ray diffraction on the < 85  $\mu\text{m}$  fraction. All samples contained quartz and clays (Henshaw 1989 further identified the clays in the suspended sediment of the Waihou River as kaolinite, halloysite, dickite, vermiculite, and smectite). In Tui Stream, goethite was present in predominantly amorphous oxides collected below the Tui mine tailings dam (WOa). The lower Tui Stream sediments (Site W19) comprised quartz-clay-tridymite-feldspar. Waihou and Ohinemuri River sediments also included tridymite, derived from the acid volcanics of the catchment, as well as feldspars and chlorite. The suspended sediment had the same mineral assemblage as sediment on the banks of the estuary.

To determine the proportion of trace metals bound to oxides and acid-soluble sediments dissolved during sediment digestion, selected samples were also completely digested using  $\text{HNO}_3$  and HF to ensure complete breakdown of silicate minerals. Fe, Cu, Pb, and Zn concentrations in the  $\text{HNO}_3$ /HF digest were very similar to those of the  $\text{HNO}_3$  digest, indicating that these metals were bound predominantly in the non-silicate phases. Mn and Cr, on the other hand, appeared to be at least partly contained within the clays or other insoluble components.

### **Trace metal concentrations**

#### *Tui Stream*

Concentrations of Fe, As, and Pb in sediments of Tui Stream decreased from the tailings dam to the junction with the Waihou River (Fig. 3 and



**Fig. 3** Metal concentrations in the sediments of Tui Stream (dashed lines) as a function of distance from the junction with the Waihou River (0 km). Metal concentrations in the Waihou immediately up and down stream of the junction are shown as a solid line. Three samples from the dam seepage: W0a, W0a-2 and W0b, have been averaged to give the first data point. The tailings dam seepage joins the main stream at c. -3.5 km, between the first two data points for Tui Stream (refer Appendix 1 for individual site data).

Appendix 1). Cu, Mn, Cr, and Zn sediment concentrations increased from the dam to Sites W23 and W20, then decreased between Site W20 and the junction with the Waihou River. Measurable Cd levels occurred in only a few samples in the Waihou Catchment, and these were all in Tui Stream. Cd concentrations were measured in

sediments from Sites W0a (5.4 mg kg<sup>-1</sup>), W0b (8.2 mg kg<sup>-1</sup>), W20 (27 mg kg<sup>-1</sup>) and W19 (6.9 mg kg<sup>-1</sup>). Tay (1980) noted a positive correlation for Cu, Cd, and Pb concentrations versus Fe concentrations in Tui Stream sediment. Cu and Cd concentrations measured in the Fe-rich sediments for this study (Sites W0a, W0a-2 and W0b) did not support this observation.

*Ohinemuri River*

Like the Tui Stream sediments, the Ohinemuri River sediments contained higher concentrations of Fe, Cu, Pb, As, and Zn than those of the Waihou River (Fig. 4 and Appendix 1): the difference being most significant for Zn, Pb, Cu, and As. Variations in Pb and As sediment concentrations may have reflected the contributions of tributaries of the Ohinemuri River such as Comstock Stream, which enters the river between Sites W9a and W9b. The Comstock Stream has high concentrations of As in the sediments (1440 mg kg<sup>-1</sup>: Livingston 1987) and in the waters (175 µg kg<sup>-1</sup>: Livingston 1987). The Cd concentrations of sediments in the Ohinemuri River (and in the Waihou River and all tributaries other than Tui Stream) were below the detection limit of 3 mg kg<sup>-1</sup>.

In the Ohinemuri River sediments, Cr concentrations were only marginally elevated above those of the Waihou River, and Mn concentrations were lower than those of the Waihou River sediments. It would appear that these two metals are not derived from sources in the Ohinemuri River catchment.

*Waihou River*

A grain size analysis of sediment samples from the Waihou River showed a general trend of fining towards the coast. This is consistent with the transition from a relatively fast-flowing inland river to a wide estuary environment. Longitudinal profiles of trace metal concentrations in Waihou River sediments showed a general increase towards the coast, but became more erratic in the tidal region down stream from Site W5a at the high-tide saline interface (Fig. 5 and Appendix 1). As a measure of the degree of metal enrichment in the estuary, ratios of average sediment metal concentrations in the tidal region (between Sites W5a and W6b) to metal concentrations in the upper Waihou River (Site W21), were calculated. The enrichment ratios ranged from 1.8 to 2.6 for Fe, Cu, Cr, and Zn, and were 4.2 for As, 5.2 for Mn,



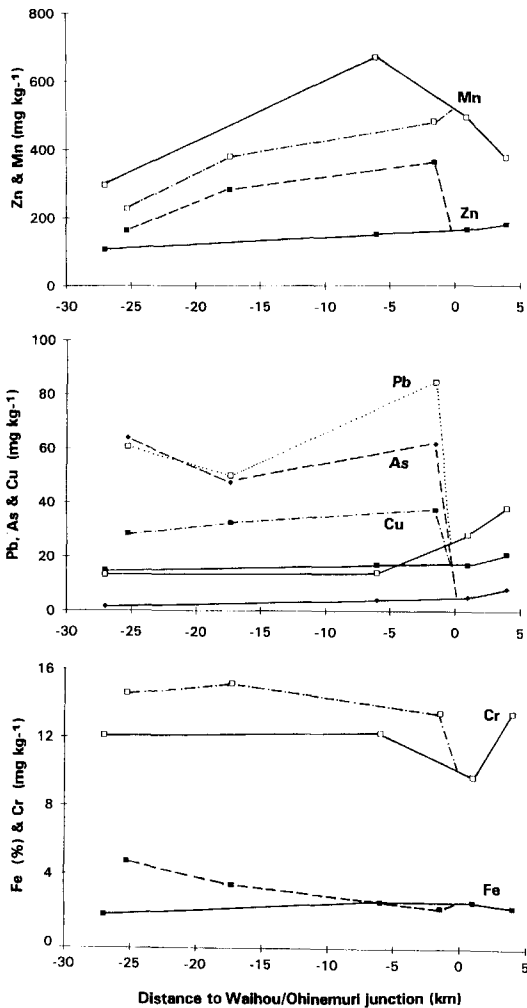


Fig. 4 Metal concentrations in the sediments of the Ohinemuri River (dashed or dotted lines) as a function of distance from the junction with the Waihou River (0 km). Metal concentrations in the Waihou immediately up and down stream of the junction are shown as a solid line (refer Appendix 1 for individual site data).

and 20.8 for Pb. Evidently Pb is accumulated to a significant degree in the estuary.

An increase in Pb, Zn, Cu, and As sediment concentrations was noted immediately down stream from the junction with the Ohinemuri River, 30 km from the Tui Stream junction (Distance = 0 on Fig. 5). This corresponds to the influx of Ohinemuri River sediment carrying relatively high concen-

trations of these metals. Sediment metal concentrations between Kopu Bridge and the coast were often lower than those immediately above the bridge. As these lower estuary sediments (e.g., Sites W25 and W26) contained marine organisms, it is likely that metal-bearing river sediments are being diluted with coastal sediment from the Firth of Thames close to the river mouth.

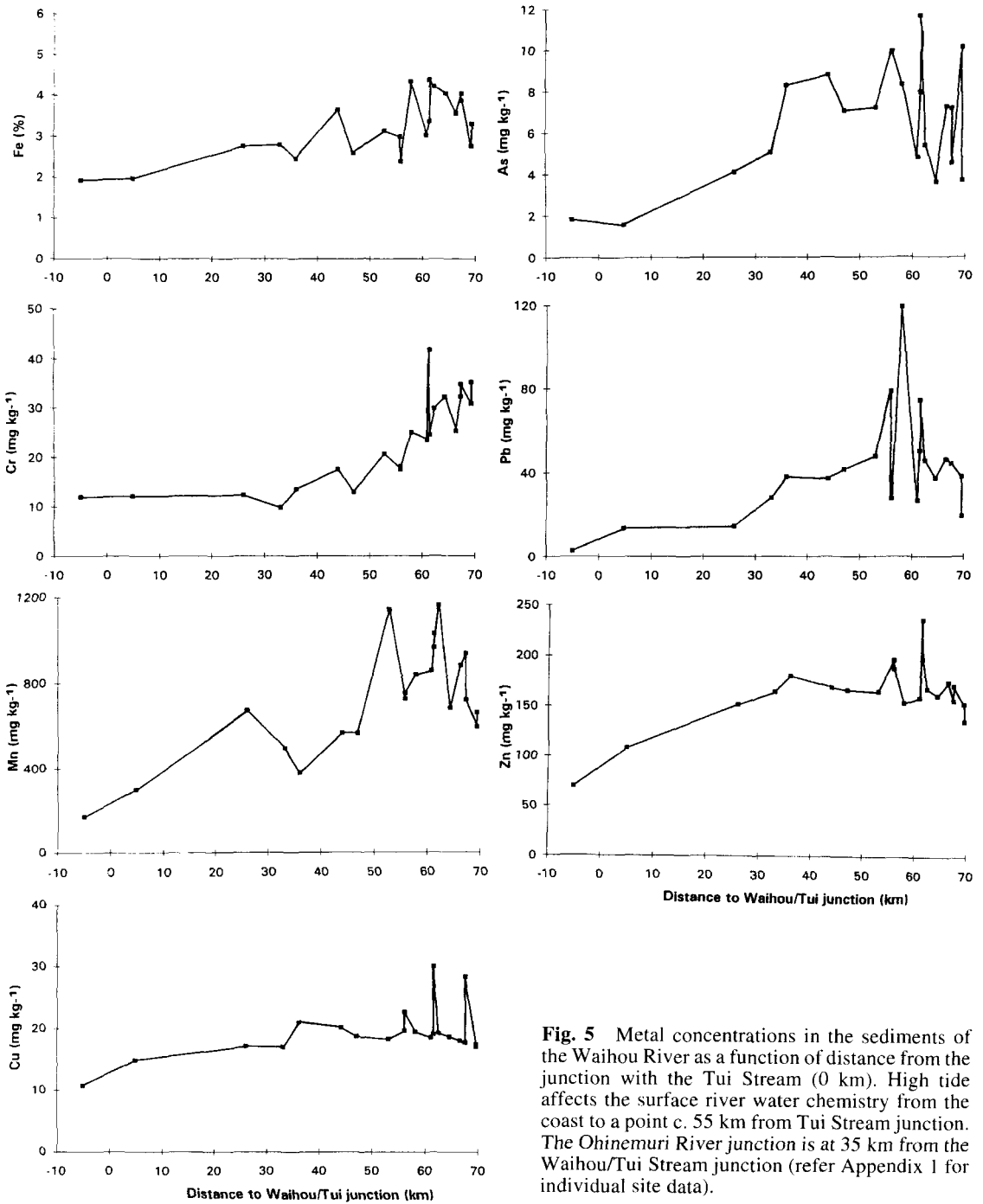
To compare estuary and seawater sediment metal concentrations, sediment (and water) samples were collected from Tararu beach in the Firth of Thames (Site W27). Sea water at Site W27 contained very similar metal concentrations to estuarine waters at Site W24 (Table 1), which seemed unusual as some dilution of the metal-bearing estuarine waters in the coastal waters might have been expected. Likewise, sediment at Tararu Beach did have higher concentrations of Cu, Pb, Mn, and Zn than were typical for either the Waihou estuary (e.g., at Site W25 and W26) or the mouth of Coromandel Harbour (Leipe & Healy 1992). It is likely that these sediments, and perhaps waters, were contaminated by municipal effluent from the township of Tararu.

Concentrations of trace metals in Waihou and Ohinemuri River sediments were correlated with Fe and total organic carbon (TOC) concentrations. TOC concentrations ranged from 0.71 to 3.11% in sediments of the Waihou River. Correlation coefficients suggested a positive relationship for Fe/Cu, Fe/Pb, Fe/Zn, Fe/Mn, Fe/Cr, and Fe/TOC. Of these, Pb, Mn, and Cr show the greatest tendency towards a linear relationship with Fe. The apparent lack of correlation between As and Fe concentrations was surprising as it suggests that As behaves more independently of Fe than of the other trace metals.

In a previous analysis of suspended sediment in the lower Waihou River, Henshaw (1989) showed that the sediment comprised organic carbon (2.4–3.0%), Al (79–112 mg kg<sup>-1</sup>), Fe (4.2–4.5%), Zn (163 mg kg<sup>-1</sup>), and Pb (69 mg kg<sup>-1</sup>). These values for TOC, Pb, and Zn concentrations are similar to those of the bed sediment sampled from the tidal region of the river in this study.

### Core sediment chemistry

Four short (20 cm) cores were taken at Sites W4b, W10, W11, and W13 and analysed for Fe, Cu, Zn, and Pb at 5 cm depth intervals (Table 2). The cores taken at Sites W4b, W10, and W13 showed no significant trends for metal concentrations with depth, perhaps reflecting the long period of natural



**Fig. 5** Metal concentrations in the sediments of the Waihou River as a function of distance from the junction with the Tui Stream (0 km). High tide affects the surface river water chemistry from the coast to a point c. 55 km from Tui Stream junction. The Ohinemuri River junction is at 35 km from the Waihou/Tui Stream junction (refer Appendix 1 for individual site data).

and mining-related contamination of this catchment. However, in the core taken from Site W11b, Zn, Pb, and Cu concentrations were significantly lower at the base of the core (15–20 cm). It is not certain

if these lower levels represent a time before land clearance (and therefore increased erosion of mineralised ground) or mining activities, or if they are due to some other change in riverine or coastal

conditions. Detailed age dating and sedimentological studies would be required to establish the cause.

### Metal source

Metal/Cu ratios in sediments can be used to suggest possible metal sources in the Waihou catchment, on the basis that ratios in the Waihou sediments will reflect those of the tributary from which the sediments have been derived (Table 3). This assumes mainly conservative behaviour of the metals concerned; a reasonable assumption as long as waters of similar chemistry are compared (i.e., the lower regions of the tributaries and the fresh waters of the Waihou River). Metal contributions from tributaries other than the Ohinemuri River and Tui Stream appeared to be minor. In the Komata River (Site W8), for example, sediment metal concentrations were not significantly higher than those of the Waihou River sediments.

**Table 2** Trace metal concentrations (% for Fe; mg kg<sup>-1</sup> for Cu, Pb, Zn) in the < 85 µm fraction of core sediments in the Waihou River, at 5 cm depth intervals from the surface.

	Fe	Cu	Zn	Pb
Site W11b				
0–5cm	2.64	16.5	259	67.2
5–10	2.66	25.6	200	100.6
10–15	2.50	20.0	146	73.0
15–20	2.39	8.2	64.3	24.6
Site W13				
0–5cm	2.92	29.8	276	60.5
5–10	2.92	23.5	185	78.0
10–15	3.04	17.8	179	75.4
15–20	2.70	18.1	201	79.4

With the exception of Pb/Cu, metal/Cu ratios in the upper Waihou River (above the Ohinemuri River junction) did not change at the Tui Stream junction. Pb/Cu ratios down stream of this junction were higher than at Site W21, and closely resembled those of sediments in Tui Stream, identifying this stream as a source of Pb and Cu in the upper Waihou River. It has already been noted that the Ohinemuri River appears to contribute Pb, Zn, As, and Cu to the Waihou River (Fig. 5). The ratios of Pb and Zn to Cu in sediment immediately below the Ohinemuri River junction support the hypothesis that these metals are derived from the Ohinemuri Catchment. However, the ratio of As/Cu in sediments of the Waihou River were lower than in those of the Ohinemuri River, suggesting that As has perhaps been preferentially redissolved from the sediments in the Waihou River. Mn and Cr are clearly not derived from the Ohinemuri River nor from Tui Stream, as the Mn/Cu and Cr/Cu ratios in the Waihou River sediments were higher than in those of the tributaries, but similar to those of sediments in the upper Waihou River at Site W21.

### DISCUSSION

Trace metals are transported in both dissolved and particulate forms in the Waihou River catchment. The main chemical processes affecting metal transport will be therefore those influencing the stability of dissolved metal complex species; and of particulates or particulate surfaces and the metals bound to them. As there were no major redox changes noted in waters of the catchment and estuary, metal transfer into, and retention on sediment would have primarily resulted from adsorption rather than precipitation processes. Chemical conditions did not favour precipitation

**Table 3** Sediment metal/Cu ratios for the Waihou River, Tui Stream, and the Ohinemuri River.

Region	Pb/Cu	Zn/Cu	As/Cu	Mn/Cu	Cr/Cu
Waihou at W21	0.3	7	0.2	16	1.1
<i>Lower Tui Str. at W19</i>	0.8	14	0.1	6	0.4
Waihou at W1	0.9	7	0.1	20	0.8
Waihou at W2b	0.8	9	0.2	39	0.7
<i>Lower Ohinemuri R. at W9a</i>	2	10	1.6	13	0.4
Waihou at W3a	2	10	0.3	29	0.6
Waihou at W3b	2	9	0.4	18	0.6
Waihou at W4a	2	8	0.4	28	0.9
Waihou at W4b	2	9	0.4	29	0.7

of metal salts other than the oxides of iron and manganese. Even in the dam waters at the head of Tui Stream where metal concentrations were high, the high acidity ensured that the metals remained dissolved.

Typical adsorbing surfaces in a natural fresh water/sea water system include hydrous iron, aluminium and manganese oxides, organic substrates, and silicates such as clays. Henshaw (1989) noted that the capacity of the suspended Waihou River sediment to adsorb Zn was similar to that of aged hydrous Fe-oxide, and that Zn was at least partly associated with the "Fe-, Mn-oxides" fraction of the sediment. In the Waihou River catchment, sediments contained between 1.9%–43% non-silicate Fe, which was almost certainly present as amorphous iron oxide. Clays were also abundant and TOC concentrations were only slightly less than those of Fe, at 0.7–3.1%. Although metal bound to clays and organics in sediments and suspended sediments may have been desorbed during acid digestion, the components themselves would not have been dissolved. As an adsorbing surface Mn-oxide is less likely to be of importance as Mn concentrations in the sediment were low (< 6% of the Fe concentration).

The degree of metal adsorption can be modelled using surface complexation constants. In a natural system, such calculations must take account of competitive ion adsorption and dissolved metal complexing, as well as maintaining a mass balance of all ions and adsorbing surfaces. Although surface complexation data is often unavailable or inconsistent for many metal-surface reactions, Dzombak & Morel (1990) have compiled a database of adsorption onto hydrous iron oxide surfaces (HFO); the geochemical modelling program MINTEQA2 (Allison et al. 1991) uses these data to model metal adsorption using a diffuse layer adsorption model. MINTEQA2 simultaneously determines dissolved metal speciation and metal adsorption by treating adsorption as a surface complexing reaction which competes with other complexing reactions (e.g., the formation of metal-chloride or -carbonate complexes). In this way, MINTEQA2 allows for the effects of changing water chemistry on adsorption processes, particularly as it influences dissolved metal complexing and oxide surface charge.

Measured partitioning of trace metals between the dissolved and acid-soluble particulate phase in Waihou catchment waters (Table 1) has been compared to that predicted by MINTEQA2 for

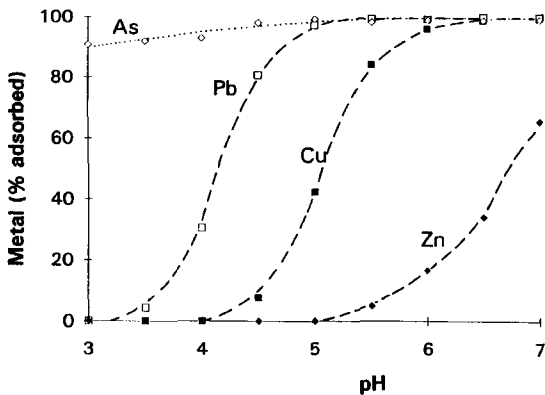


Fig. 6 MINTEQA2 modelled adsorption of Cu, Pb, Zn, and As from Tui tailings dam seepage (Site WOa), in the presence of abundant HFO (0.1 m), as pH is raised to that of Tui Stream.

these waters when HFO is the main adsorbent. Where consistent results were obtained, it was considered likely that:

- Fe in the "acid-soluble" particulate was present as HFO;
- HFO was the most active adsorbing surface in the suspended sediment;
- metal concentrations were regulated by adsorption onto HFO.

It should be noted that MINTEQA2 did not predict that Mn would adsorb onto HFO. The presence of Mn in the particulate phase (Table 1) is likely to result from precipitation of Mn-oxide as noted above. Also, MINTEQA2 does not include the facility to model Cr adsorption. No attempt has been made to calculate Cr adsorption using individual surface complexation constants, as an isolated calculation is misleading in this context.

#### Tui Stream

At Tui dam, trace metals were entirely dissolved, occurring as free metal ions or oxyanions (e.g., As) or as sulphate complexes. Although As might be expected to adsorb onto HFO under acid conditions, the tailings dam seepage was too acidic to precipitate or stabilise HFO. Down stream at Site W23, however, the pH had risen to 7.03 and dissolved Fe had clearly been precipitated as HFO. The concentrations of Cu, Pb, Zn, and As had been considerably lowered, with metals occurring in

both dissolved and particulate-bound states. The amount of dissolved metal removed by adsorption, or by precipitation, during mixing of the tailings dam seepage and Tui Stream can be estimated if the dilution factor is known. The concentrations of  $\text{SO}_4$ , Mn, and Zn can be used to estimate a dilution factor for dam seepage water in Tui Stream, assuming an upstream composition for Tui Stream similar to that of the Ohinemuri River. Mn and Zn were predominantly in dissolved form at both Sites W0a and W23, and were unlikely to have been removed from solution between these sites. Dilution factors ranged from 25 for  $\text{SO}_4$  to 30 for Zn and 34 for Mn. A similar comparison of Sites W0a and W23 concentrations for the remaining trace metals showed that 92–100% of the dissolved Fe, Pb, Cu, and As had been removed from the water column between Sites W0a and W23.

The predicted degree of metal adsorption from the tailings dam seepage onto excess HFO (as  $\text{Fe}(\text{OH})_3$ ), is shown in Fig. 6 as a function of pH between 3 and 7.03, the pH measured at Site W23. Under acid conditions the HFO surface charge is positive, adsorbing negatively charged metal ions and complexes, such as the arsenate and arsenite ions. Under neutral pH and more alkaline conditions, the surface charge becomes negative, the point of zero charge varying with solution and oxide characteristics. Metals existing in solution as positively charged ions and complexes such as Cu, Pb, and Zn are then adsorbed to different degrees. In the presence of abundant HFO and at pH = 7.03, As, Pb, and Cu would be fully adsorbed, and Zn 60% adsorbed from the dam seepage. However, once the tailings dam seepage had mixed with Tui stream, "abundant" HFO was no longer likely to be present. Modelling metal adsorption onto measured particulate Fe concentrations at Site W23, predicted that As would be fully adsorbed, Cu and Pb 20% adsorbed, and Zn entirely dissolved. Comparison with measured dissolved and particulate metal concentrations showed, that MINTEQA2 appears to underestimate the degree of adsorption for Pb and Cu. There are at least two possible reasons for this apparent discrepancy:

- there were additional adsorbing phases, possibly organics, in the suspended sediment from which metals were leached during sample acidification, or
- the HFO contained sufficient impurities to alter its adsorption properties. Amorphous Fe-oxides sampled at the tailings dam contained up to

11%  $\text{SO}_4$  (Webster et al. 1994), a composition which is typical of acid, mine-drainage Fe-oxide precipitates (e.g., Bigham et al. 1990).

Further down stream at Site W19, low particulate Fe concentrations suggest that suspended sediments have settled out in the slower flowing reaches of Tui Stream. Once again the degree Zn adsorption predicted by MINTEQA2 was consistent with measured acid soluble particulate concentrations, but Cu adsorption is underestimated.

#### *Ohinemuri River*

At Site W9b in the lower Ohinemuri River, Mn and Zn were again predominantly in dissolved form (Table 1), whereas Cu and As occurred in both dissolved and particulates states. Under conditions of pH = 7.85 and particulate Fe concentrations of  $40 \text{ mg kg}^{-1}$ , MINTEQA2 predicts that only 25% of the Cu, 8% of the Zn, and 44% of the As will be adsorbed onto suspended HFO. These predictions are broadly consistent with measured metal concentrations, although Cu adsorption is again somewhat underestimated. HFO is therefore likely to play an important role in regulating dissolved metal concentrations, and transporting trace metals in the Ohinemuri River.

#### *Waihou River*

Cu, Pb, and Zn were undetectable in the water of the upper Waihou River (Site W21). Only As concentrations could be compared with MINTEQA2 predictions, and this comparison showed consistency between measured and modelled As adsorption. In the Waihou River estuary, however, measurable metal concentrations occur in the muddy waters. When fresh water mixes with sea water the following processes may affect trace metal speciation:

- coagulation of suspended colloids which become more stable under conditions of higher ionic strength (Stumm & Morgan 1981), a process sometimes referred to as "salting out" of a colloid. Only the very fine colloidal material (clays, fine silt, and some organic matter) will be carried through an estuary into the sea;
- high ion concentrations in sea water affecting metal adsorption processes by altering surface properties or increasing/decreasing metal complexing;
- changes in pH and  $\text{dO}_2$  affecting metal chemistry. The pH of sea water is typically

slightly higher (c. 8.0) than that of freshwaters in the upper Waihou and Ohinemuri Rivers (pH = 6.9–7.2).

In the estuary down stream from Site W10, colloidal material carried in the Waihou River is visibly coagulated, "salted out" by the increasing salinity of the estuary. Although pH and HFO concentrations in the estuary were sufficiently high to encourage full adsorption of the trace metals from a fresh water, the high salinity of the estuarine waters can adversely affect metal adsorption. While sea water Cl concentrations do not appear to affect metal adsorption onto goethite (Balistrieri & Murray 1982), sea water Mg concentrations will suppress Pb, Zn, and Cd adsorption at high pH. On the other hand, sea water SO<sub>4</sub> concentrations enhance Cu and Pb adsorption (Balistrieri & Murray 1982). Sea water mixing should not, in this case, result in significant fluctuations in dO<sub>2</sub>, as no evidence was found of oxygen depleted conditions above the sediment water interface, even near the base of the estuary.

In the lower estuary at Site W24, Fe, Pb, and Zn are entirely, and Mn and Cu predominantly, bound to suspended particulates (Table 1). This is consistent with MINTEQA2 predictions for Pb and Cu adsorption onto suspended HFO, but Zn adsorption is underestimated, and As adsorption overestimated, to the same degree for both estuarine (Site W24) and sea waters (Site W27). Preliminary investigations suggest that the model maybe incorrectly compensating for the degree of Ca co-adsorption in these saline waters, and its secondary effect on As and Zn adsorption.

As the colloid settles into the estuary, trace metal concentrations increase in the bed sediment, as the proportion of fine, metal-rich, HFO-bearing particulate in the sediment increases. Metals released into the Waihou River are therefore mainly trapped within the estuary, and are likely to be removed only by physical transport of the sediment out of the estuary or perhaps by chemical leaching under more saline conditions as the sediment moves out into the Firth of Thames.

## CONCLUSIONS

In Tui Stream and the Ohinemuri River, trace metals are transported in the water column both as dissolved free metal ions or complexes, and as metals bound to suspended sediments. Zn and Mn are predominantly in dissolved form in these tributaries.

Cu, Pb, As, and Zn concentrations in the sediments of the Ohinemuri River and Tui Stream are higher than those of the Waihou River above its estuary. Although less contaminated, the Ohinemuri River is the main source of these metals in the lower Waihou River, contributing as it does a much greater volume of water and sediment than Tui Stream. Mn and Cr in the lower Waihou are not derived from the Ohinemuri River, nor from Tui Stream.

In the Waihou estuary, flocculation of the suspended particulate material leaves little dissolved Fe and Mn in solution. Pb and Zn are also predominantly, and Cu and As partially, adsorbed onto the flocculated sediment, which settles out in the slow-flowing estuary. The high proportion of fine, metal-rich sediment in the estuarine bed sediments results in high sediment metal concentrations in the Waihou River estuary.

Measured trace metal partitioning between dissolved and "acid-soluble" particulate states is generally consistent with MINTEQA2 modelled metal adsorption onto hydrous Fe-oxide in the suspended particulate. However, there are some discrepancies suggesting that some metals (particularly Cu) may also be bound to organic material and/or clays, and that MINTEQA2 may incorrectly model Zn and As adsorption from sea water.

## ACKNOWLEDGMENTS

This study was funded by a research grant from the Foundation for Research, Science and Technology (FRST). I would like to thank Dr Bruce Williamson for reviewing an early manuscript, Ms Kerry Webster, Dr Kevin Brown, Dr Mike Timperley, and Dr Catherine Butler for their field assistance, help and advice, and also Mr George Payne (NIWA), Ms Sue Courtenay (University of Auckland), staff of the Waikato Regional Council, and Dr Chris Hendy (University of Waikato).

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**APPENDIX** Metal concentrations ( $\text{mg kg}^{-1}$ ) in the  $< 85\mu\text{m}$  fraction of sediments in the Waihou River and its tributaries. Distance, distance from Waihou/Tui Junction (Tui Stream, Waihou River) or from Ohinemuri/Waihou Junction (Ohinemuri River).

	Fe (%)	Cu	Zn	Pb	Mn	Cr	As	Distance (km)
<b>Tui Stream</b>								
W 0a	43.9	455	496	1270	26.9	8.98	558	-4
W 0a-2	36.5	263	341	641	25.8	15.5	154	-4
W 0b	40.1	159	457	746	31.4	6.64	314	-4
W 23	8.63	725	6870	652	5357	53.8	49.3	-3
W 20	7.72	756	9070	601	1840	40.9	16.9	-2.5
W 19	3.80	69.1	970	53.9	399	29.3	5.97	-1.5
<b>Waihou River</b>								
W 21	1.92	10.7	69.7	2.68	172	11.9	1.83	-5
W 1	1.96	14.9	108	13.4	298	12.1	1.58	4.5
W 2b	2.75	17.2	152	14.3	671	12.3	4.10	26
W 3a	2.78	17.1	165	28.1	495	9.78	5.06	33
W 3b	2.44	21.1	181	38.3	378	13.5	8.29	36
W 4a	3.65	20.3	170	37.4	565	17.5	8.80	44
W 4b	2.58	18.9	167	41.8	564	12.9	7.04	47.5
W 5a	3.13	18.4	166	48.2	1140	20.6	7.20	53
W 5b	2.99	19.8	198	79.2	724	17.5	9.90	56
W 10	2.38	22.9	189	27.7	751	18.1	9.95	56
W 16	4.35	19.6	155	120	838	24.9	8.33	58
W 11a	3.03	18.7	160	26.7	856	23.4	4.82	61
W 11b	3.37	19.2	238	50.8	1030	41.7	7.96	61.5
W 6a	4.39	30.2	199	74.8	965	24.4	11.7	61.5
W 11c	4.23	19.4	169	46.1	1162	29.8	5.39	62.5
W 12	4.05	18.8	162	37.6	680	32.1	3.62	64.5
W 6b	3.57	18.2	176	46.7	882	25.2	7.25	66.5
W 7	4.06	17.9	157	44.7	938	32.2	7.18	67.5
W 13	3.88	28.6	172	44.8	720	34.7	4.53	67.5
W 25	2.76	17.3	154	38.5	594	30.8	10.17	69.5
W 26	3.31	17.6	137	19.5	660	35.1	3.70	69.5
W 27	5.27	237	1478	91.1	1751	37.5	9.63	
<b>Ohinemuri River</b>								
W 18	4.72	28.4	163	60.7	228	14.6	64.0	-25
W 9b	3.71	32.4	283	49.9	380	15.2	47.4	-17
W 9a	2.39	37.4	363	84.8	483	13.5	62.0	-1.5
<b>Other tributaries</b>								
W 8	3.57	25.6	69.5	4.88	714	38.4	6.43	
W 17	3.47	17.5	148	39.1	966	25.5	10.0	
W 15	4.32	16.1	135	32.3	1080	26.7	6.88	
W 14	4.29	18.6	166	41.2	783	32.5	6.08	