Heavy metals and gold in waters, sediments and aquatic vegetation from the Hauraki Goldfields area of New Zealand

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ABSTRACT

The Hauraki Goldfields area and the distribution of the heavy metals and gold from this goldfield area are reviewed.

The current environmental impact of base metal mining at the Tui Mine, Te Aroha and gold mining near Waihi, was investigated by analysis of local waters, stream sediments, and aquatic vegetation.

Analysis of waters from the Tui and Tunakohoia Streams showed concentrations of arsenic, cadmium, lead and zinc above recommended levels for potable water in the upper parts of these waterways. The discharge of these streams into the Waihou River (sampled upstream from Te Aroha and downstream to past Paeroa) did not have any significant effect on heavy-metal concentrations in this river.

Aquatic macrophytes sampled in the Waihou, Ohinemuri and Waitekauri Rivers had very high heavy-metal concentrations compared with the ambient water and should be considered as potentially useful for assessing the impact of low-metal fluxes into the waters.

Gold was determined in sediments from the Ohinemuri and Waitekauri Rivers along with other heavy metals derived from sulphide mineralisation at Waihi and Waitekauri.

Gold was detected in aquatic macrophytes from streams draining both the Martha Mine at Waihi and the Golden Cross Mine at Waitekauri and indicated the possibility of prospecting for gold by analysis of these plants.

X-ray diffraction analysis of heavy metal fractions in stream sediments showed the presence of pyrite in the upper reaches of the Tunakohoia and Tui Streams that drain the mineralised reefs and Tui tailings dam. Relatively immobile lead (galena) was

retained close to the source, whereas copper and zinc minerals were more mobile and distributed further downstream from the areas of mineralisation.

The relative mobilities of gold, copper, cadmium, lead and zinc from the Tui tailing dam (a serious environmental concern) were assessed by elution of these metals from columns containing 600 g of tailing, eluted with water, ammonium thiocyanate or ammonium thiosulphate. These elutions were carried out with, or with out, amendments. When eluted with water, the heavy metals showed a mobility sequence in the order copper>cadmium>zinc>lead>gold. After elution with 0.2% ammonium thiocyanate, there was a reduced mobility of zinc, copper and cadmium compared with the water elution and increased mobility of gold, Ammonium thiocyanate is specific in solubilising gold. Lead showed enhanced mobility, perhaps due to formation of the soluble complex ion $Pb(CNS)_4^{2-}$. Mobility for zinc was enhanced by ammonium thiosulphate.

A laboratory investigation on foam flotation was undertaken on gold, zinc, copper, lead, and cadmium in waters. A range of variables involved at their separation from dilute solutions by batch foam flotation technique was studied.

I have recently developed a method of adsorbing colloid flotation in order to concentrate gold from natural waters into a very small volume of foam prior to quantification by GFAAS.

Adsorbing colloid flotation (ACF) is a separation technique with distinct advantages for removing trace elements from natural and industrial waters. These advantages are: rapid processing, simple design, small volume of final solution, low residual concentration, flexibility of operation, and moderate cost. In this method, the substance to be removed (e.g. metal ions) is adsorbed on colloidal particles or coprecipitated on a floc produced by the addition of a flocculating agent. A surfactant is then added to adsorb on the particle or floc thus rendering it hydrophobic. The metal-loaded particle is then removed by further adsorption at the surface of rising bubbles in a flotation system. Experiments were carried out by use of a 52 mm diameter, 620 mm long glass column using a glass frit of pore size 20-40 μm for bubble generation. Cetyltrimethylammonium bromide (CTAB) a cationic surfactant, and thiourea (a complexing agent) were used either individually or in combination for removal of gold. The heavy metals included (Zn, Cu, Cd, and Pb) removed by dodecyl sulfate-Na salt (NaDS) and sodium oleate(NaO). The electrolyte tolerance of adsorbing colloid flotation of heavy metals ions (Pb^{2+}, and Cd^{2+}) from waste water was improved significantly by use of the $Fe(OH)_3$ and NaLS (sodium laurylsulfate) system for lead removal or $Al(OH)_3$ and HTMABr (hexadecyltrimethylammonium bromide) system for cadmium removal. Extraction of the gold into the foam layer was strongly dependent on the pH of the feed for which pH 11 was optimum. Adding 10 mg/L of thiourea to an equal volume of CTAB instead of CTAB alone, increased the extraction of gold to a dramatic degree. A distribution coefficient (K_d) of 46,000 was achieved under optimum conditions. The percentage extraction reached >99%. The method was applied to a number of natural waters draining gold mines and the Tui base metal mine in the Hauraki Goldfields region. Gold values reflected the presence of mineralization in the stream and river samples. It was concluded that the method may have some use in hydrogeochemical prospecting for gold.

Examples are given for the laboratory separation by foam flotation techniques of gold, zinc, copper, lead, and cadmium ions from a solution . Different technological variables that affect the process were investigated, such as concentration level, pretreatment required, pH effect, etc.

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LIST OF ABBREVIATIONS

FAAS	Flame atomic absorption spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
HGAAS	Hydride generation atomic absorption spectrometry
ICP-AES	Inductively-coupled plasma emission spectrometry
MIBK	Methylisobutyl ketone
SPT	Sodium polytungstate
ppm	Parts per million (mg per litre of solution or mg per kg of solid)
ppb	Parts per billion (μg per litre of solution or μg per kg of solid)
XRD	X-ray diffraction

Surfactant Abbreviation Key

Cationic surfactants

HTMABr	Hexadecyltrimethylammonium bromide
CTAB	Cetyltrimethylammonium bromide

Anionic surfactants

NaDS	Sodium dodecylsulfate
NaLS	Sodium laurylsulfate
NaO	Sodium oleate

SAMPLING SITES

Tunakohoia Stream (Tk).

Tk1: 70 m above adit (unmineralised water).

Tk2: Effluent from top adit.

Tk3: Just above waterfall 50m below Tk2.

Tk4: 5 m above ford (1st above gate on road to TV station).

Tk5: Top of small waterfall where domain track meets the stream.

Tk6 : Small side stream on NE side of stream with visible ochre contamination.

Tk7: Waterfall stream 100 m above confluence with Tunakohoia stream (20 m above water intake.

Tk8: In Tunakohoia Stream immediately above the confluence with the waterfall stream (70 m below Tk7).

Tk9: Ford at Domain (top of Hamilton Street.)

Tk9a: At Rata street.

Tk!0: Bridge by main Rood.

Tk11: At confluence with Waihou River.

Tui Stream (Tui)

Tui1 : At treatment plant above diversion.

Tui2 : At treatment plant below diversion.

Tui3 : Below dam, still water in sediment trap.

Tui4 : Below dam under drain exit.

Tui5 : Below dam, seepage above weir.

Tui6 : Branch on track to first sample site below dam accessed from road.

Tui7 : At end of first track below dam.

Tui8 : Just below houses on sharp bend and near road.

Tui9 : 500 m down from Tui 8.

Tui10: At ford just above golf course.

Tui11: Top third of golf course.

Tui12: At main road.

Tui13: Confluence with Waihou River.

Waihou River (Wa)

Wa1: At bridge to Mace Road

Wa2: At Te Aroha Bridge.

Wa3: 100 m downstream from Tk11

Wa4: End of Tui Pa Road.

Wa5: Turohia.

Wa6: Hubbard Road north of Paeroa

Wa7: 100 m downstream from Tui13 confluence.

Ohinemuri (Oh) and Waitekauri (Wk) Rivers from near Waihi to near Paeroa.

Oh1	0 Km at the start (170 m from the Pump house).
Oh2	7 Km from Oh1 on Ohinemuri River.
Wk3	Waitekauri River a few metres above the confluence with the Ohinemuri River.
Qh4	500 metres downstream from the Ohinemuri River confluence with the Waitekauri River.
Oh5	2.5 km from Oh4.
Oh6	2.8 km from Oh5.
Oh7	4 km from Oh6.

CHAPTER 1

1.1 GENERAL INTRODUCTION

The Hauraki Goldfield is located in the Coromandel Peninsula- Hauraki region east of Auckland City. It contains some 47 separate gold-silver deposits (Brathwaite, 1981) spread over 200 km from north to south oriented belt from Great Barrier Island to Te Puke (Fig. 1).

The greatest concentration of precious metal deposits in New Zealand is in the Hauraki Goldfield in the Coromandel Region. The main centres of mining were at Waihi, Thames, Karangahake and Coromandel (Williams, 1965). Gold was discovered in 1852 at Coromandel, and up until the cessation of large scale mining at Waihi in 1952, the Hauraki Goldfield produced 1.40 million kg of gold-silver bullion with estimated average gold: silver ratio of about 1: 4. More than 80% of this production was from one mining centre, Waihi (1.1 million kg), although other centres such as Karangahake (127 000 kg), Thames (72 500 kg), Komata (17 000 kg), Golden cross (13 000) and Coromandel (12 000 kg) were also notable producers (Fig. 1). Deposits at Maratoto and Tui were mined on a small scale from the late 1960s until 1973 and 1974 respectively, the Tui mine primarily for zinc, lead and copper (Christie & Brathwaite, 1986).

The Tui base-metal mine site near Te Aroha, New Zealand (Fig. 2) provides a graphic example of the potential hazards that are associated with many metalliferous and coal-mining operations. Major mining operations were commenced at the site during the 1960's at a time when legislation in New Zealand governing mining was antiquated and primarily aimed at the promotion of such activities rather than at environmental protection (Fyson, 1991).

The Tui Base-Metal Mine, Te Aroha is one of the most severely metal-polluted environments in New Zealand as a result of mining activities carried out some 25 years ago. During this period some 160 000 tonnes of ore were extracted from a network of un-

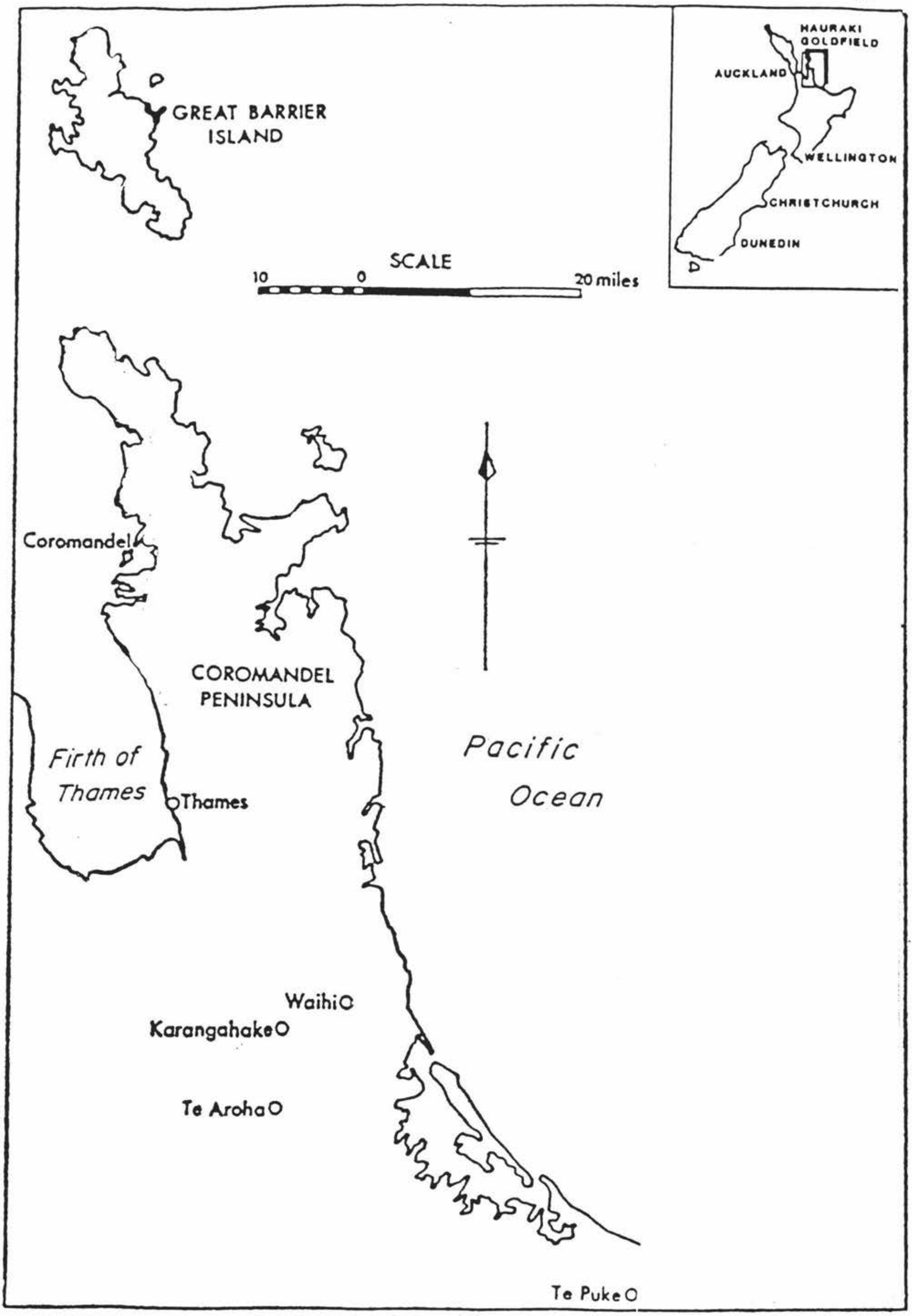


Figure 1 . Hauraki Goldfield.

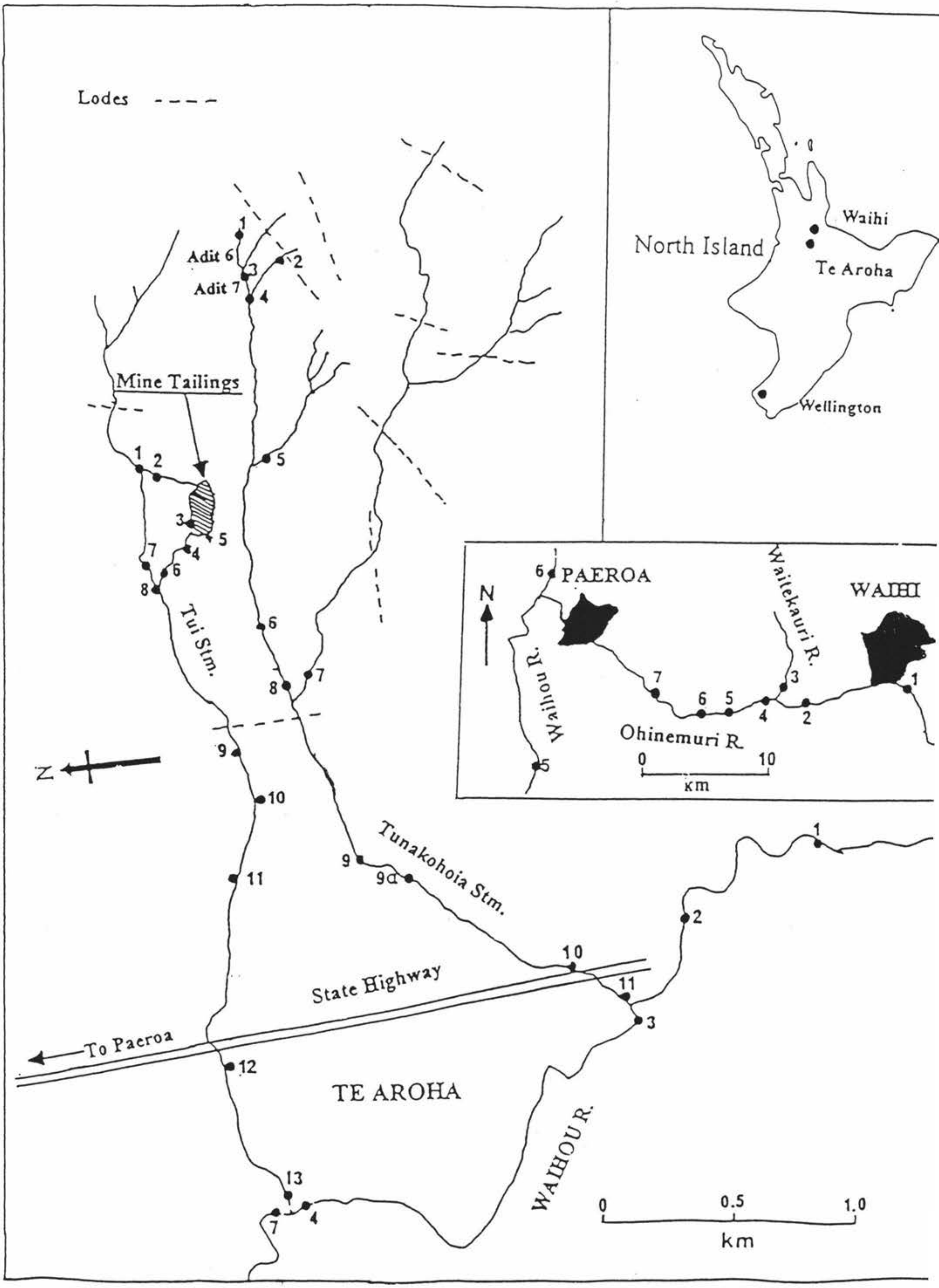


Figure 2. Map of the Te Aroha and Waihi regions showing streams and rivers sampled.

derground shafts and adits. and the deposition of 100 000 tonnes of tailings. The mine was closed in 1974 after base-metal prices fell to uneconomic levels (McGrath, 1973).

Drainage waters from the Tui mine have pH values as low as 2.6 and are heavily contaminated with metals such as Zn, Cu, Pb, Cd, and the two potential biotoxins, mercury and arsenic. Pollution problems arising from the above mining activities have been summarised by Morrell et al. (1995) and Morrell (1997), who have shown that most of the environmental degradation has been due to post-mining oxidation of remnant sulphide minerals in the mine tailings. Sulphide oxidation has not only acidified the tailings but thereby prevented vegetation from colonising the tailings dam. Acidic leachates have largely contributed to an environment inhospitable to plant growth. Some 8 years after cessation of mining, no plants have been able to establish themselves on the surface of tailings. It has also resulted in the degradation of surface and ground water via the generation of severe acid mine drainage (AMD). Acidic leachates from the mine tailings pond and highly polluted drainage from old mine shafts have seriously polluted the Tui and north Tunakohoia Streams, which were once used for the township water supply. The low pH engendered by this AMD has mobilised several toxic heavy metals that have found their way from the tailings into the local streams, waters and sediments. Heavy metals in the local waters have been reported by Livingstone (1987) , Pang (1992, 1995) and by Tay (1982).

The orebodies and enclosing host rocks have had a long history of scientific documentation (e.g., Park, 1893, 1910; Henderson & Bartrum, 1913; Cochrane, 1969; Weissberg & Wodzicki, 1970; Wodzicki & Weissberg, 1970) and have provided a fertile collecting ground for amateur mineralogists whose discoveries have added extensively to the known record. Although there have been numerous reports on the geology of the Tui Mine, there have been fewer publications dealing with the environmental impact of the mine site. One of the earliest of these was by Ward et al. (1976) who reported elevated concentrations of cadmium, copper, lead and zinc in soils, stream sediments and natural vegetation in the vicinity of the mine. A year later, Ward et al. (1977) reported elevated concentrations of copper, lead and zinc in soils and various pasture species growing in a field downslope from the tailings dam.

An MSc thesis by Tay (1980) investigated the environmental impact of heavy metal drainage from the Tui Mine and serves as a useful yardstick to gauge the current level of contamination reported in this study, compared with levels nearly 20 years ago. One of the latest detailed reports on AMD from the Tui tailings dam is the PhD thesis by Morrell (1997). The Tui Mine is a graphic example of a base metal mine that was very poorly managed in terms of environmental impact.

Specific objectives of the study presented in this thesis were the examination of the current levels of heavy-metal contamination of local waters, sediments and plants as a result of AMD from the Tui Base Mine and from Adits 6 & 7 (Fig. 2). A more limited survey was performed along the nearby Waitekauri and Ohinemuri Rivers that drain the abandoned Golden Cross Gold Mine at Waitekauri and the large opencast Martha Gold Mine at Waihi, respectively. The aim of this associated study was to establish the degree to which gold could be determined in the waters, sediments and plants in the Hauraki Goldfield area.

An additional facet of both studies was the analysis of aquatic plants to determine the presence of elements in waters at concentrations too low for conventional analytical methods. It is well known that aquatic macrophytes can concentrate trace elements from the ambient water to an extraordinary degree (Outridge and Noller, 1991) and we sought to determine the extent to which this enrichment could be used to detect the influence of heavy metal contamination from the Tui Mine, even when greatly diluted in the high-volume Waihou River. We were also interested in discovering whether metal enrichment by aquatic macrophytes would apply in the case of gold and perhaps serve as a biogeochemical method of prospecting for this element.

The Tui mine is a huge mat of finely-ground tailings derived from foam flotation separation of the mineral ore some 25 years ago. Because of the lack of clay minerals to act as a binder, the Tui tailings are very vulnerable to erosion. An engineering study conducted in 1974 suggests that "*there is an adequate factor against an overall failure of the tailing dam*". Its structural integrity was considered to be dependent on the tailings remaining largely unsaturated (Tonkin & Taylor, 1974).

The 'differential' flotation process used at the Tui mine site produced two concentrates, a zinc and cadmium concentrate, a lead and copper concentrate which also contained gold and silver (Norpac Mining Limited, undated). Waste water produced from the ore processing was first decanted and then discharged "into a stream [the Tui Stream] specified by the local Borough Council" (Norpac Mining Limited, undated). During the initial stages of the mine's development, the tailings were contained by a 5 m clay seal. This seal is situated beneath the front (western) face of the dam and is now covered by over 7 m of tailings (Tonkin & Taylor, 1974). Past reclamation efforts have been made attempting to reclaim the Tui mine site or to remedy the impact of AMD and metal-contaminated mine drainage, on ground and stream water. This has been summarised by Morrell (1997).

This thesis reports two studies. The first was on the Tui tailings, whereby the relative mobilities of Au, Cu, Cd, Pb and Zn from the Tui tailings dam (a serious environmental concern) were assessed by leaching the tailings (columns containing 600 g of material) with water, ammonium thiosulphate and ammonium thiocyanate for a total of 8 days, with and without, limestone amendments of 0.5, 1.0, and 1.5 % .

The second study was on the river and stream waters and involved the selective removal of gold and heavy-metal (Zn, Cu, Pb, and Cd) from these waters by using adsorbing colloid flotation (batch foam flotation) technique. The flotation methods were used at the laboratory scale for a specific volume of samples. I recently developed a system of adsorbing colloid flotation (Sabti et al. 1999) in order to concentrate gold into a very small volume of foam prior to quantification by GFAAS for a specific volume of the natural waters draining gold at very low concentrations and base-metal mineralisation in the Hauraki Goldfields region.

The main parameters affecting the flotation process were examined. These included reagent (collector, frother, flocculent, etc), feed concentration, pH values of the solution, ionic strength, and gas flow rate. Gold and the heavy-metal values reflected the presence of mineralisation in the stream and river samples. The method may have some use in hydrogeochemical prospecting for gold, and /or heavy metals.

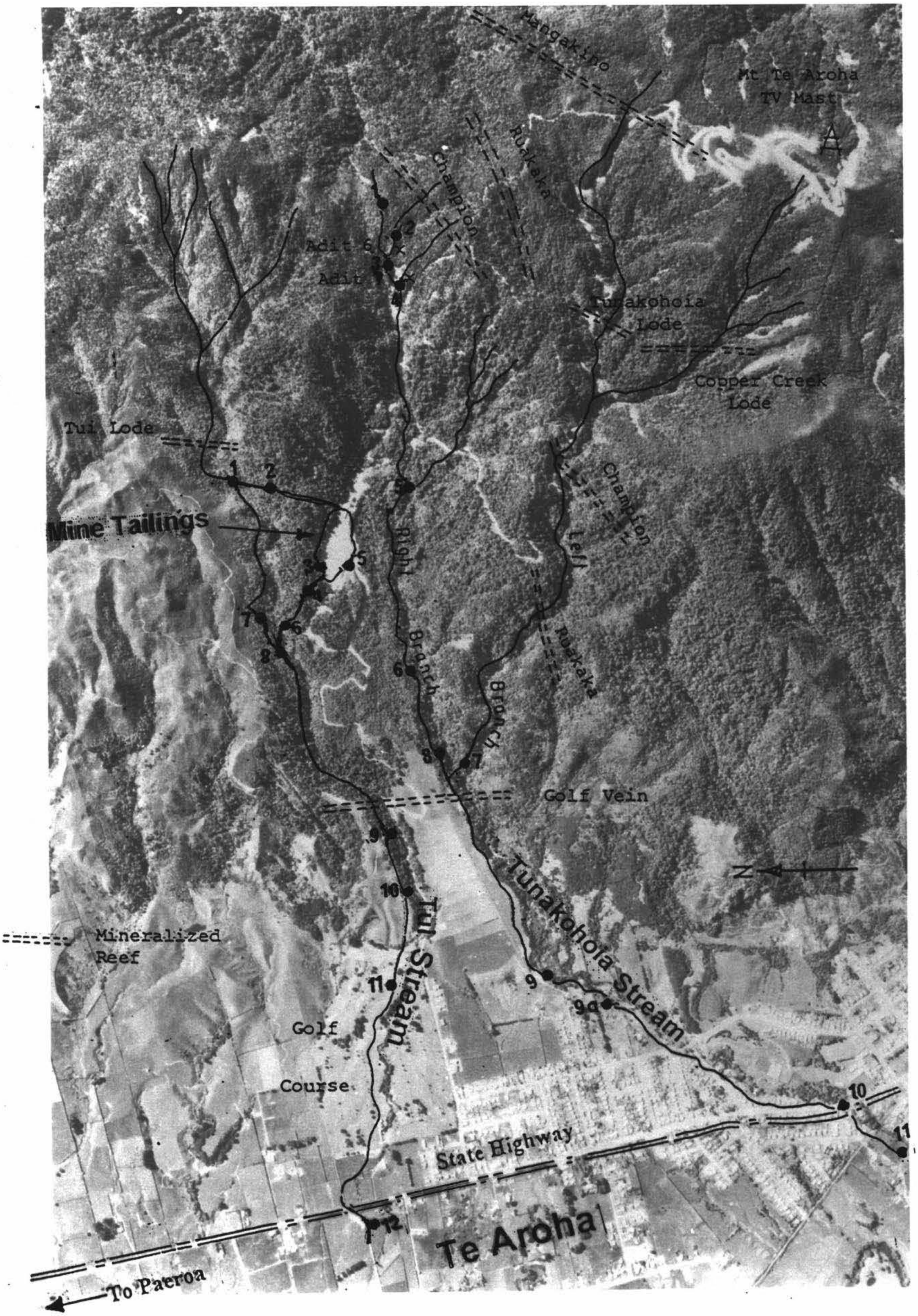
1.2 METHODS AND MATERIALS

All samples were collected from the Tui and Tunakohoia streams draining the Tui Mine and its environs. Samples were also collected along the Waihou River, into which these streams drain, and along the Ohinemuri River which drains the Martha Gold Mine at Waihi and joins the Waihou River near Paeroa (see Fig. 2 and Fig. 3 the aerial photograph, for collection sites).

Samples of water (1 L) were collected in polythene bottles and stored at 4°C. Mechanical devices such as Niskin, Nansen and Van dorn samplers (Reeves & Brooks, 1978) are required especially for sampling waters at different depths in the rivers, lakes and the ocean. However, for surficial waters in the Tui Mine drainage, it was sufficient to immerse the pretreated plastic bottles into the water and rinse several times with the sample water before it was finally collected. Analysis was carried out no later than two weeks after collection.

Sediments were collected with a sediment collector which consisted of a steel box ca 150×150×150 mm with a rope attached. This was thrown into the water from which sediments were intended to be collected. In the Tui stream, the sediments consisted largely of colloidal materials. In the Tunakohoia drainage, sampling of active sediments was made impossible by the rugged terrain and turbulent flow of the discharge.

Figure 3. Aerial photograph of the Te Aroha region showing Tui and Tunakohoia Streams sampled.


Mangakino
Mt Te Aroha
TV Mast
Champion
Ruakaka
Adit 6
Adit
1
2
3
4
Tunakohoia
Lode
Copper Creek
Lode
Tui Lode
1
2
Mine Tailings
3
4
5
5
7
6
8
Right
Branch
6
Champion
Left
Branch
Ruakaka
8
7
Golf Vein
9
10
N
Tui Stream
Tunakohoia Stream
Mineralized
Reef
11
9
9a
Golf
Course
10
11
State Highway
12
Te Aroha
To Paeroa
0
0.5
1.0
m

The fine sediments were often located only in small pockets situated behind sheltered rocks, especially along the right branch of the Tunakohoia Stream. The sediments were stored in sealed polythene bags for transport to the laboratory. Sediment samples were placed on blotting paper and left to dry for at least three weeks, lightly crushed, and sieved to mesh sizes 1-0.5 mm and <0.5 mm. Subsamples (0.5 g) were digested with 5 mL of aqua regia (1:3 nitric and hydrochloric acids) and evaporated in heating block at ca 300°C to low volume until most of the sample had dissolved. The sample volumes were then adjusted to 10 mL with deionised water, and the concentrations of arsenic, cadmium, copper, lead, mercury and zinc determined by either flame atomic absorption spectrometry (FAAS) or by graphite furnace AAS (GFAAS) using GBC instruments. Arsenic and mercury were determined either by GFAAS or by hydride generation AAS (HGAAS). The development of a hydride generation apparatus for such determinations was described by Robinson (1994).

Gold was determined by adding approximately 10 mL of aqua regia to 1 g of ground sediment sample in 50 mL Erlenmeyer flask and heating in heating block to 300°C until all the liquid volume had been reduced to ca.1 mL. After cooling, the volume was adjusted to 50 mL by (2 M) hydrochloric acid. Then 5 mL of this sample was shaken with 2 mL of methylisobutyl ketone (MIBK) and the gold determined in the organic layer by GFAAS.

Samples of aquatic plants were collected from the Waihou, Ohinemuri, and Waitekauri Rivers using a small boat anchor attached to a long line. The samples were all collected on the same day in February 1999 in order to avoid differences in metal loadings due to variations in water flow. The plants were wrapped in polythene bags upon return to the laboratory, the plant were washed by RO water. Species collected were: *Egeria densa* Planchon, *Elodea canadensis* Michaux, *Myriophyllum aquaticum* (Veil. Conc.) Verde, and *Potamogeton crispus* L. Samples were air dried and ground in a mill and the powder stored in polythene bags. Approximately 0.2 g of plant material was weighed into a 50 mL Erlenmeyer flask and 10 mL of concentrated HNO_3 was added. The samples were heated in heating blocks to ca 200°C until all the sample had dissolved. After cooling, the residues were adjusted to 10 mL with deionised water. The solutions were analysed by

FAAS and / or GFAAS as above.

To prepare the plants for gold determination, the plant material was first dried and ignited at 500°C in a test tube. This yielded an ash, or bio-ore approximately 1/15 the weight of the initial dry biomass with a gold concentration 15 times higher (Anderson et al. 1999). The ash was transferred into a conical flask, and 5 mL of aqua regia was added to the flask. After digestion on hot plate until ca. 1 mL remained, 5 mL of 2 M hydrochloric acid was added. The sample was transferred to a polythene tube and adjusted to ca. 8 mL with RO water. The volume was adjusted to 10 mL by addition of 2 mL of pre-equilibrated MIBK, and the tube capped and shaken, so that gold was selectively concentrated in a small volume of organic solvent. Only the gold would be soluble in the organic phase and hence would be separated out from the acid. The organic layer was transferred to a GFAAS cup for analysis.

The mobility of heavy metals with various solvents was tested by placing 600 g of fresh Tui tailings in 12 vertical columns, the bottoms of which were secured with a fine mesh cloth. Three columns had 0% lime , 3 had 0.5% lime, 3 had 1% lime, and the last 3 columns contained 1.5% lime. A glass beaker was placed underneath each column to collect the samples. Initially 150 mL of eluent was added to saturate the columns and then each day 50 mL of fresh eluent (water, ammonium thiocyanate, or ammonium thiosulphate) was passed through the columns and the eluates stored for chemical analysis The procedure was repeated for 8 days. Chemical analysis was performed by ICP-ES, FAAS or by GFAAS for gold determination.

X-ray diffraction analysis was carried out on sieved sediment samples in order to identify the different mineral phases present in material from the Tui and Tunakohoia Streams. The sediment samples were separated into light density (<2.8) and heavy density (>2.8) fractions using sodium polytungstate. The separated sediment samples were run as acetone slurrles mounted on glass slides and examined by a Phillips 4 kVa PW1710 X-ray diffraction instrument with a PW 1050/80 goniometer operated at 40 kV and 60 mA.