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-

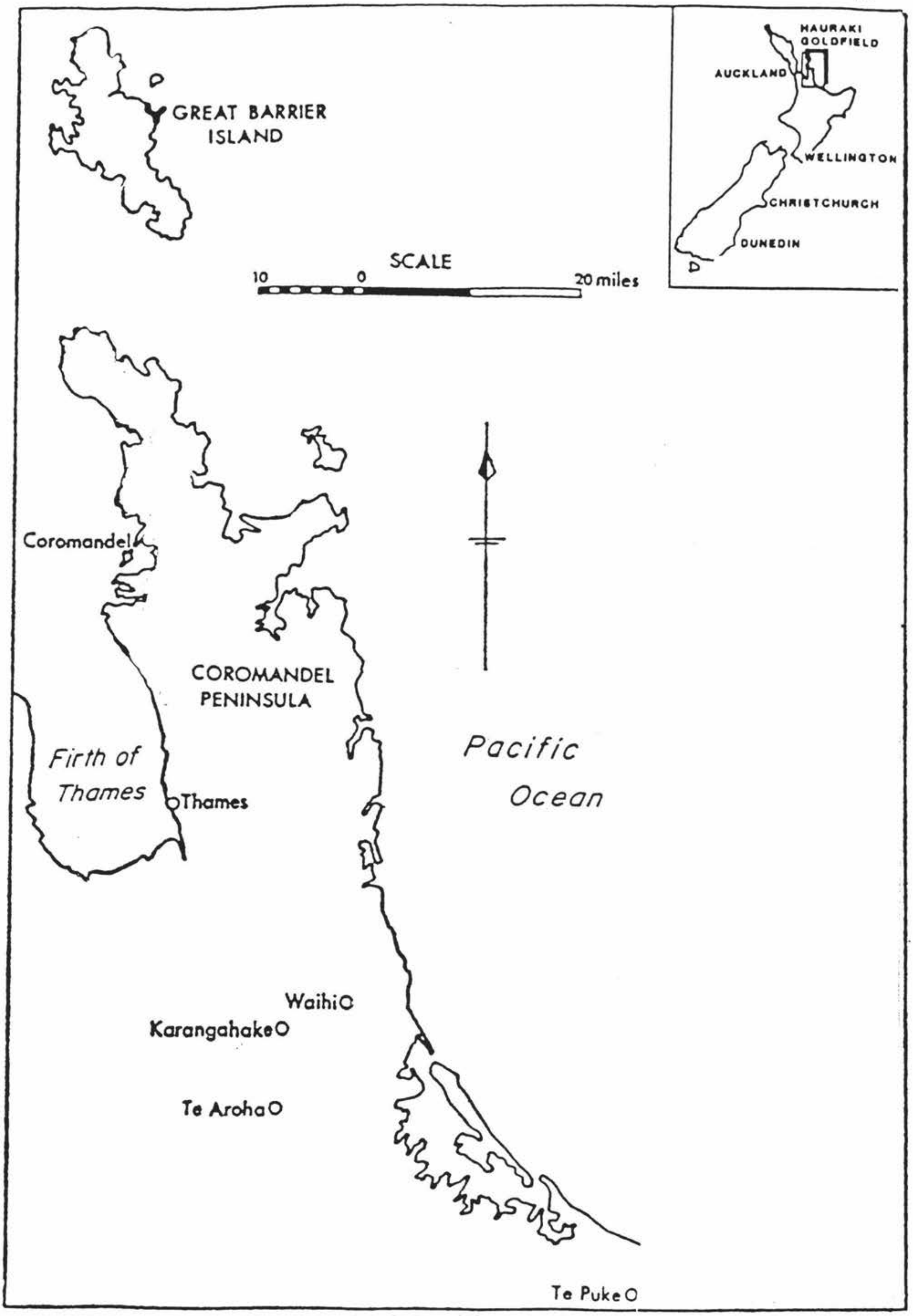

Figure 1 . Hauraki Goldfield.

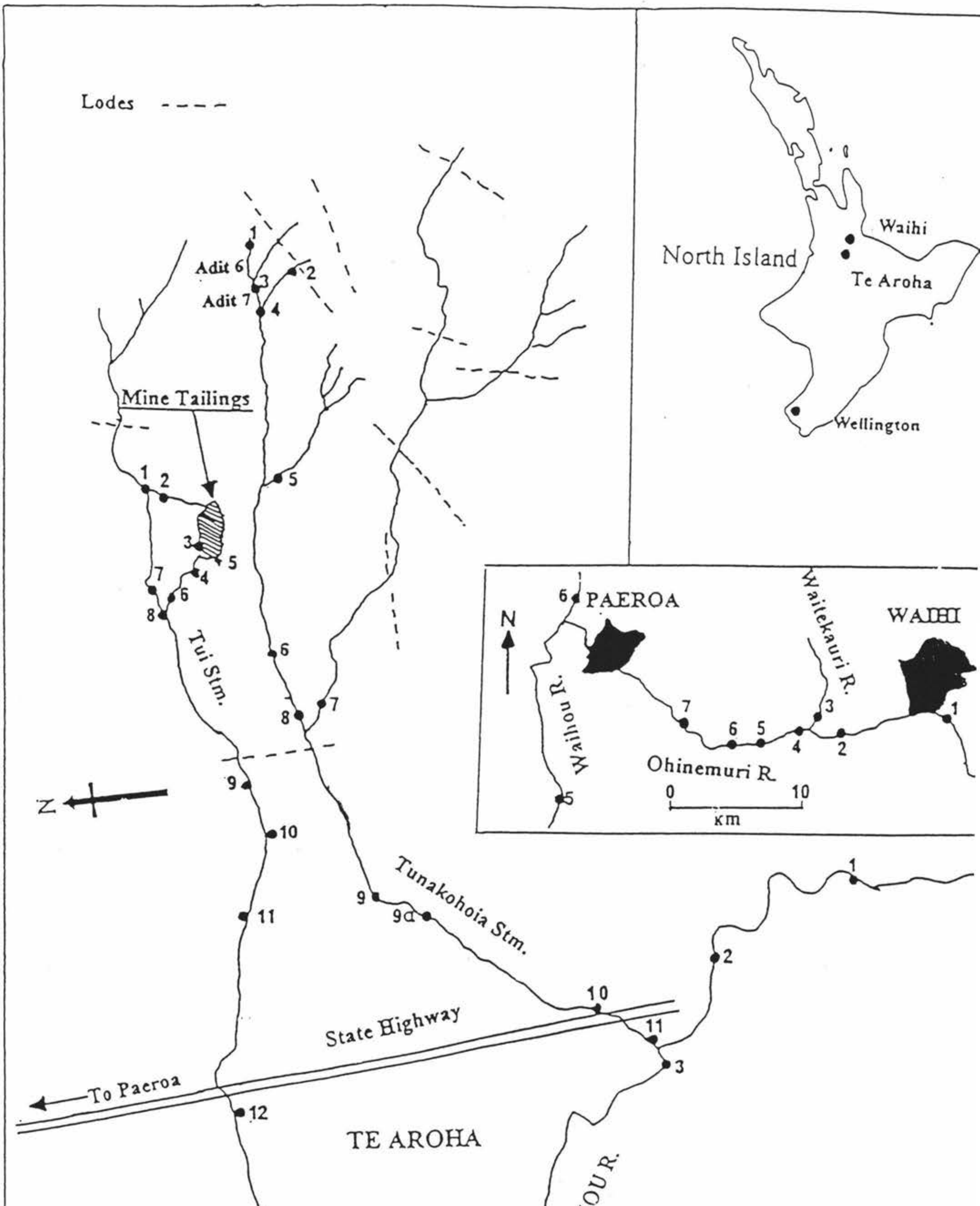

Figure 2. Map of the Te Aroha and Waihi regions showing streams and rivers sampled.

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
Tunakohoia
Lode
Copper Creek
Lode
Tui Lode
Mine Tailings
Right
Branch
Left
Branch
Champion
Ruakaka
Golf Vein
Mineralized
Reef
Tui Stream
Tunakohoia Stream
Golf
Course
State Highway
Te Aroha
To Paeroa
N
1
2
3
4
5
6
7
8
9
9a
10
11
12
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.

CHAPTER 2

2.1 LOCATION AND GEOLOGY

The Hauraki Goldfield is located in the Coromandel Peninsula - Hauraki region east of Auckland (Fig. 1). It is approximately 200 km from north to south, and up to 40 km wide, extending from Great Barrier Island in the north down to Te puke and Te Aroha in the south-west (Brathwaite et al., 1987). The region hosts two dominant types of mineralisation, disseminated 'porphyry' type and 'epithermal ' vein type (Livingston, 1987). Although both kinds of mineralisation originate from hydrothermal activity, most of the economic deposits in the region (including the Tui Mine) are epithermal. This type of mineralisation is characterised by discrete, well-defined deposits that often produce high-grade ore.

The rocks of the Coromandel-Kaimai region (Hauraki Volcanic Region) consist of a basement of Mesozoic age (= 140 million years old) greywacke sandstones, overlain by andesitic volcanic rocks of Miocene age (= 15 million years old). These in turn are overlain by younger (Pliocene, i.e., 3-5 million years) rhyolitic volcanic rocks(Christie & Brathwaite, 1986). The entire region has a tilt to the southeast, so that progressively older rocks are exposed westwards and northwards. Hence the basement greywackes are exposed in the north and west of the Coromandel Peninsula (Livingston, 1987). Limited K -Ar, fission track and palynological age data together with stratigraphic studies indicate that individual volcanic eruption episodes migrated southwards with time (Skinner, 1986; Christie & Brathwaite, 1986).

The igneous rocks of the Hauraki region were produced during the Miocene and Pleistocene by intrusive and volcanic activity occurring in a NNW trending continental margin arc. Cole & Lewis (1981) suggest that the Hauraki arc may have evolved into the presently active Taupo-Hikurangi subduction system. The change to rhyolitic volcanism that took place approximately 6 m.y. ago in the Hauraki Volcanic region is apparently related to tensional faulting in a marginal basin (Cole & Lewis, 1981). The Hauraki

Goldfield coincides with a continental margin volcanic zone (Coromandel Volcanic Zone) that consist of thin alternating beds of complexly folded Mesozoic greywackes and argillite, unconformably overlain by Miocene to early Quaternary subaerial, andesite-dacite-rhyolite volcanics and volcaniclastics (Brathwaite et al., 1987). Jurassic greywacke and argillites constitute the basement rocks of the whole region and have been folded approximately along the axis of the peninsula (Robinson, 1974). Extensive block faulting is evident in the form of normal faults within the basement rocks along NW to NNW and NE, ENE trends that gives rise to horst and graben structures (Brathwaite et al., 1987). The whole region has been tilted to the SE, exposing the Jurassic basement rocks in areas north of Thames (Hochstein & Nixon, 1979).

The overlying volcanic rocks, which range in composition from andesites to rhyolites with rare basalts, become progressively thicker and younger to the south where they merge with the Quaternary volcanic deposits of the Taupo Volcanic Zone (Wodzicki & Weissberg, 1970). In order of decreasing age, the more important volcanic units of the Hauraki Goldfield include; the Beesons Island Volcanics (dominantly andesitic Miocene rocks, ca.16 m.y.); the Whitianga Group and Minden Rhyolite (rhyolitic rocks of Pliocene age, ca. 3-5 m.y.) and the late Pliocene Omahia andesites (Adams et al., 1974). Far fewer vein deposits are found within the hydrothermally altered basement rocks and rhyolitic rocks of Pliocene age and mineralisation is absent in the Omahia andesites (Adams et al., 1974).

Immediately to the east of the Kaimai and Coromandel Ranges lies the Hauraki Depression, which is a large tectonic feature about 20-30 km wide and at least 220 km long. Hunua and Hapuakohe Ranges bound the Depression on the western and southern sides. Within the Hauraki Depression the basement greywacke rocks that form the surrounding ranges are overlain by Quaternary and Tertiary sediments with a combined thickness of up to 3 km (Hochstein & Nixon, 1979).

Based on the striking similarities of the Hauraki Depression to other well studied continental rifts, Hochstein & Nixon (1979) postulate that the southern part of the

Hauraki Depression is an active rift formed after the collision of the Indian and Pacific plates. Active faulting and shallow earthquake activity in the southern part of the depression support this theory.

The Tui Mine is located within the Hauraki Goldfield, situated at the southern end of the Coromandel Peninsula (Fig. 1) in the North Island of New Zealand. The Tui Mine is located approximately 3 km northeast of the township of Te Aroha (Fig. 2). The Mine and the tailings dam is situated on the NE flank of Mt. Te Aroha, a 960 m peak that towers above the Hauraki Plains and forms a part of the rugged Kaimai Ranges. The legacy of mining operation is a dam containing approximately 100 000 m^3 of tailings, which lies immediately below the site of old flotation plant, at approximately 350 m altitude (Plate 1). The Kaimai Range is dissected by many streams, including the Tui and Tunakohoia Sreams that flow down steep valleys adjacent to the Mine Site to their confluences with the Waihou River some 3.5 km distant (Morrell 1995).

Geological and structural mapping, at scales typically around 1:25 000, has been carried out by some surveys. Relatively cloud-free satellite imagery of the region became available in the late 1970's and provided a new tool for identifying large-scale structural features. Landsat images show some extensive lineaments, interpreted as faults, and a few large circular structures, which may represent eroded calderas (e.g. the Kapowai Caldera of Skinner, 1986). Regional magnetic and gravity data (e.g. Hunt & Syms, 1977) support these structural interpretations.

Several studies investigated the geology and mineralogy of the Tui deposits. Schofield, (1967); Cochrane (1969) , Weissberg & Wodzicki (1970), Wodzicki & Weissberg (1970), Adams *et al.*, (1974). Wodzicki and Weissberg (1970) have described the structural location of ore shoots within the Champion and Ruakaka lodes. Adams et al. (1974) reported whole-rock K-Ar ages of 17 m.y. for the Te Aroha andesites and ages of 2.5 to 7 m.y. that reflect the hydrothermal alteration. A useful review of the mine's early history and geology is included in Williams (1965). Research investigating the geology and

Plate 1. Acid Mine Drainage ponded below the Tui Tailings Dam.

mineralisation of the wider region includes that of Boyle (1979), Hochstein & Nixon, (1979), Brathwaite et al., (1987), and Christie & Robinson, (1992). Brathwaite & Christie (1996) have recently completed a geological report and map of the Waihi area, which summarise the region's stratigraphy, geological structure and economic geology.

The Tui Mine is found in country rocks of altered andesite with some breccia and tuffaceous material. Mineralogical and K/Ar dating studies have shown that the sulphide minerals were probably added to the lodes and surrounding rocks by hydrothermal solutions ascending along fissures and vein systems some 2.6 to 4.0 million years ago (Weissberg & Wodzicki, 1970; Adams et al. 1974). The major minerals of the lodes are quartz, sphalerite, galena, pyrite, kaolinite and chalcopyrite (Weissberg & Wodzicki, 1970; Robinson, 1974). Mercury and arsenic as cinnabar and arsenopyrite are also present and contribute to the biotoxicity of the AMD.

Schofield (1967) mapped the country rocks of the Tui Mine collectively as the Te Aroha andesites, a sub-unit of the Beesons Island Volcanics. In locations where the andesite is relatively unaltered, they consist of phenocrysts of plagioclase and hypersthene in a fine-grained crystalline ground mass with a pilotaxitic texture. The ground mass contains moderate quantities of microscopic quartz (Wodzicki & Weissberg, 1970).

The andesite is overlain by a 3m bed of fine-grained, moderately well layered tuff that has been so strongly hydrothermally altered that no primary minerals remain. Overlying the tuff is an 8 m bed of rhyolitic or dacitic ignimbrite. This deposits contains numerous fragments of argillite, volcanic rocks and flattened pumice, and again is highly altered (Wodzicki & Weissberg, 1970). Above the ignimbrite lies quartz bearing volcanic rock, thought to be a dacite or quartz andesite. To the south of the Ruakaka lode, a strongly altered quartz-bearing volcanic breccia probably of dacitic or quartz andesite origin, mantles the underlying units (Wodzicki & Weissberg, 1970).

2.2 MINERALOGY OF THE TUI ORE

The Tui Mine deposits are typical of the epithermal base-metal ore deposits that occur as lodes in fissures and faults in hydrothermally altered Tertiary andesitic and pyroclastic rocks (Boyle, 1979). The Tui Mine consists of two major mineralised quartz reefs (the Champion and Ruakaka) which are up to 2 m and 8 m in width respectively (Robinson, 1974). The reefs intersect in the upper levels of the mine but diverge at depth due to them dipping steeply in opposite directions. The average strike and dip of the Ruakaka and Champion reefs are N 80° E, 68° S and N 40° E, 64° NW respectively (Wodzicki & Weissberg, 1970). Surface outcropping of the reefs is extensive with the strikes of both reefs mapped for distances of over 500 m (Williams, 1965).

The reefs comprise a quartz-cemented wall-rock breccia containing a discontinuous zone of brecciated quartz cemented by sulphide minerals and a younger generation of quartz (Robinson, 1974). The minerals constituting these lodes were deposited in fault-controlled, open space filling-type environments in which fissures formed and remained open for sufficient lengths of time to enable the formation of coarse-grained sulphide minerals (Wodzicki & Weissberg, 1970). The ore at the Tui Mine is thus characterised by lenticular masses of sulphide minerals that are interspersed between barren portions of quartz and remnant andesite breccia (Robinson, 1974). The ore (defined as sulphide mineralisation with total Cu + Pb+ Zn greater than 5%) is generally coarse-grained, with 3 cm crystals of sphalerite and galena being common (Wodzicki & Weissberg, 1970).

The sulphide rich zone that forms the ore bodies varies in thickness from approximately 0.05 m to exceptionally greater than 0.9 m and has an average width in the vicinity of 0.5 m (Cochrane, 1969). The ore body in the Ruakaka lode is generally wider and more continuous than that of the Champion lode. Wodzicki & Weissberg (1970) suggest that this may be due to the Ruakaka lode's stronger normal faulting component and generally steeper dip. These factors are thought to have influenced the size and persistence of the fissures that were ultimately filled with epigenetic mineralisation (Wodzicki & Weissberge, 1970).

The Tui ore is essentially an aggregate of sphalerite (ZnS), galena (PbS), chalcopyrite ($CuFeS_2$) and pyrite (FeS_2) with subordinate marcasite (FeS_2) and tennantite ($(Cu,Fe)_{12}As_4S_{13}$) in quartz gangue (Williams, 1965). Appreciable amounts of tetrahedrite ($(Cu, Fe)_{12}Sb_4S_{13}$) and trace quantities of cinnabar (HgS) also occur in the ore (Wodzicki & Weissberg, 1970). Late stage alteration minerals include chalcocite (Cu_2S), covellite (CuS), anglesite ($PbSO_4$) and cerussite ($PbCO_3$), but these generally occur in minor quantities only (Cochrane, 1969). Sphalerite is the most abundant of the sulphide minerals in the deposits followed by galena, chalcopyrite and pyrite. Although pyrite is the most abundant sulphide, unlike the other sulphide minerals that are restricted to the lodes, pyrite is also found widely disseminated in the altered wall-rocks (Wodzicki & Weissberg, 1970). The ore yielded an approximate grade of 16.7% zinc, 7.0% lead and 0.62% copper in addition to significant quantities of gold and silver (Wodzicki & Weissberg, 1970 ; Robinson, 1974).

Quartz (SiO_2) is by far the most abundant gangue mineral in the lodes, however, well crystallised kaolinite ($Al_2Si_2O_5(OH)_4$) is also common throughout the ore body. Carbonate minerals are a minor component of the ore with only small quantities of calcite ($CaCO_3$) and siderite ($FeCO_3$) present (Cochrane, 1969). In all, over 70 different minerals have been identified in the ore and host rocks of the Tui Mine, making it one of New Zealand's *"most prolific mineral localities"* (Courtney et al. 1990).

Despite considerable variations in metal ratios within the different lodes, Wodzicki & Weissberg (1970) noted that textural relations between the minerals were remarkably constant, with both vein systems exhibiting the same minerals and paragenetic sequences. Mineralisation is believed to have occurred during two distinct phases. The first phase resulted in the formation of barren quartz veins varying in thickness from about 1.5 to 5 m. These quartz veins deposited along previously active fault planes and contained numerous angular shapes, highly altered wall rock inclusions. Renewed movement along the fault planes caused brecciation of the quartz and the rock wall inclusions, forming a porous zone containing numerous cavities. It was within this zone that the minerals of the second phase of mineralisation were deposited to ultimately form the Champion and Ruakaka lodes. Included in the minerals are galena, sphalerite, tennantite and cinnabar as well as at least two generations of quartz, pyrite and chalcopyrite (Wodzicki & Weissberg, 1970).

2.3 MINING HISTORY OF THE COROMANDEL REGION AND MINING AT TE AROHA.

Coromandel was the site of the first discovery of gold in New Zealand when, in 1852, Charles Ring, found a specimen of gold at Driving Creek, north of Coromandel Township. However, his find did not live up to its early promise, and Gabriel's Gully (Otago) became the first recognised goldfield, in 1861. It was not until the early 1870s that the Coromandel region became a major focus for gold exploration (Livingston,1987). Gold prospecting and mining followed kauri logging, and in the early days of gold mining, numerous small near-surface deposits yielded rich, and easily won, gold. Many of these had been formed by secondary enrichment of the gold by weathering and redeposition during prolonged erosion of gold-bearing quartz lode.

By 1880, most of these deposits were exhausted, and attention was increasingly focussed on the less widespread, but larger, lower-grade quartz-vein bodies. In 1894, the cyanide process was first used commercially in New Zealand at Karangahake. From the late 1890s to 1910, many larger vein deposits were actively worked, including those at Waihi, Karangahake, Owharoa, Waitekauri, Broken Hills, Thames, Kuaotunu and Coromandel. By the end of this period, all but the largest deposits had been exhausted of their comparatively readily won and higher-grade (i.e., profitably workable) ore, and were closed down. Of those remaining, the Waihi Mine continued in production until 1952, while others were worked until the early 1940s (e.g., Owharoa).

The closure of the Martha Mine at Waihi heralded a long hiatus in mining activity in the Hauraki region, and it was not until the late 1960s that any further mining took place. The Tui Mine at Te Aroha was redeveloped as a base-metal mine, producing 25 000 tonnes of zinc and lead-copper concentrates. Also of note at this time was a mining operation at Maratoto, were approximately 15 000 tonnes of quartz ore were extracted for silver concentrates.

The Tui mine was first opened in 1884 but the bulk of the mine's production occurred during the late 1960's and early 1970's. By the time the Mining Act (1971) was passed, considerable environmental damage had occurred at the Tui mine site and the scene was set for continued degradation (Morrell, 1997). The most promising of Te Aroha deposits was the Champion lode discovered by A. C. Cornes in 1884. The lode lay in *"inaccessible country near the Tui creek on the Karangahake Range"* (Salmon, 1963). The Champion Mine was set up at the site and after several name changes, this mine was to eventually become known as the Tui Mine. The lode was rich in Pb, and was originally mined with the intentions of supplying Pb flux for smelting gold ore from the Waiorongomai Valley, approximatelly 7 km to the west.

The mining operation at Tui was carried out underground and involved driving adits (horizontal drives) into the host rock. Upon interception of the quartz reefs hosting the sulphide ore, mining was redirected along the reefs, and high grade ore was selectively removed via adits which were developed on 5 levels and ranged in length from about 9 to 412 m (Carter & Pharo, 1965). The ore was transported from the mine adits to a flotation mill where it was first pulverised and then passed through flotation cells to physically concentrate the ore. The flotation process involved feeding finely ground ore into a series of separation tanks containing water and a variety of oil reagents. The oil reagents were formulated to selectively coat one or more sulphide mineral components of the ore. Aeration of the mixture resulted in the formation of a metal-bearing 'oil froth' at the surface of the tanks which was removed to yield the metal-concentrate (Blaiklock, 1981;

Brady & Humiston, 1982). The 'differential' flotation process used at the Tui mine site produced 2 concentrates, a zinc and cadmium concentrate and 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). Tailings from the mill are believed to have been deposited into the tailings dam as a thick slurry from a point source immediately beneath the flotation mill. During the initial stages of the mine's development, the tailings were contained by a 5 m clay barrier. This barrier is situated beneath the front (western) face of the dam and is now covered by over 7 m of tailings (Tonkin & Taylor, 1974). Thus the bulk of the tailings are, therefore, not structurally contained by a purpose-built retaining wall such as was constructed at the Waihi waste disposal site.

CHAPTER 3

THE CURRENT LEVEL OF HEAVY-METAL (Zn, Cu, Pb, Cd, Hg, AND As) CONTAMINATION AT THE TUI MINE, TE AROHA AND DETERMINATION OF GOLD FROM THE HAURAKI GOLDFIELD AREA.

3.1 Abstract

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

3.2 Introduction

The Tui Base-Metal Mine, Te Aroha (Fig. 2) 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 underground shafts and adits. The mine was closed in 1974 after base-metal prices fell to uneconomic levels (McGrath,1973).

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. Oxidation, particularly of pyrite (FeS_2) has led to acid mine drainage (AMD). The low pH engendered by this AMD has mobilised several toxic heavy metals such as arsenic, cadmium, copper, lead and zinc that have found their way from the tailings into the local streams, waters and sediments. Heavy metals in the local waters have also been reported by Livingstone (1987) and by Pang (1992, 1995).

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 my thesis, 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 aim of the work was to examine the current levels of heavy-metal contamination of local waters and sediments as a result of AMD from the Tui Mine. 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 determine the degree to which gold could be detected in the water and sediments in this river.

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 & 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.

3.3 Location and Geology

This account of the location and geology of The Tui Base Mine is based on a report by Morrell et al. (1995), as discussed in Chapter 2 (section 2.1).The site is situated in steep native bush some 3 km northeast of Te Aroha (Fig. 2). The mine comprises five levels of underground adits 500-700 m above sea level on the northwest flank of Mt. Te Aroha.

The Tui Mine is one of 47 epithermal gold-silver and base-metal deposits identified within the old Hauraki Goldfield (Robinson, 1974; Christie & Robinson, 1992). The mine occurs in country rocks consisting of hydrothermally altered andesite, with some breccia and tuffaceous material (Robinson, 1974). The volcanic rocks are of Miocene Age, and directly overlay Jurrassic greywackes of the Torlesse Supergroup (Brathwaite et al. 1987). They are grouped as the Te Aroha andesites which form part of the Beesons Island Volcanics (Robinson, 1974). The andesitic ricks of Mt. Te Aroha are separated from Quaternary alluvium of the Hauraki Rift that lies to the West, by the steeply dipping Hauraki fault (Cochrane, 1969; Hochstien & Nixon, 1979).

The two major lodes or mineralised reefs that make up the Tui Mine, are the Champion and the Ruakaka lodes. The steeply dipping lodes consist of a quartz-cemented breccia, within which is a younger, narrow zone of brecciated quartz cemented with sulphide and quartz (Weissberg & Wodziki, 1970).

Metal production from the Tui Mine during its short lifetime as shown in Chapter 2, section 2 amounted to 20,000 tonnes of copper-lead-zinc concentrate and 2.5 tonnes of gold-silver concentrate (Brathwaite et al. 1987). The ores averaged 17% zinc, 7% lead, and 0.6% copper, with the Champion lode providing about 28 g of gold and 36 g of silver for each tonne of ore (Wodzicki & Weissberg, 1970 ; Robinson, 1974).

3.4 Materials and Methods

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 for collection sites).

Samples of water (1L) were collected in polythene bottles and stored at 4°C. The sediment samples were dried and sieved to mesh sizes 1-0.5 mm and <0.5 mm and subsamples (0.5 g) were digested with 5 mL of aqua regia (1:3 nitric and hydrochloric acids) and evaporated to low volume. 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. Gold was determined by shaking the acid solution with a few mL of methylisobutyl ketone (MIBK) and then determining gold in the organic layer by GFAAS. Mercury was determined either by GFAAS or by hydride generation AAS (HGAAS).

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 December 1997 in order to avoid differences in metal loadings due to variations in water flows. Species collected were: *Egeria densa* Planchon, *Elodea canadensis* Michaux, *Myriophyllum aquaticum* (Veil. Conc.) Verde, and *Potamogeton crispus* L. Samples were air dried and subsamples digested with nitric acid and heated on a hotplate to low volume. The residues were then adjusted to 10 mL with deionised water. The solutions were analysed by FAAS and GFAAS as above.

3.5 Results and Discussion

All the heavy metal (As, Pb, Cu, Cd and Zn) concentrations in the sediments and waters in the Tui and Tunakohoia streams are summarised in Figs. 4 & 5 and are correlated with the New Zealand Ministry of Health standards for potable water (New Zealand Ministry of Health, 1995). The heavy metal (e.g. As, Zn, Cu) concentrations from the Waihou river in the sediments, waters and aquatic macrophytes (*Myriophyllum aquaticum*) are summarised in Fig. 6.

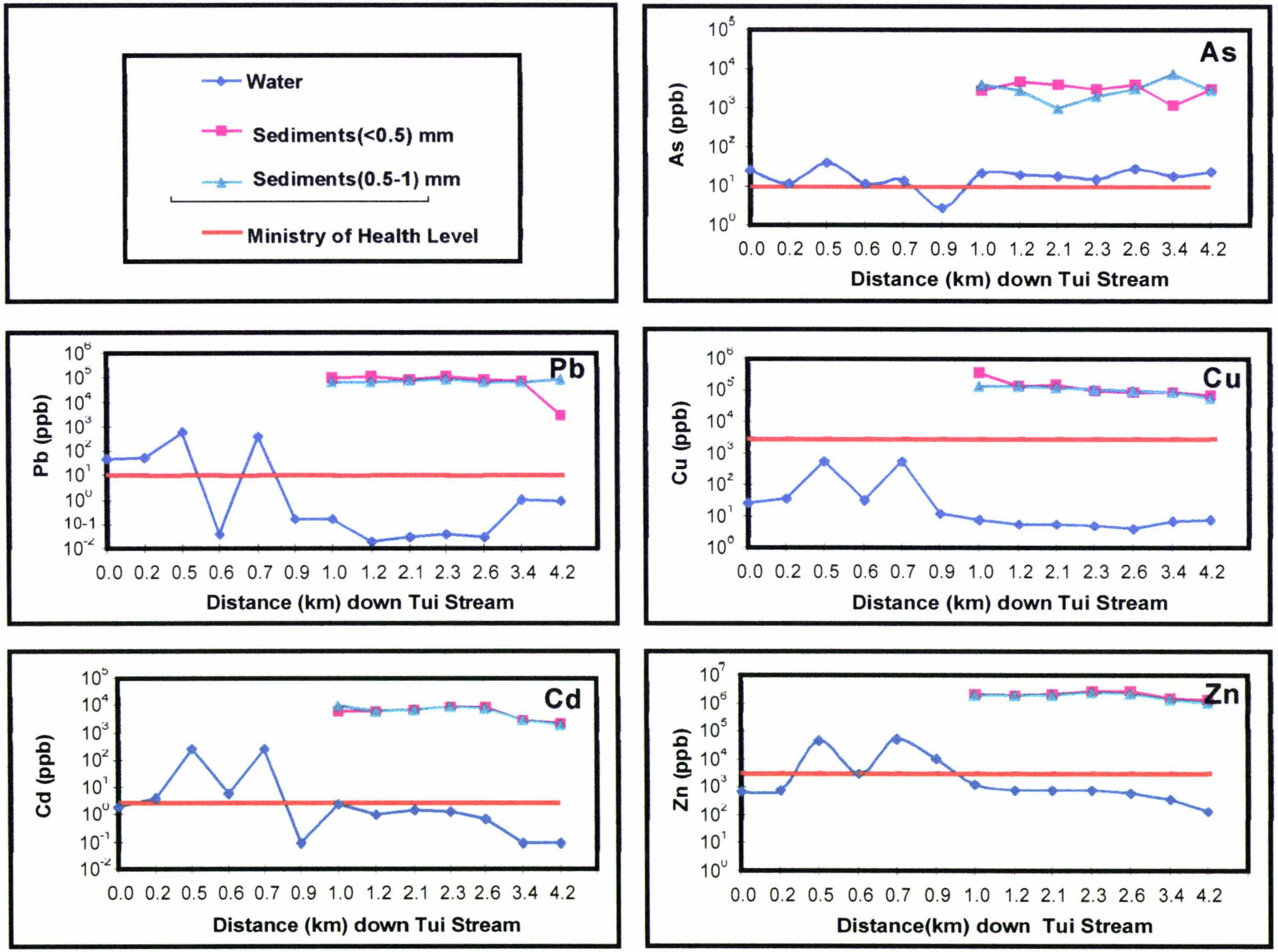

Figure 4 - Heavy-metal concentrations in sediment and water samples from the Tui Stream.

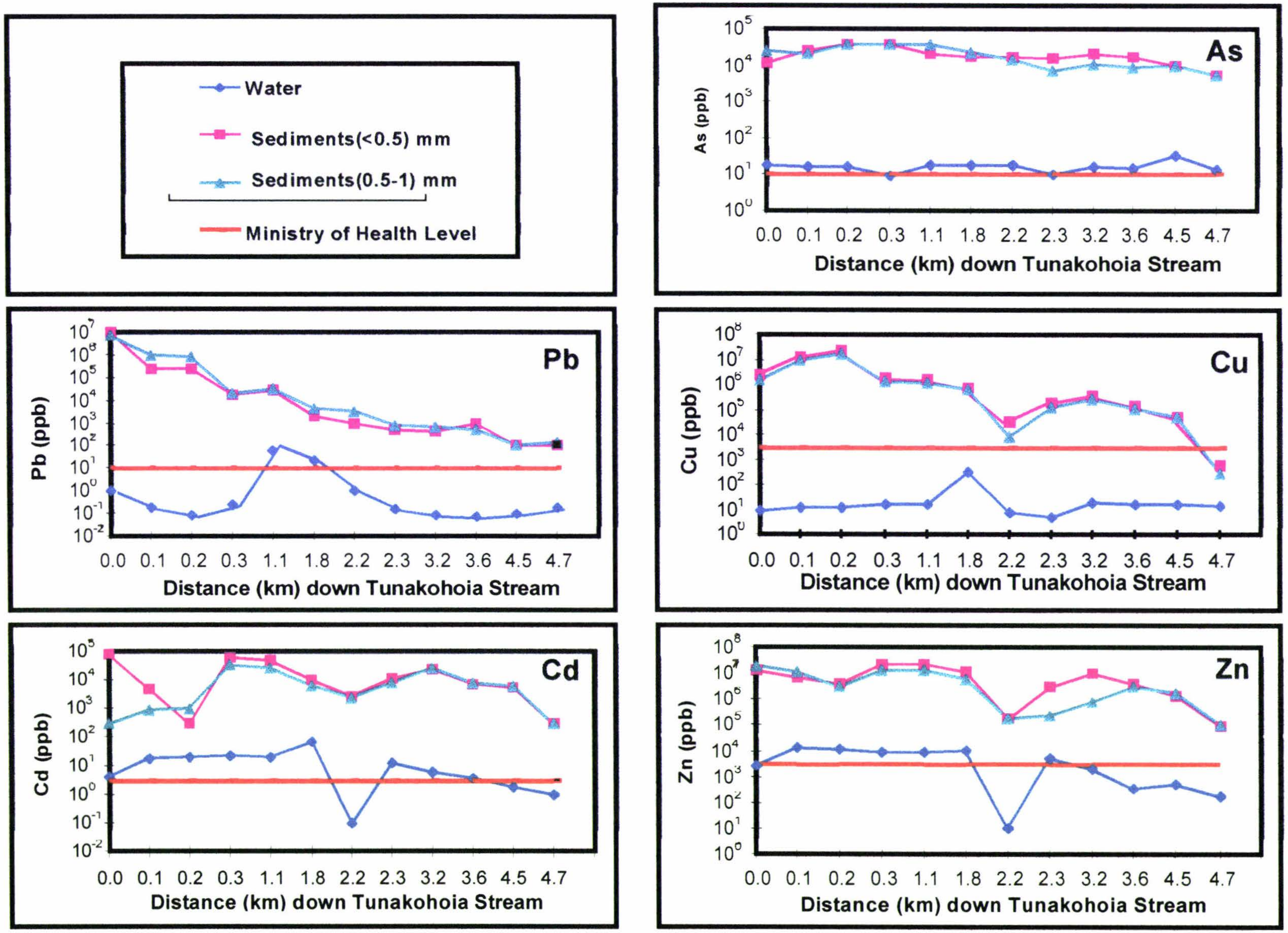

Figure 5 - Heavy-metal concentrations in sediment and water samples down the Tunakohoia Stream from adit 6.

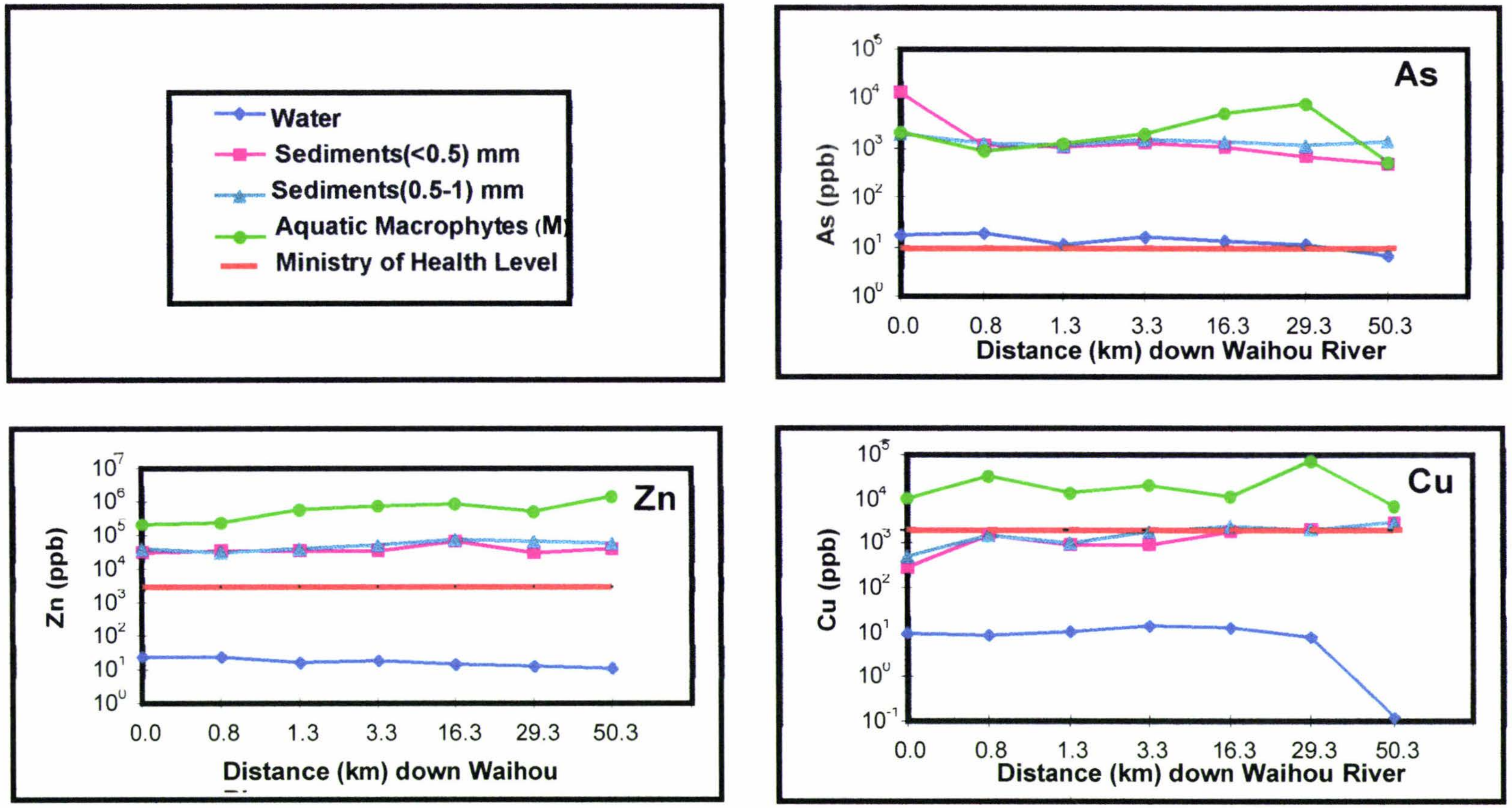

Figure 6. Heavy-metal concentration in sediments, plants and waters sampled from Waihou River, (M) = *Myriophyllum aquaticum.*

3.5 (a) Heavy metals in sediments

Elemental concentrations in sediments are shown in Figs. 7 &8. Maximum values in the Tui stream (Fig. 2) were found just below the mine tailings at sites 7 and 8 (see Fig. 1). Concentrations were always higher in the finer fractions (<0.5 mm) than in the coarser (1-0.5 mm) material. The highest values were in samples adjacent to, or just below, the Tui Mine tailings. Elemental concentration data are summarised in Table 1.

In the Tunakohoia Stream (Fig. 8), the highest values for heavy metals were found in the vicinity of the adits intersecting the Champion Reef (Tk1-4). At these sites, the highest values were: 2.14% Cu, 2.36% Zn, 65 mg/kg Cd, 0.94% Pb, 38 mg/kg As and 7.8 mg/kg Hg.

In the lower reaches of the Tui and Tunakohoia Streams (i.e. Tui10-13 and Tk12) the elemental concentrations in sediments were close to background. It is noteworthy, however, that the Tunakohoia Stream (once a source of water to Te Aroha), still has unacceptably high levels of heavy metals in the sediments (i.e. ten times background) as it entered the township at sites Tk9 and Tk10.

Correlation analysis of elemental concentration data for both sediment fractions is shown in Table 2 The data had been transformed logarithmically since all abundance data were originally lognormally distributed. Except for mercury, the other heavy metals arsenic, cadmium, copper, lead and zinc were very highly ($P<0.001$) mutually correlated between the two fraction sizes so that either fraction would have been diagnostic of the present level of pollution. Very highly significant interelemental correlations within the <0.5 mm size fraction were evident for copper vs. zinc, copper vs. cadmium, and cadmium vs. zinc. This was to be expected because of the strong geochemical association of these three chalcophile elements. Lead was, however, not strongly correlated with any element despite its high geochemical association with other chalcophile elements. This is a reflection of the much lower mobility of this element and it can be seen from Fig. 8 that in sediments from the Tunakohoia Stream, the lead concentration maximum is at site Tk1 whereas the maxima for copper and zinc occur further downstream at Tk3 and Tk4 respectively. Downstream from Tk3 there are no lead anomalies above 19 mg/kg, whereas for copper and zinc, anomalous values are found as far downstream as Tk11.

Concentrations of heavy metals and gold for the <0.5 mm fraction of sediments from the Ohinemuri River (see Fig.2 inset) are shown in Table 3. All heavy metal concentrations including gold, show anomalous values for all sediment samples at sites 1-5 and clearly reflect the influence of mining operations at the Martha Mine, Waihi, but as shown in Table 3, the concentrations for the heavy metals were much lower than in the Tui because the absence of large volume of finely ground tailings comparable to those in the Tui Mine, and the lower abundance of heavy metal sulphide in the extracted ore. It is noteworthy that a high gold value was found in sediments from the Waitekauri River draining the abandoned Golden Cross mine at Waitekauri situated upstream from this river's confluence with the Ohinemuri River, drain from natural sources.

Table 1. Summary of data for heavy metals concentrations (mg/kg) in <0.5 mm and 0.5-1.0 mm (in parentheses) size fractions of stream sediments from the Tui and Tunakohoia Streams and from the Waihou River.

	Cu	Zn	Cd	Pb	As
Tui Strm. (n=7)					
Arithmetic Mean	143 (107)	2171 (1894)	6.1 (6.6)	88 (75)	3.3 (3.6)
Median	96 (110)	2141 (1940)	6.3 (7.3)	95 (69)	3.3 (3.0)
Geometric Mean	123 (104)	2116 (1831)	5.5 (5.7)	82 (74)	3.2 (3.0)
Maximum (0.5 mm size)	363	2782	9.0	112	5.1
Minimum (0.5 mm size)	70	1447	2.4	29	1.2
Tunakohoia Strm. (n=8)					
Arithmetic Mean	3281 (2816)	6961 (5250)	22.2 (9.6)	1201(975)	18 (18)
Median	345 (183)	3766 (2428)	6.3 (4.2)	1.0 (2.5)	17 (12)
Geometric Mean	217 (139)	2342 (1694)	5.6 (3.1)	5.4 (7.0)	13 (13)
Maximum (0.5 mm size)	21,423	23,624	74	9352	38
Minimum (0.5 mm size)	0.6	87	<0.3	0.1	1.8
Waihou River (n=5)					
Arithmetic Mean	1.5 (2.0)	43.6 (53.9)	0.3 (<0.3)	4.0 (6.0)	3.4 (2.8)
Median	1.5 (1.8)	38.0 (56.0)	0.3 (<0.3)	4.0 (7.0)	1.2 (1.4)
Geometric Mean	2.8 (2.0)	41.9 (51.0)	0.3 (<0.3)	3.4 (4.5)	1.6 (1.7)
Maximum (0.5 mm size)	17	71	0.3	7.0	2.0
Minimum (0.5 mm size)	14	38	0.3	1.0	0.5

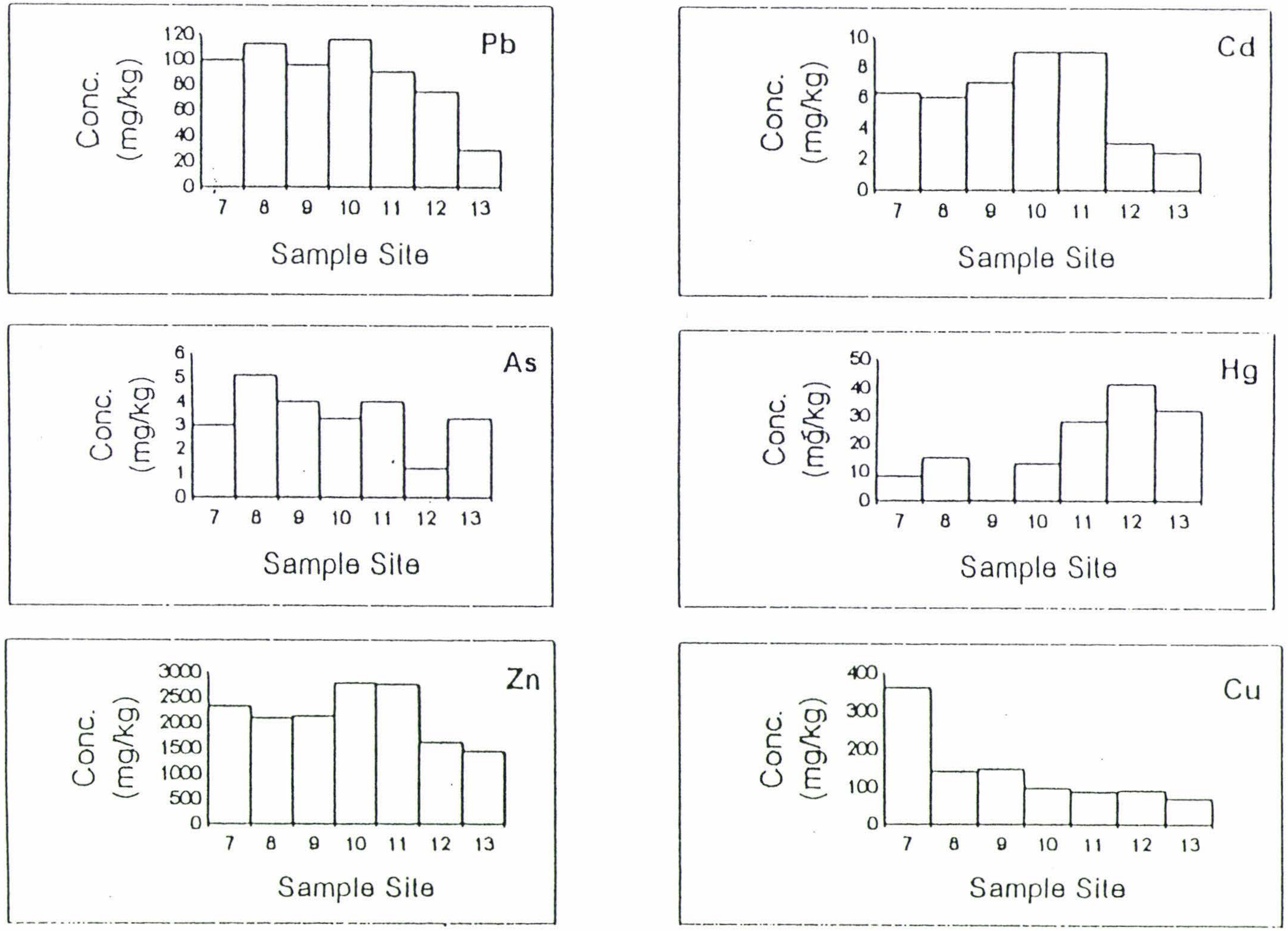

Figure 7. Heavy-metal concentrations in the <0.5 mm fraction of stream sediments sampled from the Tui Stream. See Fig. 2 & 3 for locations.

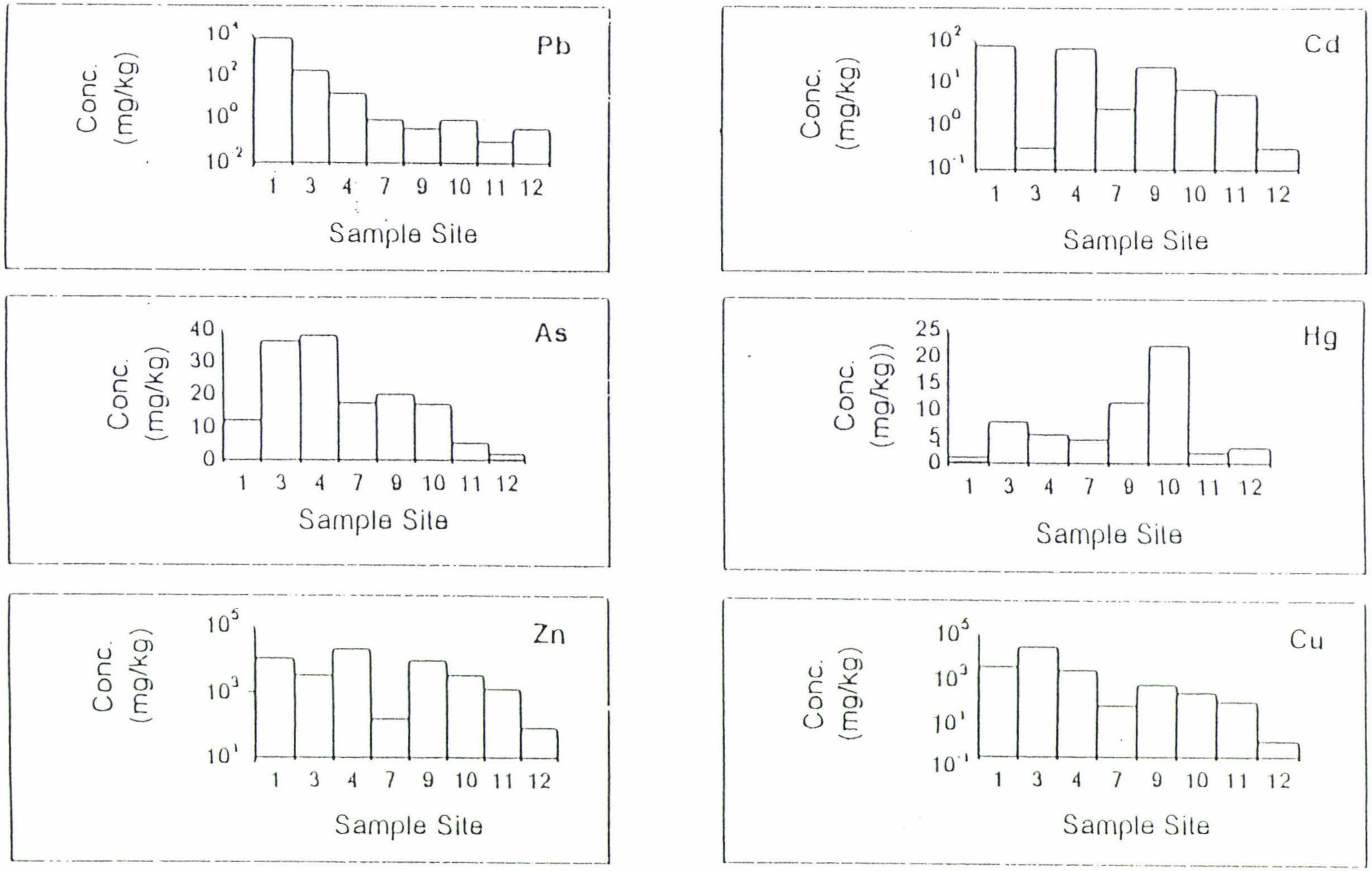

Figure 8. Heavy-metal concentrations in the <0.5 mm fraction of stream sediments sampled from the Tunakohoia Stream. See Fig. 2 & 3 for locations.

Table 2. Correlation analysis of elemental concentrations in <0.5 mm and 0.5-1.0 mm fractions of sediments from the Tui and Tunakohoia Streams and Waihou River. Asterisked headings refer to the 0.5-1.0 mm fraction.

	Cu	Zn	Cd	Pb	As	Cu*	Zn*	Cd*	Pb*
Zn	S**								
Cd	S**	S**							
Pb	S	NS	NS						
As	S*	S	NS	NS					
Cu*	S**	S**	S**	S*	S*				
Zn*	S**	S**	S**	S	S	S**			
Cd*	S*	S**	S**	NS	NS	S*	S**		
Pb*	S	NS	NS	S**	NS	S	NS	NS	
As*	S*	NS	NS	NS	S**	S*	NS	NS	NS

S** - very highly significant ($P<0.001$), S* - highly significant ($0.01>P>0.001$, S - significant ($0.05>P>0.01$), NS - not significant ($P>0.05$).

Table 3. Concentrations of heavy metals (mg/kg = ppm) and gold (µg/kg = ppb) in sediments (<0.5 mm fraction) from the Ohinemuri (Oh) and Waitekauri (Wk) Rivers near Waihi. See Fig.2 inset for locations.

Location	Au	Zn	Pb	Cu
Oh1	7	55	88	12
Oh2	163	61	32	5
Oh5	105	122	63	27
Oh6	n.d.	72	33	14
Oh7	n.d.	83	37	17
Wk3	39	125	8	24

n.d. - not determined.

3.5 (b) Heavy metals in waters

Heavy-metal concentrations in water are summarised in Table 4. The New Zealand Ministry of Health standards for potable water (New Zealand Ministry of Health, 1995) has set the following concentration limits (all in ng/mL = ppb): arsenic 10, cadmium 3 , copper 3000, lead 10, and zinc 3000.

Arsenic levels in both the Tui and Tunakohoia Streams were always somewhat above the recommended level but did not appear to have affected concentration levels in the Waihou River. Cadmium had localised high concentrations in the two streams only in the vicinity of the highly mineralised zones. Copper levels in both streams did not exceed the New Zealand health standards, even in the vicinity of the mineralised zones. Perhaps due to its insoluble nature, lead concentrations in both streams decreased rapidly to background (<1 ng/mL) within a short distance downstream from the mineralised areas. The great mobility of zinc was shown by a long dispersal pattern downstream from the mineralisation where anomalous concentrations extended as far as the confluences of the two streams with the Waihou River. A short distance downstream from the mineralisation, however, these anomalous concentrations were well below the New Zealand Ministry of Health standards.

Scientific interest in the quality at the Tui and Tunakohoia Streams stemmed largely from the fact that the streams formed an integral part of Te Aroha's town water supply between 1968 and 1979 (Fyson, 1991). Concentrations of Fe, Mn, and Cd in water collected from the former intake screen of the Tui Stream were found to exceed World Organisation (WHO) limits for drinking water by 56, 35, and 1.5 times respectively (Tay, 1980; World Health Organization, 1984a, 1984b). Although town water is no longer obtained from the Tui and Tunakohoia Streams, there is concern that shallow ground water used for domestic water supply in the tailing dam may be contaminated with heavy metals (Pang, 1995).

Several studies have been undertaken at the Tui mine site investigating various aspects of the site's hydrology and the impact of past mining activity on water quality (Tonkin & Taylor, 1974; Ward et al., 1976; Sabti et al.,1999; Tay, 1980; Pang, 1992). Research indicates that background concentrations of Cd, Cu, Pb, and Mn in ground and stream water in the vicinity of the mine site are naturally elevated due to base-metal mineralisation in the country rock (Pang, 1995). Even water taken from stretches of the Tui Stream not affected by mining and from the south branch of the Tunakohoia stream was found to contain concentrations of Cd and Pb exceeding WHO Guidelines for drinking water (Table 5).The mine adits and the tailing impoundment are the two primary sources of contaminated water in the Tui mine area.

Ground water flow modelling suggests that the northern Tunakohoia Stream may also receive drainage from the tailing dam. However, most of the highly contaminated water is believed to flow into the Tui Stream and into the ground water via fractured andesitic bedrock (Pang, 1992, 1995). Elevated levels of heavy-metals in the northern Tunakohoia Stream has rendered the stream largely devoid of life. Dilution by 'uncontaminated' water of the south branch of the Stream, however, largely mitigates these adverse environmental effects downstream of the confluence (Pang, 1995).

The Tui Stream is substantially more acidic and generally hosts higher concentrations of Fe and Mn and lower concentrations of Cu, Pb, and Zn than the Tunakohoia Stream (Table 5; Livingston, 1987; Pang, 1992). This trend may reflect the predominance of acid-generating iron pyrite (FeS_2) in the Tui tailings. Arsenic levels in the Tui Stream were found to be lower than in many streams contaminated by mining activity in the Coromandel region (Livingston, 1987). The highest value for arsenic in the Tui Stream is 42 µg/L at the Tui3 site (Sabti et al., 2000). Tay (1980) indicated that the high concentrations of metals in the lower reaches of the Tui Stream originated from acid mine drainage (AMD) emanating from the Tui tailings dam. Leachates generated by groundwater saturation of the tailing and by rainfall infiltration collect in a silt trap to form a small pond below the tailing dam (Plate 1). The water draining from the pond flows into a small stream containing diverted spring and surface water from the tailings and adjacent land. The inflow of the highly contaminated water into the Tui Stream increases its acidity and its toxicity, particularly for zinc in this stream (Livingston, 1987).

The pH values of all the stream and river water samples was in the range of 7.02 to 7.68 as shown in Table 6, with the exception of the following site numbers (Fig. 7): Tui3 (2.85) and Tui5 (2.80). These low values clearly show the high acidity of the Tui Stream in the vicinity of the Tui Mine tailings.

To summarise, it can be shown that the waters of neither the Tui nor Tunakohoia Streams are suitable as sources for potable drinking water at any point upstream from their entry into the township of Te Aroha. It does not appear however, that they have adversely affected the quality of the Waihou River for potable supply.

Table 4. Heavy-metals concentrations in waters (µg/L = ppb) from the Tui (Tui) and Tunakohoia (Tk) Streams and from the Waihou (Wa) River. See Fig.1 for locations

Location	Cu	Zn	Cd	Pb	As
Tui1	28	740	2.0	51	26
Tui2	36	790	4.0	60	12
Tui3	570	46,400	272	649	42
Tui4	32	3000	6.0	0.04	12
Tui5	570	57,600	286	426	14
Tui6	12	11,300	0.1	0.20	3
Tui7	8	1300	2.6	0.20	22
Tui8	6	850	1.1	0.02	21
Tui9	6	810	1.6	0.03	19
Tui10	5	820	1.3	0.04	15
Tui11	4	600	0.7	0.03	29
Tui12	7	370	0.1	1.04	18
Tui13	8	140	0.1	1.00	25
Tk1	40	2740	4.5	1.00	19
Tk2	30	14,000	18	15	17
Tk3	13	13,000	21	0.09	17
Tk4	18	9900	23	0.24	9
Tk5	16	9600	20	119	19
Tk6	310	11,300	73	24	19
Tk7	8	12	0.1	1.00	19
Tk8	5	5600	13	0.17	10
Tk9	20	2200	6.0	0.09	17
Tk9A	16	360	4.0	0.08	15
Tk10	17	530	1.8	0.10	35
Tk11	15	200	1.0	0.2	14
Wa1	10	25	0.1	0.06	18
Wa2	9	24	0.1	0.05	19
Wa3	11	16	1.0	0.16	12
Wa4	14	19	0.4	0.06	16
Wa5	13	15	0.1	0.03	14
Wa7	13	15	0.1	0.03	14

Table 5: Typical water quality of the tailings leachates in the Tui Stream both below and above (control) its confluence with the tailings leachates, and in the northern and southern branches of the Tunakohoia Stream below the mine site. The table also shows the World Health Organisation (WHO) guideline values for drinking water, and New Zealand Ministry of health (1995) standard for potable water. All concentrations in mg/L (ppm).

Sample Location	pH	As	Zn	Cu	Pb	Cd	Fe	Mn	Reference
Tailing Leachates	2.7 - 4.0	n.d.	224 - 302	0.84 - 9.15	0.80 - 2.68	0.35 - 0.75	737 - 906	98 - 102	Tay (1980)
	2.6 - 3.2	n.d.	70.0 - 113	0.07 - 3.13	1.30 - 2.45	0.21 - 0.56	118 - 311	26.5 - 39.0	Pang (1992)
(Tui 3 &5)* *	2.8 - 2.85	0.014 - 0.042	46.4 - 57.6	0.57	0.5	0.28 - 0.29	n.d.	n.d.	Sabti et al (2000)
Tui Stream	4.5 - 5.1	n.d.	5.1 - 11.0	0.04 - 0.27	n.d.	0.02 - 0.03	3.7 - 18.3	1.74	Tay (1980)
	6.7	n.d.	1.01	c0.02	<0.10	<0.05	0.55	0.42	Pang (1992)
	5.9 - 6.4	0.001 - 0.0015	2.08 - 17.0	0.04 - 0.23	0.02 - 0.06	<0.02	n.d.	n.d.	Livingston (1987)
(Tui 9 - 11)* *	6.9 - 7.2	0.015 - 0.029	0.60 - 1.0	<0.01	<0.01	<0.01	n.d.	n.d.	Sabti et al (2000)
Tui Stream (control)	7.1 - 7.8	n.d.	0.02	<0.03	0.02 - 0.50	<0.01	<0.03 -0.15	<0.01	Tay (1980)
	6.5	n.d.	0.1	<0.01	<0.10	<0.02	0.1	<0.05	Pang (1992)
(Tui 12&13)* *	7.2	0.018 - 0.025	0.14 - 0.37	c0.01	<0.10	<0.01	n.d.	n.d.	Sabti et al (2000)
Nth. Tunakohoia	7.4 - 7.7	n.d.	1.59 - 16.2	0.01 - 0.05	0.04 -< 0.10	0.01 - 0.13	<0.04 -0.10	<0.01 - 0.74	Tay (1980)
	7.5	n.d.	2.30 - 16.0	<0.02 - 0.11	0.11 - 0.51	<0.05 - 0.14	0.20 - 4.05	<0.09 - 1.10	Pang (1992)
(Tk1-Tk6)* *	7.0 - 7.1	0.01 - 0.019	2.7 - 14.0	0.01 - 0.3	<0.01 - 0.12	< 0.01 - 0.1	n.d.	n.d.	Sabti et al (2000)
Sth. Tunakohoia	6.7 - 7.5	n.d.	0.1 - 0.50	0.01 - <0.03	<0.03 - <0.10	0.01 - 0.02	0.03 - 0.06	0.01 - 0.05	Tay (1980)
	6.9	n.d.	<0.09	0.02	<0.10	<0.05	0.10	<0.09	Pang (1992)
(Tk9-Tk11)* *	7.2 - 7.5	0.015 - 0.035	0.2 - 2.2	0.01 - 0.02	<0.01	<0.01	n.d.	n.d.	Sabti et al (2000)
WHO guidelines	6.5 - 8.5	0.05[†]	5.0*	1.0*	0.05[†]	0.005[†]	0.3*	0.1*	WHO (1984a/b)
N.Z Ministry of Health	6.5 - 8.5	0.01	3.0	3.0	0.01	0.003	0.20	0.05	N.Z Ministry of Health

[†] Health guidelines for inorganic constituents.

*Aesthetic for chemical constituents that may affect the quality of drinking water though seldom found in toxic concentrations.

**Site shown in Figure 2.

n.d. - not determined

Measurements of pH were conducted with Radiometer pHM83 Autocal meter fitted with a Radiometer GK2401C combined glass/reference electrode, standardised with pH 4 and 7 buffers. The temperature was set at 20°C and no correction for results at field temperatures was attempted. The results for stream and river waters are shown in Table 6.

Table 6. Values of pH for the Tunakohoia (Tk) and Tui (Tui) Streams, and the Waihou (Wa) and Ohinemuri (OH) Rivers.

Site	pH
Tk1	7.02
Tk6	7.10
Tk7	7.25
Tk11	7.59
Tui1	7.12
Tui3	2.85
Tui5	2.80
Tui7	7.18
Tui8	7.00
Tui13	7.20
Wa1	7.64
Wa7	7.68
Oh5	7.14
Oh7	7.52

3.5 (c)Heavy metals in aquatic macrophytes

New Zealand possesses few species of indigenous aquatic macrophytes (Mason, 1975). This increases the opportunities for invasion by exotic species.

An aquatic plant's ability to grow successfully will depend upon its photosynthetic utilisation of available light. The penetration of light through water decreases with depth and is affected by suspended matter. Photosynthetic process are quite sensitive to change in temperature e.g. the relative activity in *Egeria densa* increases five-fold when the temperature is increased from 5 C°to 20 C°. More importantly, Changing the water temperature changes the carbon dioxide concentration which was required to maximize photosynthetic activity (Brown, 1977).

Aquatic plants are able to take up mineral nutrients from the water through both their root and leaves (Denny, 1972). Elemental abundances in aquatic macrophytes are given in Table 7. The data refer only to the Waihou River because aquatic plants were not found in the fast-running, heavily contaminated Tui and Tunakohoia Streams. In Table 7, values in parentheses are the *biological absorption coefficients* (BAC) determined by dividing each concentration in plant material by the corresponding concentration in the ambient water. These BAC values were extremely high, in some cases >100,000. The unusually high levels of element uptake by aquatic macrophytes is well known (Outridge and Noller, 1991) and in New Zealand has been studied by Robinson et al. (1995) who found well over 1000 mg/kg of arsenic in macrophytes growing in the Waikato River.

Two specimens of *Egeria densa* from the Ohinemuri and Waitekauri Rivers (sites 2 and 3 in the inset to Fig. 2) were analysed for gold and produced values of 302 and 672 μg/kg (ppb) in the dried matter. The Ohinemuri River drains the Waihi gold mine and the Waitekauri drains the abandoned Golden Cross gold mine. These results are of some significance because they indicate the possibility of using aquatic macrophytes to prospect for gold.

There are no obvious patterns among the concentrations of heavy metals (other than gold) in the aquatic plants, beyond sharp increases in differences between concentrations of arsenic, cadmium, copper and lead in samples collected at sites Wa1 (upstream from the confluence with the Tunakohoia Stream) and Wa3 (downstream from the confluence of this stream with the Waihou River). Because of the small number of samples, this relationship should be explored further before making firm conclusions, but it does appear that there might be some potential for using aquatic macrophytes to measure ultralow elemental concentrations in their ambient waters.

Table 7. Heavy-metal concentrations (µg/L = ppb) in aquatic macrophytes from the Waihou (Wa) River. Values in parentheses are the biological absorption coefficients (plant/water quotient for each elemental concentration). See Fig.2 for locations.

Element	*Myriophyllum*	*Egeria*	*Potamogeton*	*Elodea*
Cadmium				
Wa1	875 (7955)	-	360 (3273)	-
Wa2	740 (>7400)	1000 (>10,000)	-	300 (>3000)
Wa3	-	-	4500 (4500)	-
Wa4	6900 (20,294)	16,200 (47,647)	-	6700 (19,706)
Wa5	7090 (>70,900)	-	8300 (>83,000)	-
Wa6	3050	840	-	-
Wa 7	7050 (>70,500)	-	-	7450 (>74,500)
Lead				
Wa1	55,000(>110,000)	-	11,000 (>22,000)	-
Wa2	11,905 (>23,810)	11,905 (>23,810)	-	12,143 (>24,286)
Wa3	-	-	68,357(>136,714)	-
Wa4	12,025 (24,050)	21,190 (>42,381)	-	25,000 (>30,000)
Wa5	11,904 (>23,809)	-	11,428 (22,857)	11,429 (>22,857)
Wa6	65,000	7833	-	-
Wa7	11,429 (>22858)	-	-	15,000 (>30,000)
Copper				
Wa1	10,853 (>54,265)	-	13,370 (>66,850)	-
Wa2	35,000(>175,000)	85,300(>426,500)	-	199,850 (>999,250)
Wa3	-	-	15,600 (8667)	-
Wa4	20,685 (22,983)	11,814 (13,127)	-	18,400 (20,444)
Wa5	11,400 (57,000)	-	14,000 (70,000)	-
Wa6	75,700	37,600	-	-
Wa7	7,200 (60,000)	-	-	15,210 (126,750)
Zinc				
Wa1	225,000 (9000)	-	965,000 (38,600)	-
Wa2	238,095 (9921)	142,857 (5952)	-	314,285 (7543)
Wa3	-	-	434,762 (27,173)	-
Wa4	786,500 (41,395)	452,380 (8595)	-	1,090,000 (57,368)
Wa5	919,048 (61,270)	-	514,286 (34,286)	-
Wa6	500,000	686,667	-	-
Wa7	1,490,476(124,206)	-	-	704,762 (58,730)
Arsenic				
Wa1	2175 (120)	-	685 (37)	-
Wa2	876 (46)	1047 (55)	-	514 (27)
Wa3	-	-	3263 (286)	-
Wa4	1978 (122)	1010 (64)	-	2090 (133)
Wa5	5171 (366)	-	4533 (321)	-
Wa6	7700	1241	-	4219
Wa7	557 (84)	-	-	4219 (639)

A few plant species were collected from the Waihou River : *Egeria densa* Planchon, *Elodea canadensis* Michaux, *Myriophyllum aquaticum* (Veil. Conc.) Verdc, and *Potamogeton crispus* L. A complete description for these plants can be found in (Johnson,1998).

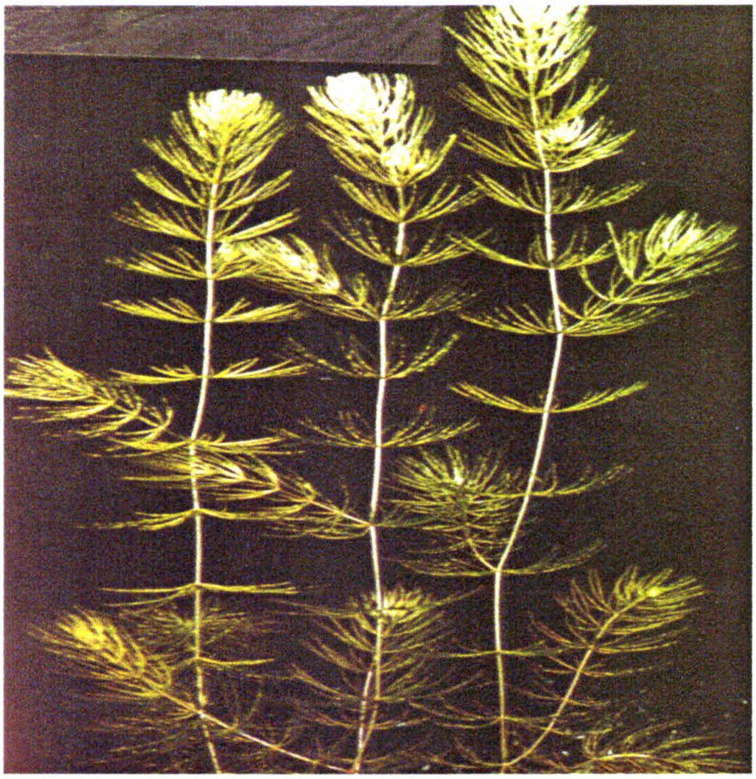

Plate. 2

Myriophyllum aquaticum (Vell. Conc.) Verdc. **(Plate. 2)**
Parrot's feather stout, light green aquatic. Stems to 2 m long, to 5 mm diam. Leaves in whorls of 5-8; bases interspersed with numerous hydathodes (filiform appendages about 2 mm long). Submerged leaves to 4 cm long with thread-like pinnae; emergent leaves to 3 cm long, thicker, comb-like, rounded in outline at tip. Flowers with trifid bracts. In New Zealand, only female flowers are found and fruit is not set. N, S. Auckland to Wellington, scattered and only locally common; one collection in Canterbury. Lakes, slow-flowing rivers and streams, pond and diches, aquatic and emergent, or extending across water surface from banks.

Plate. 3

Egeria densa Planchon (**Plate. 3**)
stems to 1.5 m long, slender, brittle, much branched, buoyant. Leaves dark grey-green, in whorls of usually 4-5 (sometimes 3-8), 10-30 mm long, abruptly narrowed to acute tip; margins sometimes with fine teeth. Abundant in Waikato lakes and scattered elsewhere; Northland, Auckland, Napier, Foxton, Marlborough. Aquatic, forming dense growths near the surface in shallow and still waters of lakes. (Native to S. America but now established in warm waters in all continents)
First noted in New Zealand in 1946 and now gazetted as a class B noxious plant

Plate. 4

Elodea canadensis Michaux (**Plate. 4**)
Canadian pond weed Stems to 6 m long, slender, brittle, much branched. Leaves dark green, often crowded, in whorls of 3 or in opposite pairs on lower stems, 6-12 mm long, rounded at tip. Flower with white petals, unisextial, to 5 mm wide, borne singly on a thread-like stalk from a sessile spathe among upper leaves. Flowering, when it occurs, shows most New Zealand plants to be female. N, S. Throughout but rare in Northland, Taranaki, and Westland. Aquatic, to 8.5 m depth, often forming dense, tall beds; in many habitats including lakes, ponds, rivers, and streams. (Native to N America but now found through much of the temperate world)
This is the most widespread of oxygen weeds in New Zealand and has established rapidly, extensively, and often unobtrusively in many waterways.

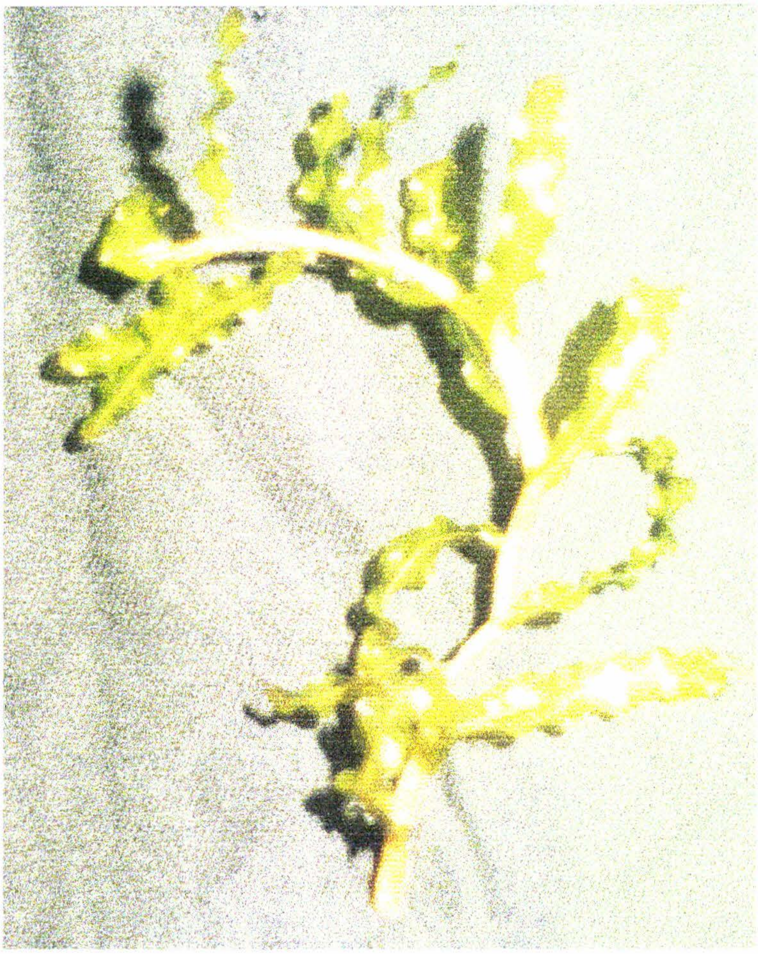

Plate. 5

Potamogeton crispus L **(Plate. 5)**

Curly pond weed Stems to 2 m or more long, often zigzagged, angled. Stipules short (to 5 mm), soon becoming fibrous. Leaves translucent, often reddish, sessile, 2-8 cm long, 4-12 mm wide, obtuse; main veins 3, Widely-spaced; margins crimped, minutely toothed towards tip. Spikes few-flowered (3-5). Achenes large (4 mm) with thick, curved beak. N,S. Auckland to Blenheim and Canterbury. In Streams, ditches, ponds, rivers, and lake, especially common in North I. (Native to Europe, Asia, Africa).

The only naturalised *Potamogeton* in New Zealand is a problem when choking waterways. Identified by the fine leaf-teeth, the undulate margins are absent as in young growth, and can be distinguished from *P. ochreatus* by the lack of numerous fine, longitudinal veins.

3.6 CONCLUSIONS

Conclusions arising from this chapter can be summarised as follows:

1. Sediments from the Tui and Tunakohoia Streams draining mineralisation near the Tui Mine still contain significant levels of heavy minerals in their upper reaches and these will continue to supply heavy-metal contamination to these waters.
2. The upper reaches of the Tui and Tunakohoia Streams have heavy-metal concentrations above the limits set for potable waters and neither is a suitable supply source for domestic water supply.
3. Discharge of the Tui and Tunakohoia Streams into the Waihou River has not had an appreciable effect on the water quality of this waterway.
4. Gold and other heavy metals are detectable in the Waitekauri and Ohinemuri Rivers draining gold mines in the Waihi area.
5. Very high relative accumulation of heavy metals in aquatic macrophytes in the Waihou, Ohinemuri and Waitekauri Rivers points to the possibility of using these plants as bioindicators of heavy-metal contamination of waters.
6. Detection of gold in aquatic macrophytes in the Ohinemuri and Waitekauri Rivers draining existing and abandoned gold mines suggests that these plants should be investigated as possible biogeochemical indicators of gold mineralisation.

CHAPTER 4

MINERALOGICAL ANALYSIS (X-RAY DIFFRACTION ANALYSIS)

4.1 Abstract.

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, and clearly has not advanced as far as the confluences with the Waihou River.

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. X-ray diffraction analysis of the heavy mineral fractions of the Tunakohoia and Tui streams, and those of the Waihou and Ohinemuri Rivers, identified 10 minerals distributed throughout these streams and rivers.

4.2 Introduction

The technique of XRD mineral identification is based on the principle that each crystalline substance has a characteristic arrangement of atoms, which diffract X-rays in a unique and hence characteristic pattern (Whitton & Churchman, 1987). XRD analysis has been used to investigate the mineralogy of ore materials. Cochrane (1969) used XRD to determine the purity of sphalerite and the presence of well-crystallised kaolinite in the Tui ore. Wodzicki &Weissberg (1970) similarly used XRD to identify quartz, chlorite, illite and interlayered illite-montmorillonite. Morrell (1997) analysed unseparated Tui mine tailings to depths from 0-600 mm and found it to consist primarily of quartz, galena, sphalerite and chalcopyrite. The presence of kaolinite or pyrite in the ore was not detected. The presence of pyrite was masked by the sphalerite which, has similar major d-spacing to pyrite. Morrell (1997) also found that the 500-600 mm sample was shown to contain a small but significant amount of pyrite, and XRD analysis of the ore sample also indicated the presence of calcite in the HMF sample, but it was not a major constituent of the Tui ore sample.

In this study, X-ray diffraction analysis was used to investigate the different mineral phases present in material from the Tui, Tunakohoia Streams, Waihou and Ohinemuri Rivers. Density separation was used to isolate the heavy mineral fraction (HMF) of rivers and streams sediments from the light mineral fraction (LMF) by using a solution of sodium polytungstate (SPT) with a bulk density of approximately 2.8 g/cm^3 (Callahan, 1987).

For the purposes of this study, the LMF is defined as the fraction of the sediments made up of particles with a density of < 2.8 g/cm^3. Conversely, the HMF is defined as the fraction of the stream sediments composed of particles with a density > 2.8g/cm^3. Half-gram river and stream samples were placed in centrifuge tubes with narrow stems. Approximately 5 ml of SPT was added to each tube and the solutions were stirred gently to disperse the grains and break up aggregates. The tubes were then centrifuged for 4 minutes at approximately 1500 rpm. The LMF of the samples was decanted from the test tubes into funnels containing filter paper (Whatman, No.1). This was achieved by creating a seal with a glass rod at the narrow section of the stem containing the HMF. The tubes were rinsed to ensure that any of the LMF adhering to the walls of the tubes was removed. The samples were rinsed thoroughly with deionised water to remove the SPT and then placed in an oven at 105°C and left to dry overnight on filter papers (Whitton & Churchman, 1987). Following the removal of the LMF, the HMF was rinsed from the bottom of the centrifuge tube with distilled water and similarly collected and dried. Both fractions of each sample were then weighed to four decimal place.

The sediments samples were run as acetone slurry mounts which were prepared by mixing ground separated sediment samples with a few drops of acetone on a glass slide before evenly distributing the slurry over the whole slide and allowing it to air-dry (Whitton & Churchman, 1987). The glass slides were examined by a Phillip's 4-kVa PW 1710 instrument with a PW 1050/80 goniometer operating at 40 kV and 60 mA and used in conjunction with a 42 sample changer system (a PW 1775 unit). A broad-focus cobalt anode tube was used and the samples were scanned from 2°to 90° 2θ. Sietronics XRD trace processing software (Version 1.0) was used to analyse the traces and to identify the mineral phase present in the tailings sample.

4.3 Results and Discussion

XRD analysis of the heavy mineral fraction (HMF) of the Tunakohioa and Tui Stream, and Waihou and Ohinemuri rivers sediments identified 10 minerals shown in Table 8 for all the minerals from the XRD traces, and its abbreviation, These included as prevalent minerals in all the rivers and streams sediments: hypersthene $(Mg, Fe^{++})_2Si_2O_6$, quartz(SiO_2), magnetite(Fe_3O_4), hornblende($Ca_2MgFe_5(SiAl)_8O_{22}.(OH)_2$), pyrite($FeS_2$), ilmenite($FeTiO_3$), cummingtonite($(Fe_{16}Mg_{14})_7(OH)_2Si_8O_{22}$, and feldspar. An increase in the relative abundance of sphalerite(ZnS), anglesite($PbSO_4$), and pyrite(FeS_2) in the upper reaches of the Tui and Tunakohioa Streams was indicated by a significant increase in the intensity of a peak corresponding to the pyrite, and clearly has not advanced as far as the confluences with the Waihou River. XRD traces of Tk1, Tui7 and Wa1 in Figures 9 (a, b, and c) contained detectable, magnetite, pyrite, quartz, hypersthenene as well as ilmenite.

The relative depletion of Cu, Zn, Cd, and Pb from the lower part of the Tunakohioa Stream, and Waihou River is, therefore, a function of stability / solubility of the various weathering products of the sulphide minerals under different pH values. The water quality studies of Tay (1980) and Pang (1992) confirmed that substantial amounts of Cu, Fe, Zn and other elements were then being leached into surface and ground water at the Tui mine site. Pang (1992) mentioned the identification of quartz, pyrite, some sphalerite and kaolinite and a little feldspar in a bulk sample of the Tui mine tailings using XRD. The intrinsic association of the quartz and pyrite explains the presence of a significant amount of quartz in the HMF of the rivers and streams sediments. Due to the comparatively high density of the heavy minerals, a relatively large amount of quartz was carried through into the HMF fraction of the sediments by sodium polytungstate solution. The presence of pyrite in the Tunakohioa stream and upper part of the Tui stream masked the sphalerite, because it has a similar major d-spacing, but heavy-liquid (tetrabromoethane) separation of sediments from the Tunakohoia stream conducted by Tay (1980) facilitated the identification of sphalerite and pyrite in the sediments. In Tay (1980), quartz, galena, sphalerite and cerussite were identified in adit No. 7 driven into the Champion Reef (Fig. 2). The XRD traces of Tui Stream sediments (taken from below the confluence of the tailing dam stream), however, did not indicate the presence of sulphide minerals despite the high concentrations of Cu, Cd, Fe, Pb, and Zn in the sediments.

Table 8. Heavy minerals identified by XRD in the <0.5 mm fraction of stream sediments from the Tui (Tui) and Tunakohoia (Tk) Streams (Te Aroha) and from the Waihou (Wa) and Ohinemuri (Oh) Rivers. See Fig. 2 for sample locations. Ang - anglesite, Cum - cummingtonite, Fel - felspar, Hbl - hornblende, Hyp - hypersthene, Ilm - ilmenite, Mag - magnetite, Pyr - pyrite, Qtz - quartz, Sph - sphalerite.

Location	Minerals									
	Pyr	Sph	Qtz	Mag	Hyp	Ilm	Ang	Hbl	Cum	Fel
Tk1	+	+	+	+	+	+	+	+	-	-
Tk7	+	-	+	+	+	+	-	+	-	-
Tk9	+	-	+	+	+	+	-	+	-	-
Tk10	+	-	+	-	+	-	+	-	+	-
Tk11	-	+	+	+	+	-	+	-	-	-
Tk12	+	-	+	-	+	+	-	+	-	-
Tui7	+	-	+	+	+	+	-	-	-	-
Tui11	+	-	+	+	+	+	-	-	-	-
Tui12	-	-	+	+	+	+	+	-	+	-
Tui 13	-	-	+	-	+	-	+	+	+	-
Wa1	-	-	+	+	+	+	-	+	-	-
Wa2	-	-	+	+	+	+	-	+	-	-
Wa4	-	+	+	+	+	-	+	-	-	-
Wa5	-	-	+	-	+	+	+	-	-	+
Wa7	-	-	+	-	+	-	-	-	-	+
Oh6	-	-	+	+	+	+	+	+	+	-
Oh7	-	-	+	+	+	+	-	+	+	-

N.B. + present, - absent.

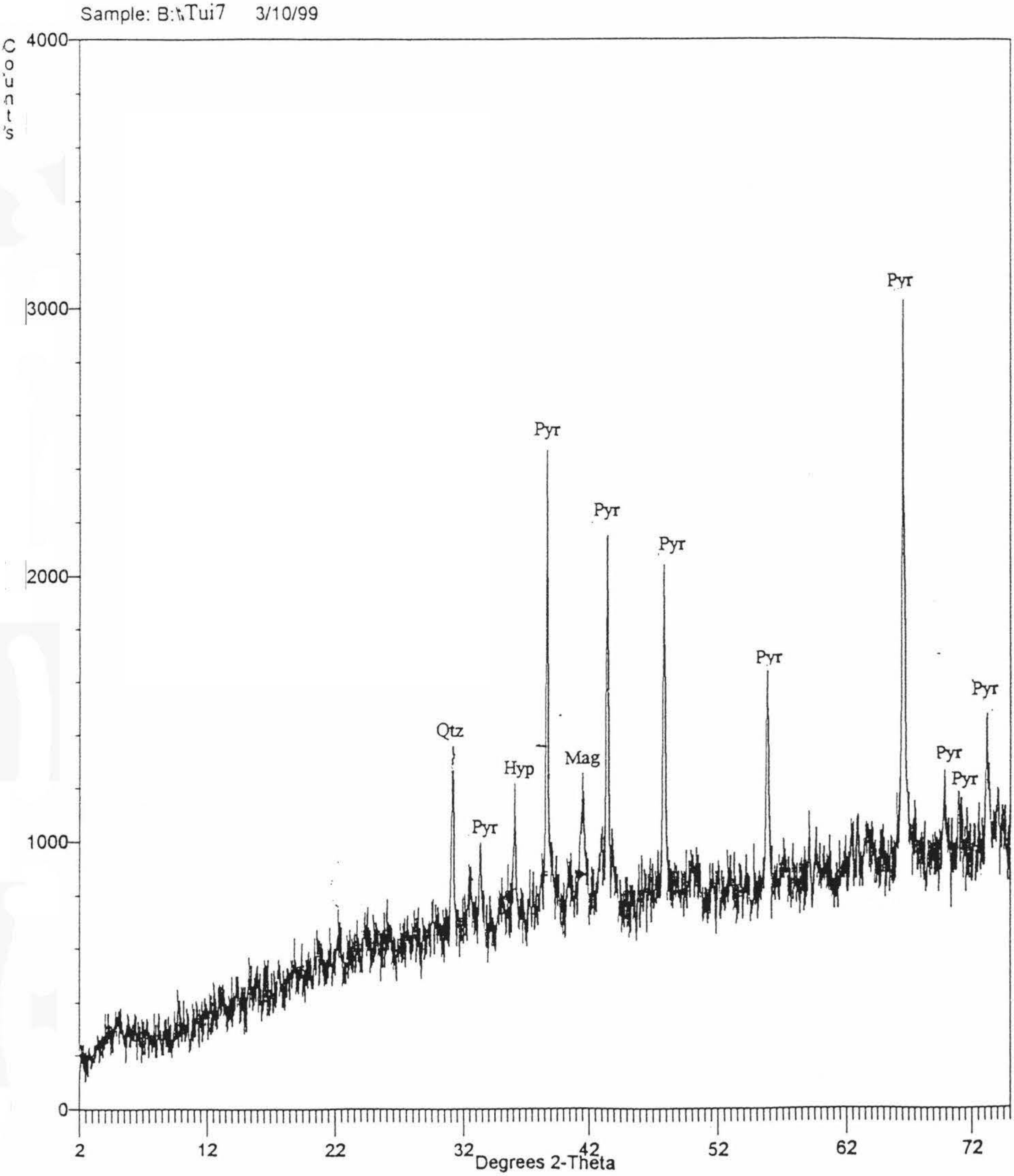

Figure 9 (a). XRD trace of a Tui7 sediment sample containing detectable pyrite (Pyr), quartz (Qtz), as well as magnetite (Mag) and Hypersthene (Hyp).

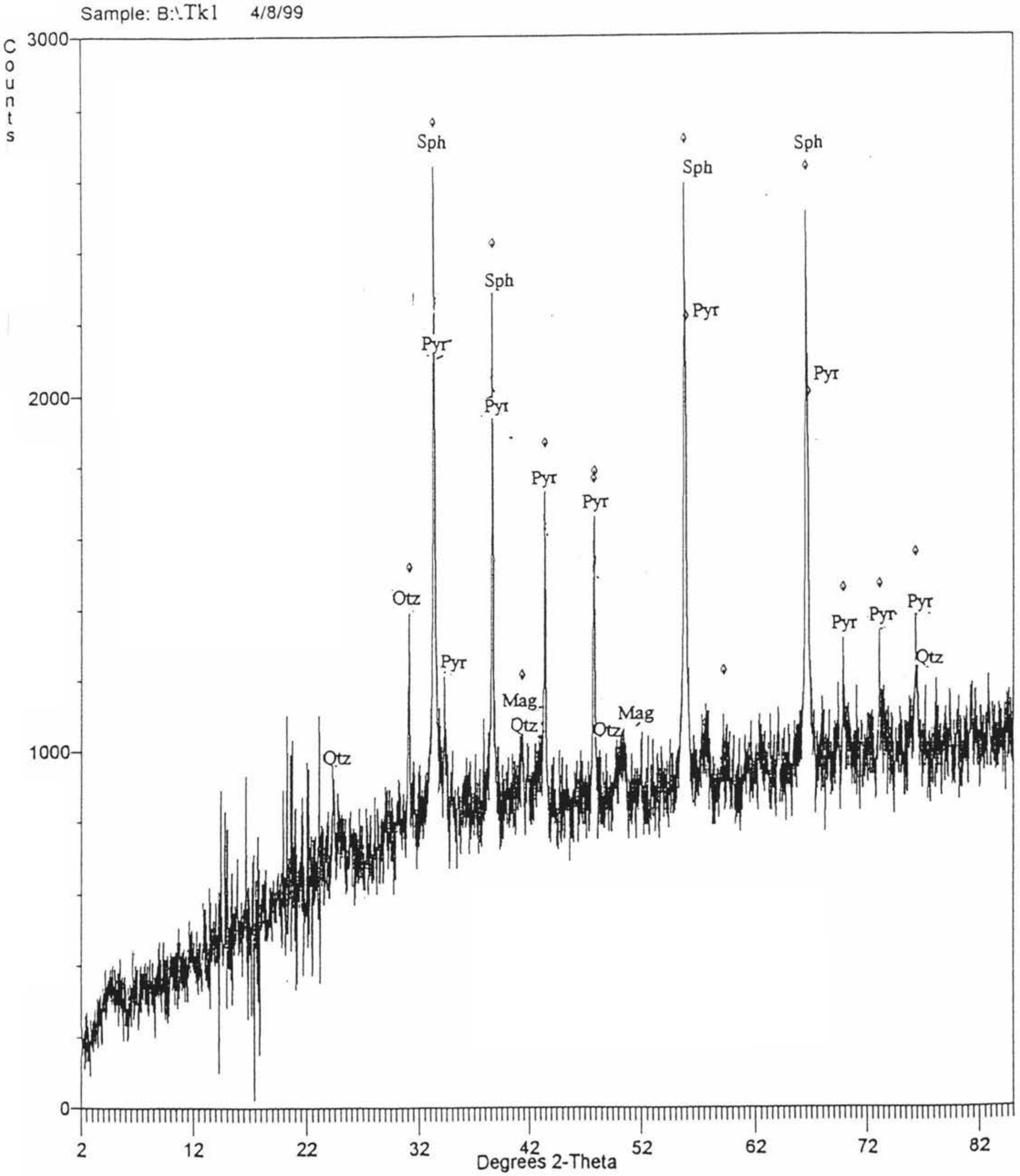

Figure 9 (b). XRD trace of a Tk1 sediment sample containing detectable pyrite (Pyr), sphalerite (Sph) as well as quartz (Qtz) and magnetite (Mag).

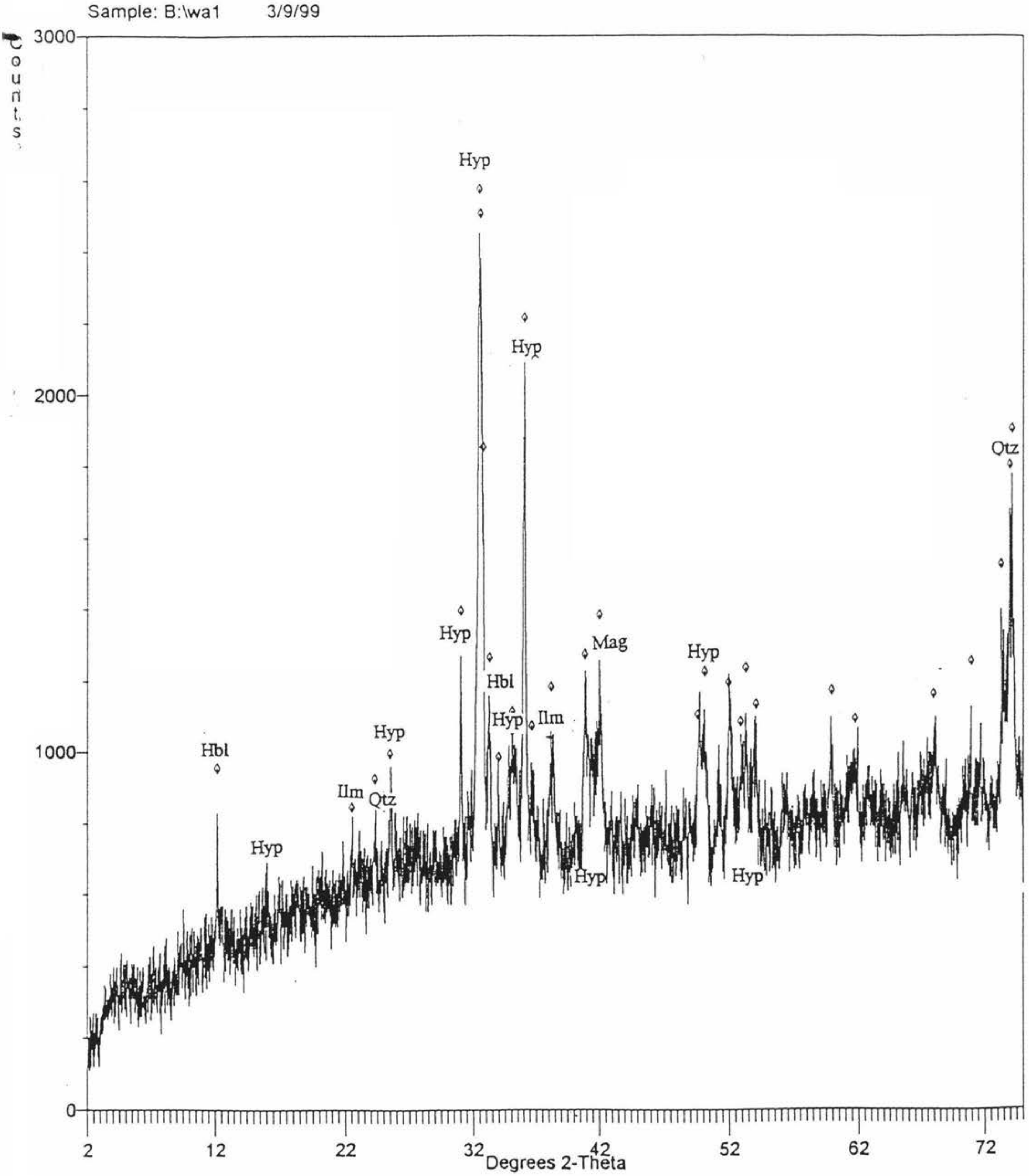

Figure 9 (c). XRD trace of a Wa1 sediment sample containing detectable Hypersthene(Hyp),quartz (Qtz), magnetite (Mag) as well as hornblende (Hbl) and ilmenite (Ilm).

CHAPTER 5

TAILINGS BASE-METAL RECLAMATION BY TUI TAILINGS COLUMN EXPERIMENS

5.1 Abstract

A series of experiments was carried out in which columns of auriferous Tui mine tailings were leached with various eluents at several pH values. The eluents included ammonium thiocyanate, ammonium thiosulphate and water. Concentrations of gold, copper, cadmium, zinc, lead and iron were determined in these leachates. Ammonium thiocyanate was more selective for gold and lead than the other eluents, ammonium thiosulphate was highly selective for zinc, and much less so for the other metals and gold. Elution of cadmium and copper by water was higher than for the other reagents. Elution of iron by water and ammonium thiocyanate was higher than the elution by ammonium thiosulphate.

5.2 Introduction

The Relative mobility of heavy metals and gold leached from the Tui tailings dam at Te Aroha was assessed by passing water and other reagents through tailings columns. These reagents were ammonium thiocyanate and ammonium thiosulphate. Since these reagents can solubilise gold, it might be expected that other heavy metals present in the substrate might also be released into the environment at the same time as gold. This is not an unreasonable concern, because gold in ores or mine tailing is frequently associated with chalcophile heavy metals such as As, Cd, Cu, Pb or Zn (Msuya et al, 2000).

Concern about the environmental effects of induced phytomining are centred around two main problems: the actual toxicity of the reagents used, as well as the toxicity of heavy metals released by these chemicals. Ammonium thiocyanate has toxicity over 200 times less than that of cyanide, and is graded 3 on the toxicity class (Merck Catalogue 1999). Ammonium thiosulphate is over 1000 times less toxic than cyanide and is degraded quickly to class 5 sulphate. These reagents have low toxicity, as has been shown by Hung and Pavlostathis, (1997) and are also readily broken down in the environment.

The above experiments carried out in the absence of, or with different limestone rates (0.5, 1.0, and 1.5%). Even 0.5% lime is enough to increase the pH of the tailings to 7 as is shown in Table 9.

Chemically induced uptake of gold by plants has recently been reported by Anderson et al.(1998) who have subsequently (Anderson et al. 1999; Brooks et al. 1999; Msuya et al. 2000) investigated further, the possibility of producing a crop of gold (photomining) by inducing gold uptake by several plants after mobilisation of the gold by reagents such as ammonium thiocyanate and ammonium thiosulphate.

Ammonium thiocyanate acts to make the gold soluble in the soil. Once this gold is in the soil solution, a plant has little choice but to take up the soluble complex as a function of transpiration. The gold is then accumulated in the living tissues.At the point where the plant stops accumulating gold, the biomass is harvested and burnt.This yields an ash or 'bio-ore' that is concentrated in the metal. The bio-ore is then processed to yield the final, golden metallic product (Anderson et al. 1999).

5.3 Materials and Methods

5.3a Tui base metal mine tailings

The Tui Base-metal Mine at Te Aroha, New Zealand is one of the most severely metal-polluted environments in that country as a result of mining activities carried out some 25 years ago. The tailings from the Tui mine are auriferous and contain on average about 0.5 to 1.0 mg/kg gold that is readily extractable into ammonium thiocyanate. Anderson et al. (1998) were able to extract 22.6% of this gold from 1 g of tailings into 10 mL of 2 g/L thiocyanate. This tailings material was therefore selected for the following leaching experiments, because its gold content and its high content of readily leachable heavy metals such as Cd, Cu, Pb, Fe and Zn. Pollution problems arising from the above mining activities as referred to in the introduction of this thesis, have been summarised by Morrell et al. (1995) and (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. Oxidation, particularly of pyrite (FeS_2), has led to acid mine drainage (AMD). The low pH engendered by this AMD has mobilised several toxic heavy metals such as As, Cd, Cu, Pb and Zn that have found their way from the tailings into the local, streams, waters, sediments and plants.

5.3b Design of leaching experiments.

12 columns were packed with 600g of Tui tailings contained in polypropylene cylinders of 250 mm length, and 50 mm inside diameter. The bottom of each cylinder was covered with 0.1 mm nylon gauze. The tailings were amended with different lime (as $CaCO_3$) rates: 3 columns with 0% lime, 3 columns with 0.5% lime, 3 columns with 1.0% lime and 3 columns with 1.5% lime. RO water and solutions (2g/L) of ammonium thiocyanate or ammonium thiosulphate were passed through each of the columns for a period of 8 days at a rate initially of 150 mL to saturate the columns and then each day 50 mL of fresh eluent. The eluates were collected in beakers placed underneath each column and stored at 4°C before chemical analysis. To avoid decomposition of the metal complexes, the extractants were shielded from light.

5.3c Chemical analysis of leachates

The individual daily leachates were analysed for Cd, Cu, Pb, and Zn by flame atomic absorption spectrometry (FAAS) using a GBC 909 atomic absorption spectrometer capable of determining down to 0.5 mg/L (ppm) of metals other than gold in the solution. Gold was quantified using a GBC System 3000 graphite furnace atomic absorption spectrometer (GFAAS) with limit of detection of about 5 µg/L (ppb). The same instrument was used to determine the heavy metals with concentrations below the limit of detection of the FAAS instrument.

Multielement analysis of four leachates from four columns, three of them without lime, the first one leached by $Na_2S_2O_3$, the second one leached by NH_4SCN the third one leached by H_2O, finally with 1.5% lime leached by $Na_2S_2O_3$ was carried out by using inductively-coupled argon plasma atomic emission spectrometry (ICP-AES).

5.4 Results and discussion

The mobility of heavy metals and gold leached from the Tui tailings dam was assessed by passing water and other reagents through tailings columns as described above. The results are shown in Table 9. The results of ICP-AES data are presented in Table 10.

When leached with water, copper appeared to be the most mobile among the heavy metals in the tailings. After the first day, its concentration reached 226 mg/L and levelled off to about 4 mg/L after only 4 days. This eluted copper was, however, only the soluble fraction of the tailings after oxidation of the sulphide and therefore did not represent the whole of the copper content. The experiment did, however, indicate the relative mobility of oxidised copper in comparison with other oxidised heavy metals. The cadmium showed a maximum of 0.985 mg/L after 2 days of leaching with water and there was a steady decrease thereafter. It appears to be slightly less mobile than copper in sharp contrast to zinc that despite its geochemical similarity to cadmium, leached at a much slower rate that did not appear approach a limiting value even after 8 days. Lead was the least mobile among the heavy metals, despite being by far the major constituent of the tailings, so that its concentration in the water eluate fractions increased only slightly over the 8-day period. This is because lead remains insoluble after oxidation from sulphide to sulphate unlike the other three heavy metals.

Elution of the tailing columns with ammonium thiocyanate (Fig. 10) showed similar elution patterns for cadmium, copper and zinc compared with water, though on a reduced scale. Although it might be supposed that thiocyanate would be a better eluent than water for this purpose, it must be appreciated that copper thiocyanate is relatively insoluble. In the case of lead, there was a threefold enhanced elution of this element with thiocyanate. This is probably because of formation of a complex ion with the formula $Pb(CNS)_4^{2-}$. Elution of the column with 2 g/L thiocyanate was effective in removing a large part of the gold that is found at concentrations from 0.1 to 0.5 mg/kg in the tailings that had a pH of 2.4. As will be seen from Fig. 11. the highest gold concentration (318 µg/L) was found in the eluate of the second day of elution, The concentrations decreased steadily thereafter to a final value of 53 µg/L after 8 days. This elution was highly dependent on pH, because addition of 0.5% lime to the material (pH 5.2) reduced the maximum gold concentration to only 15 µg/L at day 2 and only 2.6 µg/L after addition of 1% lime (pH 7.5). When the column was eluted with 4 g/L ammonium thiocyanate, the gold concentration at day 1 of the elution period, increased to 1223 µg/L and to 1082 µg/L at day 2 as shown in Fig. 11.The gold values extracted by 4 g/L from the first day into the last day number eight were: 1223, 1082, 599, 419, 323, 195, 319, and 166 respectively.

Increasing concentrations of thiocyanate extraction in the range of 1 to 10 g/L (Msuya et al, 2000) resulted in a corresponding increase in the amount of gold removed from the tailings. There was no corresponding increase in removal of the other four elements, thus confirming the selectivity of thiocyanate for gold phytomining.

Elution with sodium thiocyanate (Fig. 10) produced patterns somewhat different from those of the other eluents. Thiosulphate was non-selective for gold, but zinc mobility increased dramatically with most of the removal in the first day. After only four days, the concentration decreased from a maximum of 580 mg/L to a limiting value of only about 4 mg/L for unlimed tailings by elution with sodium thiosulphate. A similar pattern was evident for cadmium and copper. In the case of lead, there was no obvious significant removal and the concentrations gave a plateau of only about 3 mg/L. Gold was not removed to any significant degree when this eluent was used. Addition of lime to the tailings decreased the elution and 0.5% lime is enough to increase the pH to 7. At this pH, thiosulphate removed a very small amount of heavy metals. With addition of lime, extraction of the gold and the elements Zn, Cu, Pb and Cd decreased as a function of increasing the pH because the solubility of most metals increases as pH decreases, so the production of acid tends to increase the rate of dissolution of metals.

Table 9. The metal concentrations and pH measurements of the Tui tailings after 8 days leaching with water and ammonium thiocyanate and ammonium thiosulphate) with absence or presence of different limestone rates (0,0.5, 1.0,1.5), gold concentrations in µg/L, and all the heavy metal concentrations in mg/L.

	Zn Concentration			Cu Concentration			Pb Concentration			Cd Concentration			Au Concentration			Fe Concentration			Ph Measurement			%Lime
Day	H_2O	NH_4SCN	$Na_2S_2O_3$	H_2O	NH_4SCN	$Na_2S_2O_3$	H_2O	NH_4SCN	$Na_2S_2O_3$	H_2O	NH_4SCN	$Na_2S_2O_3$	H_2O	NH_4SCN	$Na_2S_2O_3$	H_2O	NH_4SCN	$Na_2S_2O_3$	H_2O	NH_4SCN	$Na_2S_2O_3$	
1	3.200	1.000	580.000	226.000	120.00	137.00	2.000	3.200	1.000	0.564	0.523	0.349		181.520		102.20	95.75	63.11	2.11	2.19	2.33	0% Lime
2	3.250	2.380	55.000	42.900	15.700	15.000	2.210	3.250	2.380	0.985	0.750	0.478		318.400		33.41	79.51	46.27	2.48	2.42	2.63	
3	6.100	2.850	16.000	8.200	5.690	4.270	3.160	6.100	2.850	0.138	0.092	0.113		206.150		4.35	46.09	44.56	2.57	2.55	2.80	
4	8.170	2.760	11.000	5.800	4.650	2.110	3.600	8.170	2.760	0.092	0.028	0.027		234.783		2.49	34.54	27.34	2.66	2.63	2.90	
5	9.220	2.660	4.000	4.360	3.010	1.260	3.770	9.220	2.660	0.069	0.014	0.017		104.150		2.21	27.97	14.18	2.70	2.70	2.95	
6	10.860	2.540	4.000	3.830	2.090	0.920	3.720	10.860	2.540	0.038	0.009	0.004		80.400		2.20	23.02	4.21	2.68	2.76	2.96	
7	13.200	2.890	3.000	3.760	1.670	0.810	4.460	13.200	2.890	0.049	0.024	0.023		70.500		1.18	19.81	1.23	2.60	2.73	2.96	
8	14.430	3.100	3.000	3.450	1.390	0.790	4.790	14.430	3.100	0.030	0.010	0.010		52.667		1.31	17.34	0.89	2.55	2.75	2.99	
1	21.900	89.000	67.000	0.100	0.290	0.100	0.610	3.450	0.300	0.024	0.875	0.153				0.002	0.002	0.001	5.20	6.36	5.45	0.5% Lime
2	16.000	16.000	11.000	0.100	0.140	0.070	0.460	0.850	0.640	0.176	0.306	0.140		15.000		0.003	0.002	0.042	7.19	7.27	7.09	
3	9.000	9.000	5.000	0.040	0.110	0.050	0.930	0.730	0.510	0.098	0.160	0.147		11.444		0.001	0.001	0.001	7.36	7.54	7.71	
4	5.000	5.000	2.000	0.030	0.110	0.200	0.720	0.680	0.640	0.078	0.135	0.157		11.120		0.048	0.002	0.025	7.42	7.50	7.95	
5	3.000	3.000	0.900	0.050	0.110	0.260	1.010	0.700	0.770	0.059	0.070	0.146		4.612		0.007	0.136	0.222	7.64	7.31	7.83	
6	3.000	5.000	2.000	0.030	0.100	0.400	1.470	0.830	0.910	0.054	0.053	0.120				0.001	0.123	0.052	7.42	7.32	7.85	
7	3.000	4.000	2.000	0.010	0.090	0.550	1.300	0.830	0.960	0.047	0.052	0.095				0.001	0.042	0.064	7.76	7.34	8.02	
8	2.000	3.000	1.000	0.070	0.120	0.560	1.190	1.180	3.470	0.041	0.040	0.087				0.050	0.022	0.002	7.81	7.34	8.10	
1	4.000	6.000	5.000	0.280	0.230	0.150	0.570	1.320	0.200	0.113	0.144	0.088				0.001	0.001	0.001	7.10	6.92	7.49	1.0% Lime
2	4.000	8.000	4.000	0.100	0.210	0.090	0.610	0.750	0.560	0.068	0.131	0.059		2.588		0.001	0.001	0.001	7.78	7.54	7.76	
3	3.000	5.000	2.000	0.060	0.190	0.070	0.550	0.950	0.820	0.036	0.107	0.071		1.352		0.001	0.001	0.001	8.06	7.60	8.10	
4	2.000	3.000	1.000	0.040	0.160	0.550	0.420	1.000	0.450	0.046	0.118	0.083		0.020		0.004	0.035	0.014	8.06	7.54	8.15	
5	1.000	2.000	0.600	0.040	0.170	1.690	0.600	0.900	0.620	0.031	0.101	0.109				0.079	0.085	0.013	7.88	7.37	8.01	
6	0.900	1.000	0.400	0.040	0.120	2.730	0.600	1.010	0.640	0.037	0.086	0.130				0.064	0.083	0.014	7.73	7.24	8.00	
7	2.000	1.000	1.000	0.050	0.120	2.940	0.550	0.830	0.680	0.032	0.094	0.132				0.001	0.001	0.001	8.06	7.20	8.22	
8	2.000	2.000	0.700	0.060	0.160	2.920	0.860	0.780	0.900	0.062	0.064	0.115				0.001	0.033	0.001	8.06	7.19	8.17	
1	0.700	0.700	0.600	0.120	0.190	0.330	2.500	0.500	0.660	0.033	0.034	0.034				0.001	0.001	0.045	7.14	6.79	7.21	1.5% Lime
2	0.300	0.700	0.300	0.070	0.180	0.200	0.590	0.800	0.570	0.190	0.048	0.020				0.019	0.001	0.051	8.00	7.67	8.02	
3	0.600	0.900	0.200	0.050	0.160	0.090	0.550	0.480	0.650	0.002	0.030	0.011				0.006	0.004	0.030	8.23	7.64	8.07	
4	0.500	0.700	0.200	0.030	0.160	0.110	0.670	0.800	0.400	0.002	0.014	0.027				0.029	0.001	0.042	8.18	7.54	8.11	
5	0.300	0.300	0.200	0.040	0.140	0.250	0.500	0.810	0.600	0.002	0.018	0.045				0.011	0.001	0.001	8.00	7.58	7.98	
6	0.200	0.200	0.100	0.050	0.120	0.490	0.460	0.800	0.680	0.007	0.003	0.040				0.001	0.001	0.001	8.15	7.56	7.94	
7	0.400	0.300	0.100	0.050	0.120	1.000	0.630	0.820	0.730	0.007	0.022	0.039				0.012	0.526	0.092	8.26	7.50	8.10	
8	0.400	0.100	0.200	0.060	0.130	1.140	0.480	0.200	0.930	0.002	0.021	0.072				0.061	0.001	0.283	8.21	7.54	8.03	

Table 10. Multielement analysis for heavy-metal concentrations within eluates of four columns of Tui Tailings for the second day leachates, as determined by ICP-AES. Data in parentheses represent the concentrations also determined by FAAS. Unit of measurement are mg/L (ppm).

Element	**$Na_2S_2O_3$ 0% Lime**	**NH_4SCN 0% Lime**	**H_2O 0% Lime**	**$Na_2S_2O_3$ 1.5% Lime**
Zn	50.2(55)	4(2.38)	5(3.25)	0.30(0.3)
Cu	15.0(15)	15.7(15.7)	42.9(42.9)	0.14(0.2)
Pb	2.2(2.38)	3.3(3.25)	2.3(2.21)	<0.1(0.57)
Cd	0.47(0.478)	0.79(0.75)	1.00(0.98)	<0.01(0.02)
Mn	1.2	2.8	2.5	0.22
Fe	42.0(46.3)	79.2(79.5)	28.8(33.4)	<0.01(0.05)
As	<0.03	<0.03	<0.03	<0.03
K	4.4	12.6	6.3	15.2
Mg	7.7	18.1	20.8	38.3
S	750	1107	562	756
Ca	26.5	59.2	77.1	479
Al	31.4	102	96.1	<0.1

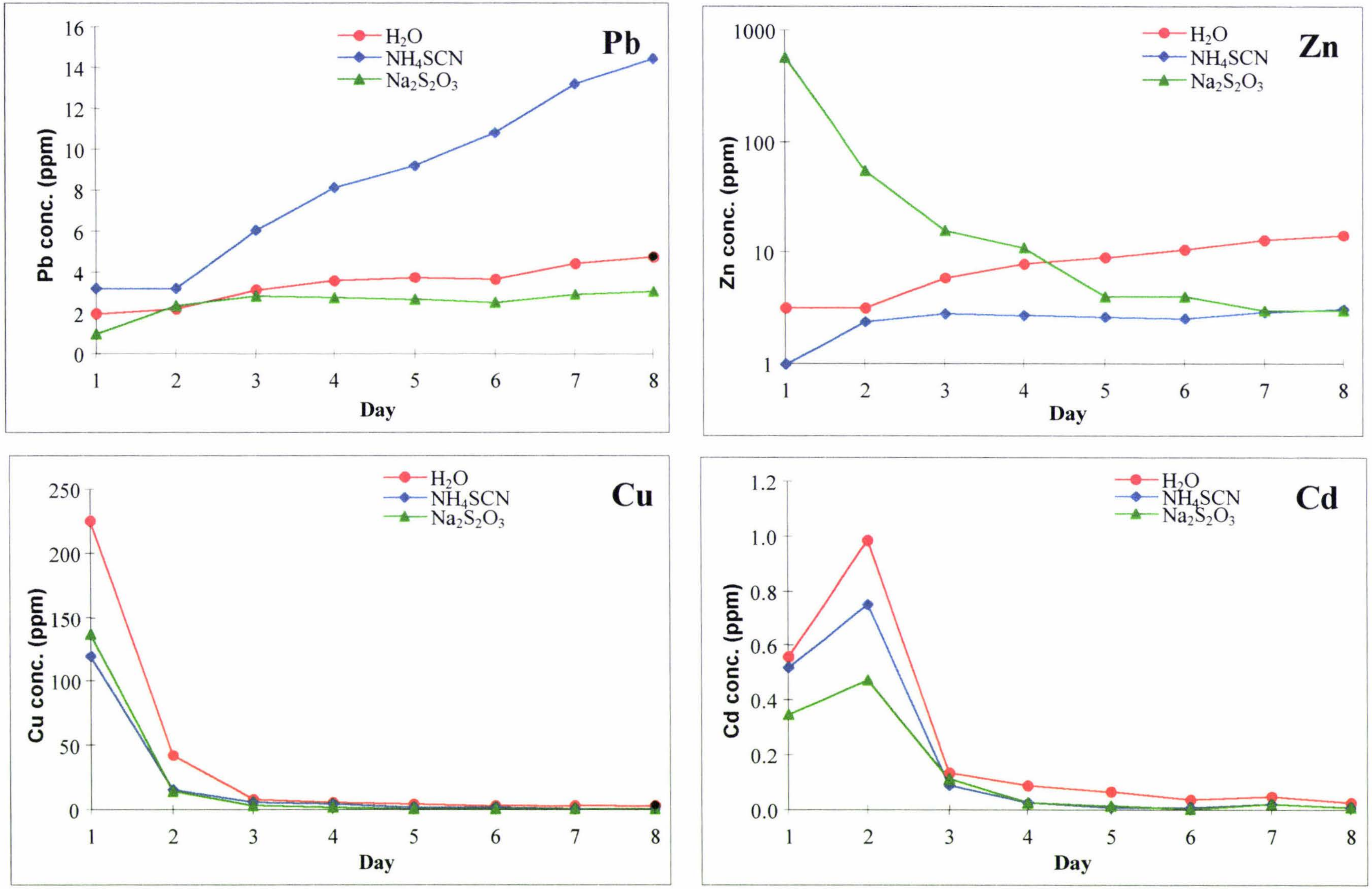

Figure 10. Elution curves for four heavy metals removed from Tui tailing by water, 2g/L ammonium thiocyanate and 2 g/L ammonium thiosulphate.

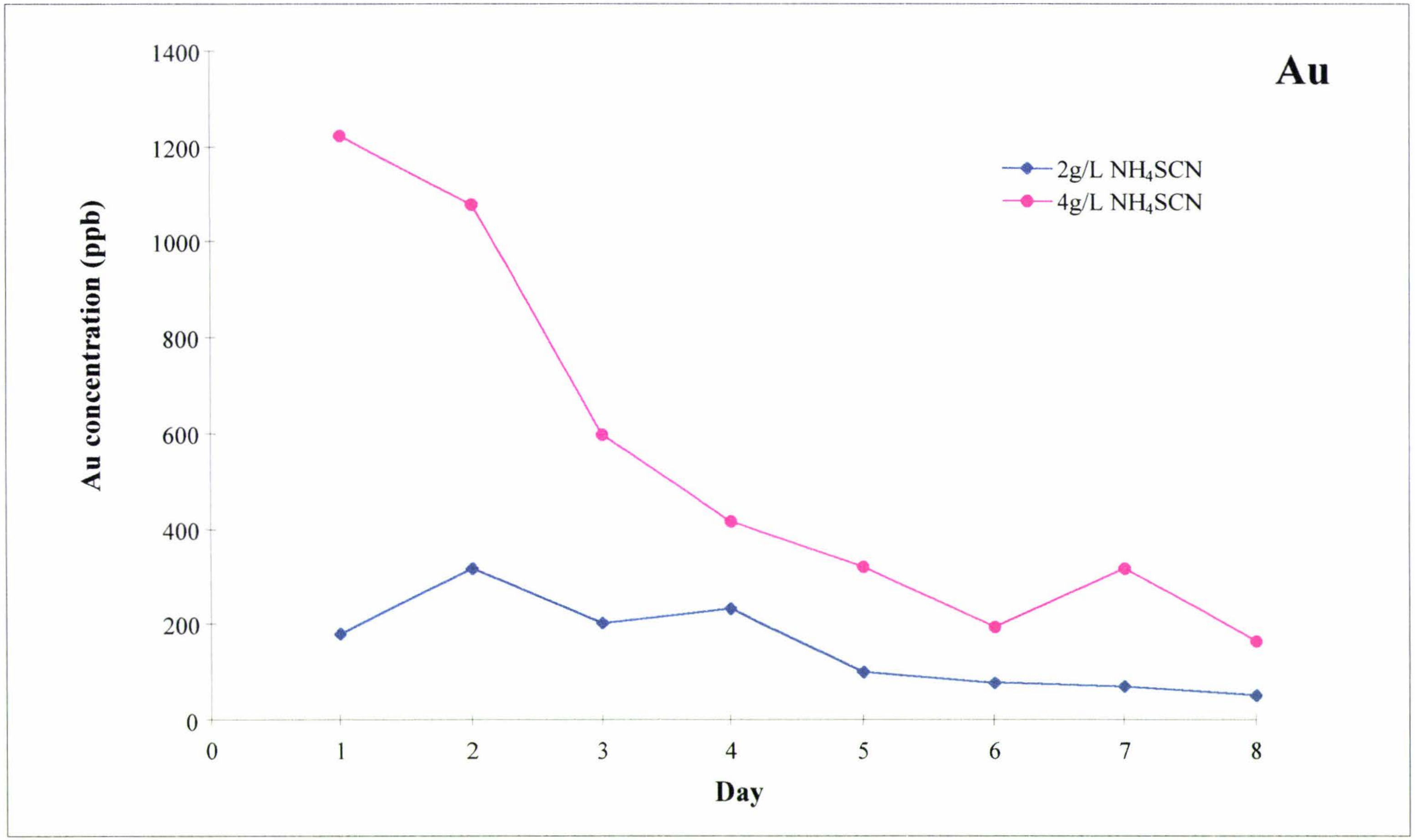

Figure 11. Elution of gold from Tui tailings with two different concentrations of ammonium thiocyanate in the absence of lime.

CHAPTER 6

GOLD AND HEAVY METAL (Zn, Cu, Pb, AND Cd) REMOVAL FROM NATURAL WATERS BY ADSORBING COLLOID FLOTATION

6.1 Abstract

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, moderate cost. It eliminates the difficulties associated with separation of colloidal precipitates, and allows for the use of very large volumes of samples, thus increasing the preconcentration factor. 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) was used as a cationic surfactant, alone or in combination with thiourea (a complexing agent) for removal of gold. The feed concentrations of these reagents were in the range 10 to 70 mg/L (ppm) at various pH values and air flow rates. 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. Gold values reflected the presence of mineralisation in the stream and river samples. The flotation techniques may have some use in hydrogeochemical prospecting for gold.

Laboratory experimental work was carried out for multielement removals of the heavy metals Zn, Cu, Pb, and Cd from a dilute aqueous solutions at different concentrations using different experimental parameters and different systems. The main parameters affecting the flotation process for the heavy metal Zn, Cu, Pb, and Cd were examined. These included reagents (collector, frother, flocculent, etc.), feed concentrations, pH values of the solution, ionic strength, gas flow rate, as applied to the separation of heavy metals from dilute aqueous solutions, and hydrogeochemical or environmental origins. The metal ions Zn^{2+} Cu^{2+}, Pb^{2+} and

Cd^{2+} with different concentrations (50 mg/L, 500 μg/L, 50 μg/L) were removed by the dodecyl sulfate-Na salt (NaDS) and sodium oleate(NaO) system.

The electrolyte tolerance of adsorbing colloid flotation of heavy metal ions (lead, and cadmium) from waste water was improved significantly by use of the $Fe(OH)_3$ +NaLS (Sodium lauryulsulfate) system for lead or the $Al(OH)_3$+ HTMABr (hexadecyltrimethyl-ammonium bromide) system for cadmium.

High quantities of the reagents used for higher feed concentrations, precipitate flotation proved to be better at lower consumption of surfactant. A large excess dosage of surfactant resulted in larger residual concentrations due to the competition between the species and the surfactant ions for the places on the surface of the rising bubbles, so that the degree of separation decreased.

The obove method was applied to a number of natural waters draining the Tui base-metal (Pb, Zn, Cu, and Cd) mine, Te Aroha and Golden Cross gold mine in nearby Waihi. Gold values reflected the presence of mineralisation in the stream and river samples. This method for Zn, Cu, Pb and Cd has clear potential for monitoring environmental pollution of drinking water. It was concluded that separation processes can be utilised to separate the metals Zn, Cu, Pb and Cd or to enrich rare metals such as gold.

6.2 Introduction

Laboratory experimental work was carried out for the removal of gold and each of the heavy metals Zn, Cu, Pb, and Cd from very dilute aqueous solutions of these elements, stream and river waters by using an adsorbing colloid flotation technique for preconcentration.

The determination of gold at very low abundance (<1 μg/L = ppb) has long been a problem in geochemistry. It has to date, been impossible to use gold concentrations in natural waters as a means of geochemical exploration because of this low abundance encountered in such samples. Perhaps one of the most sensitive procedures to emerge during the past 20 years has been a combination of solvent extraction and graphite furnace atomic absorption spectrometry (GFAAS). Brooks et al. (1981) used a combination of extraction with methylisobutyl ketone and GFAAS in which gold was extracted from natural waters as the chlorocomplex after addition of hydrochloric acid to the sample. Using two-litre samples and a two-step extraction system, these authors claimed to be able to detect as little as 0.001 µg/L gold in the sample. The method was however cumbersome and because the distribution ratio (K_d) of gold between the aqueous and organic phases was only 4500, the percentage extraction (E) was only about 95% when gold was extracted from 1 L of water into 10 mL of organic solvent. Zoubolis et al. (1993) have used a flotation procedure to extract gold from thiourea solutions at various pH values and by use of several surfactants such as cetyltriammonium bromide (CTAB) and sodium dodecylsulphate (SDS). They reported recoveries of over 95%. Other workers Galvin et al (1992) and Ghazy (1989) have used other flotation systems for gold recovery but recoveries were only of the order of 80%.

Sabti et al. (1999) have been recently developed a system for adsorbing colloid flotation in order to concentrate gold from natural waters into a very small volume of foam prior to quantification by GFAAS. This technique was used to determine gold at very low concentrations in natural waters draining gold and base-metal mineralisation at Te Aroha. Flotation techniques also eliminated the difficulties associated with separation of colloidal precipitates and allow for the use of very large volumes of samples, thus increasing the preconcentration factor. The extensive literature in this field has been reviewed by Huang, (1992); Grieves (1962, 1975); Grieves et al. (1979); Sebba (1962); Mizuike (1983); Lemlich (1972); Somasundaran (1975); Clarke & Wilson (1983); and Caballero et al. (1987).

The serious health problems presented by environmental contamination with heavy metals have been reviewed elsewhere (Friberg et al. 1971). Numerous techniques have been studied and developed to remove metal ions from aqueous solutions (Patterson & Minear 1975, Huang, 1983). The most common method is chemical precipitation (typically by hydroxide, carbonate, or sulfide compounds), but this often produces troublesome amounts of bulky sludge. Other available techniques include ion exchange, reverse osmosis, and adsorption on activated carbon, but these methods are usually relatively expensive (Leu, 1994). Foam flotation techniques have a distinct advantage by using this method to remove a small volume of the foam layer with high concentrations of the target elements. Laboratory experimental results on batch foam flotation for removal of gold gave dramatic results with very high concentrations of gold in the foam layer as measured by (FAAS) and very low concentrations for the residual, which were below the limit of detection by (GFAAS). Laboratory experiments were also carried out on removal of heavy metals by using different systems and these gave good results for removal of the above metals.

6.3 Methods and Materials

6.3a Definition of terms

K_d = distribution coefficient, given by concentration of gold in foam divided by the concentration of gold in the residual liquid.

E = percentage extraction, given by $100K_d/[K_d + (V_r/V_f)]$ where V_r and V_f are the respective volumes of the residuals and foam after flotation. This equation used to measure E in the case of gold.

Re = percentage recovery or removal, given by $(1- (C/C_o))\times 100$ where C_o is the initial concentration and C the final (Zouboulis et al. 1990). This equation used to measure the Re in the case of heavy-metal.

6.3b Methodology

The process flow diagram is shown in Fig. 12 and is based on the fact that surface-active materials tend to concentrate at the gas-liquid interface. When air is bubbled through the solution, the surface-active material adsorbs on the surface of the rising bubble which then separates it from the solution. If the substance to be removed is not surface-active, it can be made so through union with, or adsorption of, a surface-active material.The experimental equipment consisted of a standard laboratory glass column with a glass frit having a porosity range 20-40 µm fused into its base. A modified PVC U-bend, was used as part of the foam collection unit. Foam passing through a PVC tube attached at the end of the U-bend was collected in a plastic beaker. Air flow rate from the pressure regular was controlled using a rotameter (GGC-Elliot, England). The initial mixing stage had a duration of 10 min with simultaneous pH control. Measurements of pH were made with a digital pH meter and the pH was modified by sulphuric acid or sodium hydroxide. The optimum pH value was found to be 11.0, for gold preconcentration, and for the heavy-metals Zn, Cu, Pb and Cd. The pH was adjusted by the same reagents. A series of experiments was carried out at different pH values. The results are presented in Tables 13, 14 and 15.

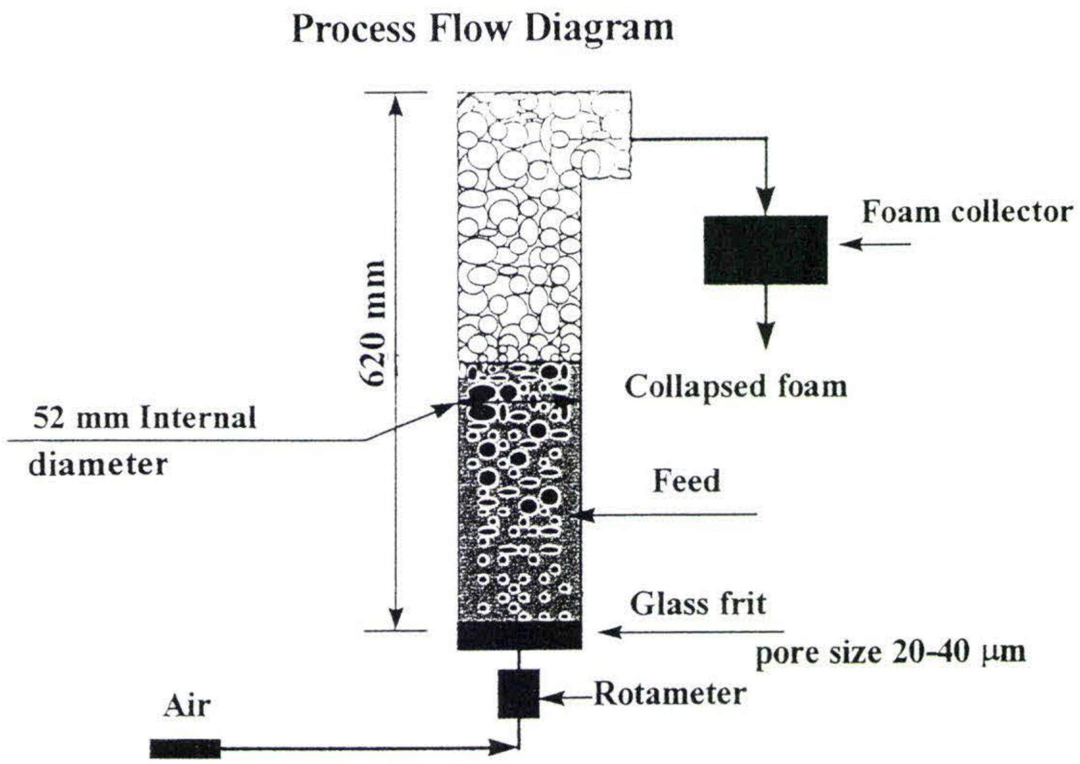

Figure 12. Process flow diagram for removal of gold from feed solutions by adsorbing colloid flotation.

Use was made of cetyltrimethylammonium bromide (CTAB) as a cationic surfactant both with and without added thiourea to act as an additional collecting agent for gold removal. After each experiment, the concentration of gold in the foam layer was determined by flame atomic absorption spectrometry (FAAS) because the levels of gold were high enough for this purpose. Where necessary, the gold concentrations in the residual liquid and the low concentration of gold in the foam were determined by GFAAS that afforded a much higher degree of sensitivity.

Laboratory experiments carried out by using dodecyl sulfate-Na salt (NaDS) and sodium oleate were used as frother and collector for multielement (Zn, Cu, Pb, and Cd) removal. Many runs were made using Fe(III) as effective flocculent and different surfactants (see Table 11 for abbreviations) using different initial feed concentrations (50 mg/L, 50 µg/L and 500 µg/L). Different factors affecting the batch foam flotation system for these metals were: volume of the feed, concentration of the feed, pH, ionic strength, length of the column, air flow rate, type of surfactant and its concentrations. The feed had volumes of 800 mL for low feed concentrations, and 250 mL for high feed concentrations. The duration of the flotation times were 30-45 minutes, and retention times up to 1 h were needed. Air flow rates differ with the concentration of the feed. The foam should be relatively dry as high gas flow rates resulted usually in the formation of large amounts of wet foam, indicating a volume of entrained water, which is difficult to handle.

An important parameter affect the batch foam flotation method is the length of the column. A longer column is required to allow the foam sufficient time to drain before removal from the system in order to obtain dry foam. The required pH is differs with different metals as is shown in Tables 13-15. The pH was adjusted by ($NaOH$ or H_2SO_4) in order to ensure complete precipitation of metal ions with the floc. The pH will determine the sign and the magnitude of the electric charge on a variety of inorganic particulates. Ionic strength adjustment was by use of $NaNO_3$ or Na_2SO_4, and many runs were made using different molarities of $NaNO_3$ or Na_2SO_4 for ionic strength adjustment. The solutions were also stirred for 10 min to allow the reaction to proceed to completion before treatment by foam flotation.

Use of $Fe(OH)_3$ and NaLS (sodium laurylsulfate) improved removal of lead, and using the system $Al(OH)_3$ and HTMABr (hexadecyltrimethylammonium bromide) improved cadmium removal. Minimal concentrations of these surfactant used in the system, resulted in better separation efficiency.

Table 11. Surfactant Abbreviation Key

Cationic Surfactants

HTMABr	Hexadecyltrimethylammonium bromide
(CTAB)	Cetyltrimethylammonium bromide

Anionic Surfactants

NaDS	Sodium dodecylsulfate
NaLS	Sodium laurylsulfate
NaO	Sodium Oleate

6.4 Result and Discussion.

6.4.1a *Effect of pH on removal of gold from the feed*

A series of experiments with pH values of 5, 6, 7, 8 and 11 in the feed was carried out by use of 800 mL of deionised water containing 500 µg/L of gold, 10 mg/L of CTAB and 10 mg/L of thiourea. The air flow rate was 3L/h. The data are shown in Fig. 13. Values of K_d increased from 75 to 46070 as the pH increased from 5 to 11. In the same pH range, E increased from 2 to 95%. The extraction of gold is clearly very pH-dependent and all further experiments were carried out at pH 11.

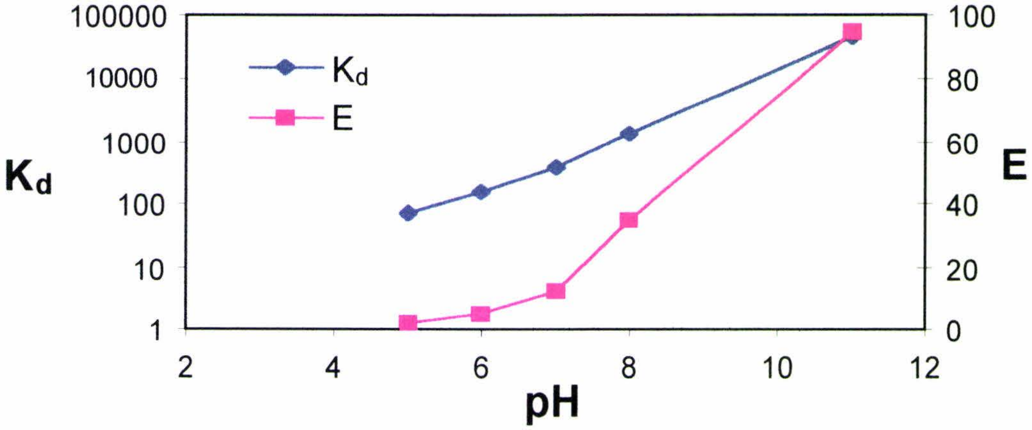

Figure 13. Effect of pH on removal of gold from a feed containing 500 µg/L Au and with 10 mg/L CTAB and thiourea.

6.4.1b. *Effect of air flow rate on removal of gold from the feed.*

The effect of air flow rate is shown in Fig. 14. Conditions were as for Fig. 2 except that the gold concentration in the feed was only 50 µg/L. There is a clear pattern, as might be expected, for a decrease in K_d (from 44,000 to 284) as the flow rate increased from 3 to 15 L/h. The corresponding values for E were 96 to 47%, where E = percentage extraction given by $100K_d/[K_d + (V_r/V_f)]$ where V_r and V_f are the respective volumes of the residuals and foam after flotation.

6.4.1c. *Effect of a CTAB/thiourea mixture on removal of gold from the feed.*

When CTAB (10 mg/L) was used alone, K_d was only 913 (E= 79%). However, a combination of both CTAB and thiourea had a dramatic effect on gold removal from the feed.

This is shown in Fig. 15. For 10 mg/L each of both reagents at pH 11, K_d increased to 46,070. With 20 mg/L and 70 mg/L of each, there was a decrease in K_d to respectively 5000 and 22. For E in the same range, values were 99.9 and 22%. The air flow rate was 0.05 L/min.

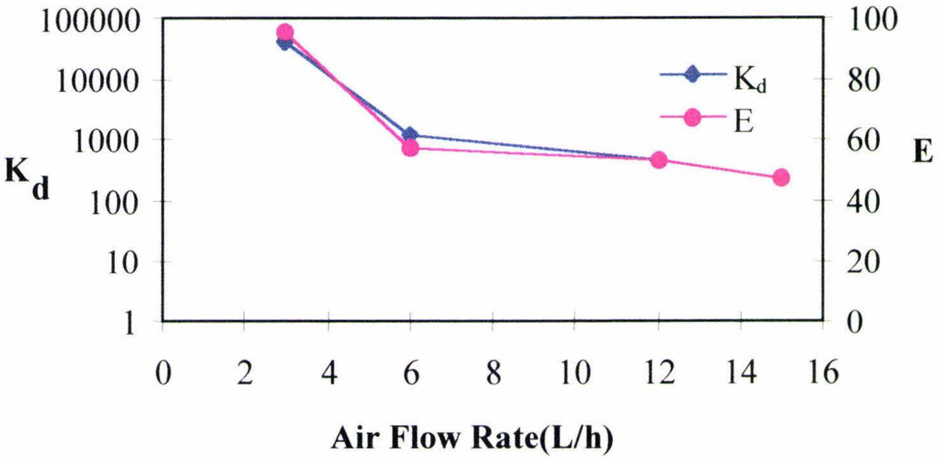

Figure 14. Effect of flow rate on removal of gold from a feed containing 50 μg/L of this element. Conditions as for Fig.13.

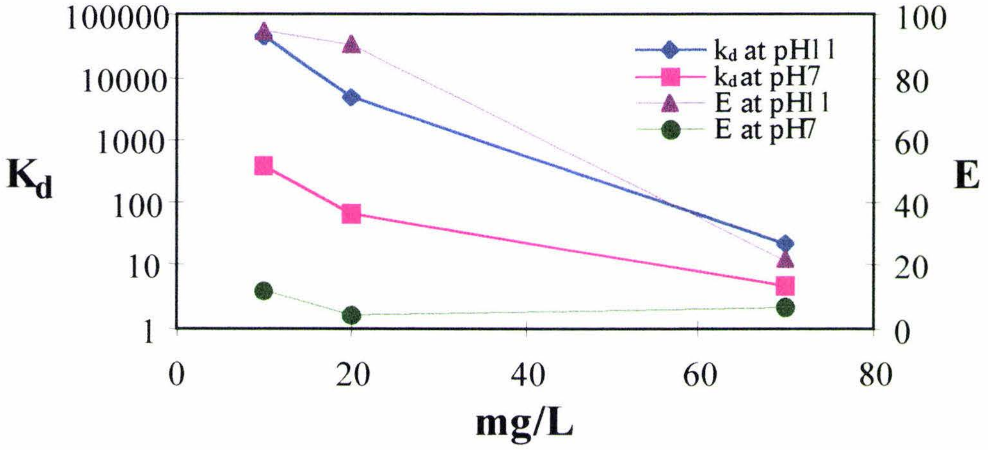

Figure 15. Effect of various mixtures of CTAB and thiourea on removal of 500 μg/L gold from the feed at pH11 and pH7, air flow rate 0.05 L/min.

6.4.1d. *Practical applications of adsorbing colloid flotation for gold.*

Adsorbing colloid flotation was applied to determination of gold at very low abundance in a stream draining a base metal mine at Te Aroha (Tui Stream) and a river (Ohinemuri) draining the Martha and Golden Cross gold mines in nearby Waihi.

Gold was determined in the foam and the residual concentration calculated from knowledge of K_d and the volume of the foam and residual solutions. The pH of the feed was adjusted to 11 before flotation. The data are shown in Table 12. The final column (gold in feed) is the original gold concentration in the stream water supplied as feed for the flotation process.

The high values of gold in sample Oh 3 related to the presence of the Golden Cross mine near the Waitekauri River. The sample was taken a few metres above its confluence with the Ohinemuri River that drains the Martha Gold Mine at Waihi. The lowest gold value (Oh 4) was for a sample taken from the Ohinemuri River about 500 metres downstream from its confluence with the Waitekauri River.

Table 12. Gold in natural waters (μg/L) as determined by adsorbing colloid flotation

Site	Foam vol (mL)	Au in foam	Resid. vol (mL)	Au in residue	Au in water
Tui 3	0.4	425	249.6	0.09	0.68
Oh 1	0.8	1,266	799.2	0.08	1.26
Oh 2	0.8	1,324	399.2	0.04	2.64
Oh 3	0.5	116,000	799.5	2.52	75.0
Oh 4	0.7	755	799.3	0.03	0.69

The following is a worked example to explain the calculation for Tui 3 above. This is based on a distribution coefficient for gold of 46 000 as measured from the experiments on Figures 14 & 15.

425 μg/L gold in 0.4 mL foam

425/ 46000 = 0.0092 μg/L in 249.6 mL residual after flotation

Total gold in the foam = 0.4 × 425 = 170 ng

Total gold in the residual = 0.009×249.6 = 2.246 ng

Total gold in the system = 170 +2.24 = 172.24 ng

The water originally contained 172.24/ 250 = 0.68 ng/mL = 0.68 μg/L

6.4.2. Results and discussion for heavy-metal (Zn, Cu, Pb and Cd) removal.

"Re" the percentage recovery or removal, is given by$(1- (C/C_o))\times100$ where C_o is the initial concentration and C the final (Zouboulis, et al, 1990). Laboratory experiments were carried out by using dodecyl sulfate-Na salt (NaDS) and sodium oleate as frother and collector for multielement (Zn, Cu, Pb, and Cd) removal. Many runs were made using Fe(III) as effective flocculent by using different initial feed concentrations (50 mg/L, 50 μg/L and 500 μg/L). The best removal percentage was for a feed concentration of 50 mg/L. The best removal percentage for zinc and copper was by use of NaDS and NaO. Use of $Fe(OH)_3$ and NaLS (sodium laurylsulfate) improved the lead removal, and using the system $Al(OH)_3$ and HTMABr (hexadecyltrimethylammonium bromide) improved the cadmium removal percentage.

6.4.2a. *Removal of heavy metals (Zn, Cu, Pb and Cd) from a feed concentration of 50 mg/L.*

The effect of various surfactants on concentrations of metals in the residue and percentage of metal removed from a feed concentration of 50 mg/L is shown in Table 13.

A series of experiments was carried out in which feed concentrations of 50 mg/L for four heavy metals were used with different surfactants and with different concentrations by using Fe (III) as flocculent for a feed volume 250 mL. After a series of trials with different pH values, pH 9 was found to be the optimum. Higher concentrations of metals using a low air flow rate (3L/h), improved removal of the heavy metals and obtained a dry foam layer. The best removal for zinc and copper was by use of NaDS and NaO, and the best removal percentage for lead was by use of $Fe(OH)_3$ and NaLS. The best removal percentage for cadmium was by $Al(OH)_3$ and HTMABr.

6.4.2b. *Removal of heavy-metals (Zn, Cu, Pb and Cd) from a feed concentration of 500μg/L.*

The effect of various surfactants on concentrations of metals in the residue and the percentage of metals removed from feed concentrations 500 μg/L (ppb) is shown in Table 14. This series of experiments was carried out on a feed volume 250 mL for the four metals.

Presented values are for the best removal percentage and lowest concentration for the residual by using pH 8.5, air flow rate 6 L/h, and a flotation duration time 30-45 minutes.

Table 13. Removal of heavy-metals (Zn, Cu, Pb and Cd) from a feed concentration of 50 mg/L

Element	Surfactant type, conc. (mg/L)	Ionic strength adjustment (M)	Residual Conc. (mg/L)	Removal (%)
Zn	NaDS(40),NaO(10)+ Fe(III) (100)	$NaNO_3$(1.5 M)	1.7	96.6
	NaLS(100)+$Al(OH)_3$ (100)	$NaNO_3$(0.05 M)	3	94
Cu	NaDS(20),NaO(10)+ Fe(III)(100)	Na_2SO_4(0.6 M)	2.3	95.4
	NaLS(100)+$AL(OH)_3$ (100)	$NaNO_3$(0.05 M)	26	48
Pb	NaDS(60),NaO(10)+ Fe(III)(100)	$NaNO_3$(1.5 M)	2.47	95
	$Fe(OH)_3$(100)+NaLS (30)	$NaNO_3$(0.02 M)	0.15	99.7
Cd	NaDS(90), NaO(20) + Fe(III) (30)	$NaNO_3$(0.1 M)	0.65	93.5
	$Al(OH)_3$(10)+HTMABr (50)	$NaNO_3$(0.01 M)	0.07	99.3

Table 14. Removal of heavy-metals (Zn, Cu, Pb and Cd) from a feed concentration of 500 μg/L

Element	Surfactant type, conc. (mg/L)	Ionic strength adjustment (M)	Residual conc. (mg/L)	Removed (%)
Zn	NaDS(20),NaO(10) +Fe(III)(20)	$NaNO_3$(0.02 M)	0.07	86
	HTMABr(30)+ $Al(OH)_3$ (20)	_	0.3	40
Cu	NaDS(20),NaO(10) + Fe(III)(20)	Na_2SO_4(0.01 M)	0.1	80
	HTMABr(30), $Al(OH)_3$ (20)	_	0.23	54
Pb	NaDS(20), NaO (10)+ Fe(III) (20)	$NaNO_3$(0.01 M)	0.214	58
	HTMABr(30)+ $Al(OH)_3$ (20)	_	0.15	70
	$Fe(OH)_3$(20)+NaLs (10)	$NaNO_3$(0.02 M)	0.05	90
Cd	NaDS(20),NaO(10) + Fe(III) (10)	$NaNO_3$(0.02 M)	0.16	68
	$Fe(OH)_3$ (20)+ NaLS(10)	$NaNO_3$(0.01 M)	0.1	80
	HTMABr(30)+ $Al(OH)_3$ (10)	_	0.035	93

6.4.2c. *Removal of heavy-metals (Zn, Cu, Pb and Cd) from a feed concentration of 50µg/L.*

The effect of various surfactants on concentrations of metals in the residue and percentage of metals removed from feed concentrations of 50 µg/L (ppb) are shown in Table 15 . Using 20 mg/L of NaDS and 10 mg/L NaO gave a good removal of zinc and copper 90%, 86% respectively), but a lower removal percentage for the other metals. Other conditions were pH 7.5, feed volume 800 mL, air flow rate 15 L/h, flotation duration time 45 minutes, and use of 0.01 M $NaNO_3$ for ionic strength adjustment.

Table 15. Removal of heavy-metals (Zn, Cu, Pb and Cd) from a feed concentration of 50 µg/L.

Element	Surfactant type, conc. (mg/L)	Ionic strength adjustment (M)	Residual conc. (mg/L)	Removal (%)
Zn	NaDS(20),NaO(10) +Fe(III)(10)	$NaNO_3$(0.01 M)	0.005	90
	NaLS(10)+AL$(OH)_3$ (20)	$NaNo_3$ (0.01 M)	0.03	40
Cu	NaDS(20),NaO(10) + Fe(III)(10)	Na_2SO_3(0.01 M)	0.007	86
	NaLS(10)+AL$(OH)_3$ (20)	$NaNO_3$(0.01 M)	0.037	26
Pb	NaDS(20),NaO(10) + Fe(III)(10)	$NaNO_3$(0.01 M)	0.012	76
	HTMABr(10) +Al$(OH)_3$(10)	_	0.006	87.6
	Fe$(OH)_3$(30)+NaLS (10)	_	0.0045	91
Cd	NaDS(20), NaO(10)+ Fe(III) (10)	$NaNO_3$(0.01 M)	0.02	60
	Fe$(OH)_3$(30)+ NaLS (10)	_	0.009	82
	HTMABr(10)+ Al$(OH)_3$(10)	_	0.005	90

6.4.2d. *Effect of surfactant concentration on the cadmium residual concentration and its percentage removal*.

There was a clear pattern for an increase in percentage removal (up to 99%), and decreasing values for the residual concentrations with decreasing surfactant (NaDS and NaO) concentrations in the presence of Fe(III) 30mg/L and 0.1 M $NaNO_3$ for ionic strength adjustment on the cadmium feed concentration of 10 mg/L. Other conditions were air flow rate 0.05 L/min, feed volume 250 mL, pH 10.5. The results are shown in the Table 16.

Table 16. Effect of surfactant concentration on the cadmium residual concentration and percentage removal from a feed concentration of 10 mg/L.

Surfactant Conc. (mg/L)	Residual conc. (mg/L)	Removal (%)
NaDS(200),NaO(60)	4.7	53
NaDS(140), NaO(40)	2.6	74
NaDS(90), NaO(20)	0.1	99

6.4.2e. *Effect of pH on the cadmium residual concentration and its percentage removal*.

A few experiments on cadmium feed concentrations were carried out by use of 800 mL of deionised water containing 500 μg/L of cadmium, 20 mg/L of NaDS and 10 mg/L of NaO in the presence of Fe(III) 20 mg/L and (0.01 M) $NaNO_3$ for ionic strength adjustment. The air flow rate was 15 L/h. The data are shown in Table 17. The removal percentage increased to 86% as the pH increased to 9 and the corresponding values for residual concentrations decreased.

Table 17. Effect of pH on the cadmium residual concentration and its percentage removal from a feed concentration of 500 μg/L.

Cd conc. (μg/L)	pH	Residual conc.(μg/L)	Removal (%)
500	3.5	445	9
500	7.5	290	42
500	9	70	86

6.4.2f *Practical applications of adsorbing colloid flotation for heavy-metals (Zn, Cu, Pb and Cd).*

Adsorbing colloid flotation was applied for separation of heavy-metals from the Tui (Tui) and Tunakohoia Streams (Tk) draining the base-metal mine at Te Aroha. The best removal of zinc and copper was with NaDS and NaO in the presence of Fe(III) as flocculent. The dosage of Fe(III) differed with the concentration of the metals in the feed. The best removal for cadmium and lead was with HTMABr and $Al(OH)_3$, with an air flow rate of 3L/h for high feed concentrations, and 15L/h for low feed concentrations. In Tk-6, the surfactant concentration was sufficient for removal of copper, but not enough for removal of zinc. The pH of the feed was adjusted before flotation. The data are shown in Table 18.

Table 18. Application of adsorbing colloid flotation to the removal of heavy-metals (Zn,Cu, Pb and Cd) From waters draining the Tui base metal mine at Te Aroha.

Site	Element, initial conc. (µg/L)	Surfactant types, conc. (mg/L)	Residual (µg/L)	Removal (%)
Tui-3	Zn (46400)	NaDS(40), NaO(10)+ Fe(III) (100)	700	98.5
	Cu (570)		300	47.4
	Pb (649)	HTMABr(20)+ $Al(OH)_3$(10)	50	93
	Cd (272)		35	88
Tui-5	Zn (57600)	NaDS(40), NaO(20)+ Fe(III) (100)	600	99
	Cu (570)		75	86.9
	Pb (426)		60	86
	Cd (286)		130	55
TK-1	Zn (2740)	NaDS(30), NaO(10)+ Fe(III) (40)	74	97.3
	Cu (40)		10	75
	Pb (1)		n.d	n.d
	Cd (4.5)		n.d	n.d
TK-2	Zn (14000)	NaDS(30), NaO(10)+ Fe(III) (30)	340	97.6
	Cu (30)		24.4	19
	Pb (15)		13.9	10
	Cd (80)		15.2	15.6
Tk-3	Zn (13000)	$Al(OH)_3$(10)+ HTMABr (10)	12000	8
	Cu (13)		3.15	76
	Pb (0.09)		n.d	n.d
	Cd (60)		9.5	84.2
Tk-6	Zn (11300)	NaDS (30), NaO(10)+ Fe(III) (20)	1500	86.8
	Cu (310)		32	89.7
	Pb (23.35)		22..33	5
	Cd (73)		35.6	52
Tk-10	Zn (530)	NaDS(20), NaO(10)+ Fe(III) (20)	0.05	90.6
	Cu (17)		n.d	n.d
	Pb (0.1)		n.d	n.d
	Cd (1.8)		n.d	n.d

CHAPTER 7

CONCLUDING SUMMARY

Conclusions arising from this study can be summarised as follows:

Sediments from the Tui and Tunakohoia Streams draining mineralisation near the Tui Mine still contain significant levels of heavy minerals in their upper reaches and heavy metals continue to leach from these minerals into streams waters. These will continue to supply heavy-metal contamination to these waters.

The upper reaches of the Tui and Tunakohoia Streams have heavy-metal concentrations above the limits set for potable waters. Neither will be a suitable supply source for domestic water supply.

Discharge of the Tui and Tunakohoia Streams into the Waihou River has not had an appreciable effect on the water quality of this waterway. Arsenic concentrations are, however, somewhat higher, or close to, the recommended maximum concentration for potable water.

Gold and other heavy metals are detectable in the Waitekauri and Ohinemuri Rivers draining gold mines in the Waihi area. Very high relative accumulation of heavy metals in aquatic macrophytes in the Waihou, Ohinemuri and Waitekauri Rivers points to the possibility of using these plants as bioindicators of heavy-metal contamination of waters.

Detection of gold in aquatic macrophytes in the Ohinemuri and Waitekauri Rivers draining existing and abandoned gold mines, suggests that these plants could be useful biogeochemical indicators of gold mineralisation. Uptake values for plants sampled from the Waihou river were: 16 mg/L for cadmium in *Egeria dense*, 68 mg/L for lead in *Potamogeton crispus*, 200 mg/L for copper in *Elodea canadensis*. 1490 mg/L for zinc in *Myriophyllum aquaticum*, 8 mg/L for arsenic and 42 mg/L for mercury in *Myriophyllum aquaticum. Egeria densa* from the Ohinemuri and Waitekkauri Rivers (site 2 and 3 in the inset to Fig. 2) contained respectively 302 and 672 μg/L gold in the dry matter.

Chemical treatments of Tui tailings by use of two reagents (ammonium thiocyanate, and ammonium thiosuphate) indicated that thiosulphate removed inordinately high amounts of zinc at low pH (2.33), and thiocyanate was highly selective for removal of gold at pH 2.42, compared with cadmium, copper, lead and zinc. With addition of lime to give a pH of 7, the extraction with the two reagents decreased to less than 50%. The two reagents have low toxicity, and are readily broken down in the environment.

Treatment of waters from the rivers and streams by adsorbing colloid flotation technique gave dramatic results for the gold pre-concentration by using the cetyltrimethylommonium bromide (cationic surfactant) and thiourea (complexing agent) system, and good results for the heavy metal (Zn, Cu, Pb and Cd) removal with different systems by changing different parameters for different feed concentrations.

The limit of detection for gold in the foam layer was of the order of 2 µg/L. Assuming a foam volume of 1 mL and feed volume of 800 mL, this would equate to a limit of detection of 2.5 ng/L (ppt). It has been shown that aquatic plants such as *Egeria densa* contained 302 and 672 µg/kg of gold at sites Oh 2 and Oh 3 respectively. The sediment at Oh 2 contained 163 µg/kg of gold. The high values for gold in natural waters from the Ohinemuri River are reflected in the inordinately high values obtained for sediments and aquatic vegetation.

It is concluded that adsorbing colloid flotation has potential for determining gold concentrations in natural waters as a means of hydrogeochemical prospecting for this element. The recent dramatic rise in the price of gold should encourage such prospecting in the future. The method is quick, simple and inexpensive and should have applications for many elements other than gold, such as the platinum group metals and heavy metals such as cadmium, copper, lead and zinc. For heavy metals such as cadmium, copper, lead and zinc, the method has clear potential for monitoring environmental pollution.

REFERENCES

Adams G.J.D., Wodzicki A. and Weissberg B.G. 1974. K-Ar dating of hydrothermal alteration at Tui Mine, Te Aroha, New Zealand. *New Zealand Journal of Science* 17: 193-199.

Anderson C.W.N., Brooks R.R., Stewart R.B. and Simcock R. 1998. Harvesting a crop of gold in plants. *Nature* 395, 553-554.

Anderson C.W.N., Brooks R.R., Stewart R.B., Msuya F.A., and Sabti H. 1999. Growing a Crop of Gold, in Palmerston North Conference 1999: *Geological Society of New Zealand Miscellaneous Publication 107A.*

Brady J.E. and Humiston G.E. 1982. *General Chemistry - Principles and Structures*, 3rd edn. Wiley, New York.

Brathwaite R.L. 1981. Size patterns of gold-silver deposits in the Hauraki Goldfield, Coromandel Peninsula. *Proceedings of Australasian Institute of Mining and Metallurgy Conference*. (NZ Branch):11p.

Brathwaite R.L., Christie A.B. and Skinner D.N.B. 1987. The Hauraki Goldfield - regional setting, mineralisation and recent exploration. In: (Kear,D. ed.) *Mineral Deposits of New Zealand*. Australasian Institute of Mining and Metallurgy, Melbourne, 45-56.

Brathwaite R.L. and Christie A.B. 1996. Geology of the Waihi Area. Institute of Geological and Nuclear Sciences Limited, Lower Hutt, New Zealand. Geological Map 21. Scale 1: 50 000.

Blaiklock K. 1981. The environmental impact of mining. *New Zealand Environment* 29: 616.

Boyle R. W. 1979. The Geochemistry of Gold and its Deposits (together with a chapter on geochemical prospecting for the element). *Canadian Geological Survey*, Bulletin # 280.

Bradshaw A.D. and Chadwick M.J. 1980. The Restoration of land. *The Ecology and Reclamation of Derelict and Degraded Land.* Studies in Ecology Volume 6. Blackwell, Oxford.

Brathwaite R.L., Christie A.B. and Skinner D.N.B. 1987. The Hauraki Goldfield - regional setting, mineralisation and recent exploration. In: (Kear,D. ed.) *Mineral Deposits of New Zealand.* Australasian Institute of Mining and Metallurgy, Melbourne, 45-56.

Brooks R.R., Chatterjee A.K. and Ryan D.E. 1981. Determination of gold in natural waters at the parts-per-trillion level (pg. cm^{-3}) level, *Chemical Geology.* **33**pp. 163-169.

Brooks R.R., Anderson, C.W.N., Stewart, R.B. and Robinson, B.H. 1999. Growing a crop of a metal. *Biologist* 46: 201-205.

Brown J..M.A. 1977. The physiology, ecology and succession of lake weeds with respect to increasing nutrient in N.Z. lakes. Paper presented to a symposium on lake weed: Friend or Foe? Nature conservation council, Hamilton, 29 July .

Caballero M., Lopez R., Cela R. and Perez-Bustamante J.A. 1987. Preconcentration and determination of metals in synthesic sea water by flotation with inert organic collectors, *Analytica Chimica Acta*, 196, 287.

Callahan J. 1987. A non toxic heavy liquid and inexpensive filters for separation of mineral grains. *Journal of Sedimentary Petrology* 57: 765-766.

Carter L. and Pharo C.H. 1965. The Tui Mine, Te Aroha. *Tane* 2: 55-59.

Christie A.B. and Brathwaite R.L. 1986. Epithermal gold-silver and porphyry copper deposits of the Hauraki Goldfield- a review, in *Guide to the Active Epithermal (Geothermal) Systems and Precious Metal Deposits of New Zealand*, (Eds. R. W. Henley, J.W. Hedenquist and P.J. Roberts) Monograph Series on Mineral deposits No. 26: 129-145, (Gebrüder Borntraeger: Berlin).

Christie. A.B. and Robinson,B.W. 1992. Regional sulphur isotope studies of epithermal Au-Ag-Pb-Zn-Cu deposits in the Hauraki Goldfield, South Auckland. *New Zealand Journal of Geology and Geophysics* 35: 145-15.

Clarke A.N. and Wilson D.J. 1983. *Foam Flotation: Theory and Applications*, Marcel Dekker, New York.

Cochrane R.H.A. 1969. *Geology of the Tui Mine, Mt. Te Aroha*. MSc. Thesis, University of Auckland, New Zealand.

Cole J.W. and Lewis K.B. 1981. Evolution of the Taupo-Hikurangi Subduction System. *Tectonophysics* 72: 1-21.

Courtney S. F., King p. and Rodgers K.A. 1990. A Check List of Minerals from the Tui Mine, Te Aroha, New Zealand. *New Zealand Natural Sciences* 17: 95-98.

Denny P. 1972. Sites of nutrient absorption in aquatic macrophytes. *Journal of Fcology.* 60: 819-29.

Friberg L.T. 1971. *Cadmium in the Environment*, CRC press, Cleveland.

Fyson H. 1991. The Tui Comes Home to Roost. *Terra Nova* September: 41-44.

Galvin K.P. Nicol S.K. and Waters A.G. 1992.Selective ion flotation of gold. *Colloids and Surfaces* 64, pp. 21- 33.

Ghazy S.E., El. Tanbouly M.A. and Kenawy I.M. 1989. Flotation of gold from aqueous solutions and natural waters. *Arabian Journal of Science and Engineering.* **14**: 459-462.

Grieves R.B. 1970. Foam Separation Processes. *Journal of Water Pollution.*. 42, 336.

Grieves R. B. 1975. Foam separation, *Chemical Engineering Journal.* 9. 93.

Grieves R.B., Walkowiak.W. and Bhattacharyya.D. 1979. Foam fractionation selectivity sequences of quaternary ammonium surfactants for simple and complex anions: areview, in *In Recent Development in Separation Science*, volume 5, lin, N.N.,Schultz J.S. Dranoff J.S. and Somasundaran P.,Eds.;CRC Press: Boca Raton

Henderson J. and Bartrum J.A. 1913. *The Geology of the Aroha subdivision, Hauraki, Auckland.* In: *New Zealand Geological Survey Bulletin* 16, government Printers, Wellington.

Hillel D. 1992. *Out of the Earth: Civilization and the life of the Soil.* University of California Press, Los Angeles.

Hochstein M.P. and Nixon I.M. 1979. Geophysical study of the Hauraki Depression, North Island, New Zealand. *New Zealand Journal of Geology and Geophysics* 22: 1-19.

Huang S.D. 1992. Flotation. *In Preconcentration Techniques for Trace Elements*, Z.B. Alfassi and C. M. Wai (eds), CRC press, Boca Raton, pp. 276-299.

Huang J.C. 1983. An innovative coprecipitation technique for removing heavy metals, EPA Report 600/2-28-053, US EPA, Cincinnati, Ohio.

Hung C. H. and Pavlostathis S.G. 1997. Arobic degradation of thiocyanate. *Water Research*. 31: 2761-2770.

Hunt T. M. and Syms M.C. 1977. *Magnetic Map of New Zealand, 1:250 000,Total Force Anomalies*. Sheet 3. Auckland.

Johnson P. N. 1998. *Wetland Plants in New Zealand*. Lincoln, Canterbury, New Zealand.

Lemlich R. 1972. Adsubble methods, *In Recent Development in Separation Science*, Volume 1, Li, N. N., Ed., CRC Press, Cleveland.

Leu M.H., Chang J.E. and Ko M.S. 1994. Removal of heavy metals from a chelated solution with electrolytic foam separation. *Separation Science and Technology*, 29: 2245-2261.

Livingston M.E. (ed). 1987. *Preliminary studies on the Effects of Past Mining on the Aquatic Environment*, Coromandel Peninsula. Water & Soil Miscellaneous Publication No. 104. Water and Soil Directorate, Ministry of Works, Wellington, New Zealand.

Main J.V. 1979. Precious metal bearing veins of the Maratoto-Wentworth area, Hauraki Goldfield, New Zealand. *New Zealand Journal of Geology and Geophysics* 22: 41-51.

Mason R. 1975. The macrophytes In ,Jolly, V.H. and Brown, J.M.A.,(eds.) *New Zealand lakes*. Oxford University Press, 231.

McGrath T. 1973. State holds key to fate of Te Aroha mine. *New Zealand Herald* 21/11/73.

Merck Catalogue. 1999. Chemicals Reagents. Merck KGaA, Darmstadt, Germany.

Mizuike A. 1983. *Enrichment Technique for Inorganic Trace Analysis*, Springer-Verlag, New York, Chapter 10.

Morrell W.J., Gregg P.E.H., Bolan N. and Horne D. 1995. Potential for revegetating base-metal tailings at the Tui mine site, Te Aroha, New Zealand. *Proceedings of the 1995 PACRIM Congress 19-22 November.* Australasian Institute of Mining and Metallurgy, Carlton, Australia.

Morrell W.J. 1997. *An Assessment of the Revegetation Potential of Base Metal Tailings from the Tui Mine, Te Aroha, New Zealand.* PhD Thesis, Massey University, Palmerston North, New Zealand.

Msuya F. A., Anderson C.W.N., Brooks R.R. and Sabti H. 2000. Environmental consequences of chemically induced phytomining for gold. *Journal of Geochemical Exploration* (in press).

Msuya F. A., Brooks R.R. and Anderson C.W.N. 2000. Chemically induced uptake of gold by root crops: its significance for phytomining. *Gold Bulletin.* (in press).

New Zealand Ministry of Health. 1995. *Standards for Potable Water.* New Zealand Ministry of Health, Wellington.

Norpac Mining Ltd. (undated) Tui Base Metal Mine & Mill. Publicity Pamphlet (c. 1970).

Outridge P.M. and Noller B.N. 1991. Accumulation of toxic trace elements by freshwater vascular plants. *Reviews of Environmental Contamination and Toxicology 121*:63.

Pang L. 1992. *A Hydrogeological Study of Heavy Metal Contamination in the Groundwater of the Te Aroha Area.* University of Waikato, Hamilton.

Pang L. 1995. Contamination of groundwater in the Te Aroha Area by heavy metals from an abandoned mine. *New Zealand Journal of Hydrology 33*: 17-34.

Park. J. 1893. On the occurance of some rare minerals in New Zealand. *Transactions and Proceedings of the New Zealand Institute* 26: 365-367.

Park. J. 1910. *The Geology of New Zealand: an Introduction to the Historical, Structural and Economic Geology*, Whitcombe and Tombs, Wellington, 488pp.

Patterson J. W. and Minear R. A. 1975. *Heavy Metals in the Aquatic Environment* (P. A Krendel, Ed.), Pergamon press, Oxford.

Reeves R.D. and Brooks R.R. (1978). *Trace Element Analysis of Geological Materials.* New York, Wiley- Interscience. 402p.

Ritcey G.M. 1989. *Tailings Management- Problems and Solutions in the Mining Industry*, vol 6. Elsevier, Amsterdam.

Robinson B.W. 1974. The origin of mineralisation at the Tui Mine, Te Aroha, New Zealand in light of stable isotope studies. *Economic Geology* 69: 910-925.

Robinson B.H. 1994. *Pollution of the Aquatic Biosphere by Arsenic and other Elements in the Taupo Volcanic Zone*. MSc Thesis, Massey University, Palmerston North, New Zealand.

Robinson B.H.,Outred H.A., Brooks R.R. and Kirkman, J.H. 1995. The distribution and fate of arsenic in the Waikato river system, North Island, New Zealand. *Chemical Speciation and Bioavailability* 7: 89-96.

Sabti H., Hossain Md.M., Brooks R.R. and Stewart R.B. 2000. The current environmental impact of base-metal mining at the Tui Mine, Te Aroha, New Zealand. *Journal Royal Society of New Zealand* (in press).

Sabti H., Hossain Md. M., Brooks R.R and Stewart R.B. 1999. Selective removal of gold from natural waters by adsorbing colloid flotation, Massey university, Palmerston North, 2nd Annual Postgraduate Colloquium, Institute of Natural Resources.

Sabti H., Brooks R.R., Stewart R.B. and Hossain Md. M. 1999. Distribution of heavy metals, including gold, in the Hauraki goldfield area, in *Proceedings of Conference of the Geological Society of New Zealand* Miscellaneous Publication 107A.

Salmon J. H. M. 1963. *A History of Gold-Mining in New Zealand*. Government Printer, Wellington.

Schofield J.C. 1967. Sheet 3-Auckland. "Geological map of New Zealand 1: 250,000", Department of Scientific and Industrial Research, Wellington.

Sebba F. 1962. *Ion Flotation*; Elsevier: New York.

Skinner D.N.B. 1986. Neogene Volcanism in the Hauraki Volcanic Region. *In*: Smith I.E.M. (ed) Late Cenozoic volcanism of New Zealand. *Bulletin of the Royal Society of New Zealand*, 23.

Somasundaran. P. 1975. Separation using foaming techniques. *Separation Science*. 10. 93.

Tay K.A. 1980. *Geochemistry and Environmental Impact of Discharge of Heavy Metals from the Tui Mine and its Tailings.* MSc Thesis. University of Waikato. Hamilton. New Zealand.

Tonkin and Taylor. 1974. Hauraki Catchment Board Stability Study of Norpac Mine Tailing Dam. Unpublished report prepared for the Hauraki Catchment Board. Te Aroha. New Zealand.

Ward N.I., Brooks R.R. and Reeves R.D. 1976. Copper, cadmium, lead and zinc in soils. stream sediments. waters and vegetation around the Tui Mine. Te Aroha. *New Zealand Journal of Science 19*: 81-89.

Ward N.I., Brooks, R.R. and Roberts, E. 1977. Contamination of a pasture by a New Zealand base-metal mine. *New Zealand Journal of Science 20*: 413-419.

Weissberg B.G. and Wodzicki A. 1970. Geochemistry and hydrothermal alteration and origin of sulphide mineralisation at the Tui mine, Te Aroha, New Zealand. *New Zealand Journal of Science 13*: 36-60.

Whitton J.S. and Churchman G.J. 1987. Standard Methods for Mineral Analysis of Soil Survey Samples for Characterisation and Classification in NZ Soil Bureau. NZ Soil Bureau Scientific Report 79. NZ Soil Bureau, Department of Scientific and Industrial Research, Lower Hutt.

Williams G.J. 1965. *Economic Geology of New Zealand*, vol 4. Australasian Institute of Mining & Metallurgy, Melbourne.

Wodzicki A. and Weissberg B.G. 1970. Structural Control of Base Metal Mineralisation at the Tui Mine, Te Aroha, New Zealand. *New Zealand Journal of Geology and Geophysics* 13: 610-630.

World Health Organisation (1984a) *Guidelines For Drinking-Water Quality*, Vol 1.World Health Organisation, Geneva.

World Health Organisation (1984b) *Guidelines for Drinking-Water Quality*, vol 2. World Health Organisation, Geneva.

Wu X. and Liang S.C. 1990. Enrichment of trace amounts of gold, silver, palladium and platinum by precipitate flotation. *Fresenius Journal of Analytical Chemistry* 336: 120-123.

Zouboulis A.I., Kydros K.A. and Matis K.A. 1993. Recovery of gold from thiourea solutions by flotation. *Hydrometallurgy* 34: 79-90.

Zouboulis A.I., Matis K.A. and Stalidis G. A. 1990. Parameters influencing flotation in removal of metal ions. *Environmental Studies* 35: 183-196.