Pollution of the Aquatic Biosphere by Arsenic and other Elements in the Taupo Volcanic Zone

A thesis presented in partial fulfilment
of the requirements for the degree of Master
of Science in Biology at Massey University

Brett Harvey Robinson
1994

Massey University
New Zealand

Abstract

An introduction to the Taupo Volcanic Zone and probable sources of polluting elements entering the aquatic environment is followed by a description of collection and treatment of samples used in this study.

The construction of a hydride generation apparatus for use with an atomic absorption spectrophotometer for the determination of arsenic and other hydride forming elements is described. Flame emission, flame atomic absorption and inductively coupled plasma emission spectroscopy (I.C.P.-E.S.) were used for the determination of other elements.

Determinations of arsenic and other elements were made on some geothermal waters of the area. It was found that these waters contribute large (relative to background levels) amounts of arsenic, boron and alkali metals to the aquatic environment. Some terrestrial vegetation surrounding hot pools at Lake Rotokawa and the Champagne Pool at Waiotapu was found to have high arsenic concentrations.

Arsenic determinations made on the waters of the Waikato River and some lakes of the Taupo Volcanic Zone revealed that water from the Waikato River between Lake Aratiatia and Whakamaru as well as Lakes Rotokawa, Rotomahana and Rotoehu was above the World Health Organisation limit for arsenic in drinking water (0.05 g/mL) at the time of sampling.

Arsenic accumulates in the sediments of the Waikato River and Lakes of the Taupo Volcanic Zone. The levels were variable, but characteristically around 100 g/g.

Trout taken from the Waikato River and some lakes in the Taupo Volcanic Zone, had flesh arsenic concentrations of the same order of magnitude as the water from which they were taken. Trout from Lakes Rotorua, Rotoiti and Rotomahana contained average flesh mercury concentrations above the World Health Organisations limit for mercury in foodstuffs (0.5 g/g). There were positive correlations between weight, length and flesh mercury concentration.

Freshwater mussels from Lakes Rotorua and Tarawera had arsenic concentrations above the World Health Organisations limit for arsenic in foodstuffs (2 g/g). Shellfish taken from the mouth of the Waikato river and from Raglan were below the World Health Organisation's limit for arsenic and mercury.

Aquatic macrophytes from the Waikato River had arsenic concentrations many times greater than the water from which they were taken. Some samples of *Ceratophyllum demersum* had arsenic concentrations above 1000 g/g dry weight.

Water cress from the Waikato River at Broadlands and Orakei Korako contained on average 400 g/g and 30 g/g arsenic respectively. An experiment was conducted on the uptake of arsenic by water cress. It was found that water cress does accumulate arsenic if placed in an arsenic solution.

Acknowledgements

I would like to express thanks to my supervisors, Prof. RR Brooks, Dr HA Outred and Prof. J Kirkman, for their advice, assistance and encouragement throughout the period of this work.

I am greatly indebted to the New Zealand Department of Health for a grant towards operational costs.

Thanks are also due to DJ Stack and the staff at the Eastern Region Fish and Game Council, Rotorua for the collection of trout from the Waikato River and nearby streams.

Julie Hanna, Tania Reihana, and Craig Simpson are also thanked for their assistance and advice on the location and collection of samples.

I acknowledge the receipt of a MURF scholarship for operational expenses.

Table of Contents

List of Figures

List of Tables

Chapter 1: General Introduction and Methods

1.1 Introduction

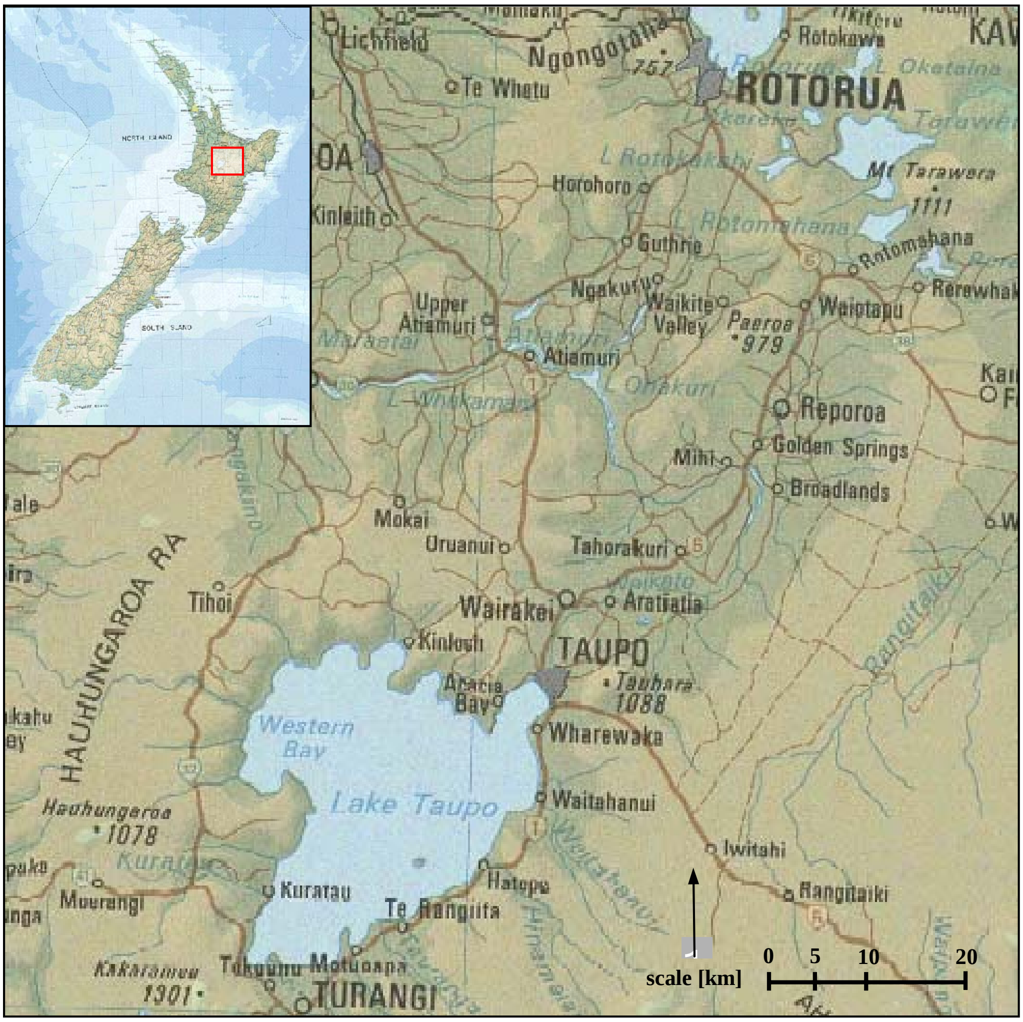
The Taupo Volcanic Zone covers an area of 6000 square kilometres in the central North Island, New Zealand. It extends from White Island south-west to Mount Ruapehu in a long narrow belt, (Fig. 1). The area features five active volcanoes, from north to south these are: White Island, Mt Tarawera, Mt Tongariro, Mt Ngauruhoe and Mt Ruapehu.

Geologically, the Taupo Volcanic Zone forms a trough some 3.5 km deep filled with volcanic material. On each side of the trough there are faults bordering uplands of greywacke covered with flat - topped, tilted layers of ignimbrite (Thornton, 1985). This is manifested in gravitational, seismic and magnetic anomalies (Modriniak and Studt, 1959). The area is rich in hydrothermal activity, abounding in hot springs, geysers and mud pools. Such areas occur in specific fields of geothermal activity.

The Taupo Volcanic Zone contains at least 32 natural lakes, which include Lake Taupo the largest lake in New Zealand, and Lake Rotorua. New Zealand's longest river, the Waikato, flows out of Lake Taupo, through several geothermal fields and north westward to the Tasman sea.

The area has been extensively modified by humans. The modification is in some ways similar to that in other parts of the country *i.e.*: (1) removal of native vegetation to use the land as farmland and urban areas, (2) exploiting the Waikato River system both as a water source and as an energy source by damming, (3) adding material to waterways of the area as a means of disposing of waste and (4) introduction of alien flora and fauna. The unique geothermal features of the area have also been used by humans to modify the environment in ways that are unique to the Taupo Volcanic Zone, *i.e.*: (1) using the naturally occurring geothermal hot water; this usually involves piping or channelling the water, (2) drilling bores down into the geothermal field to extract high pressure hot water and steam; this is then used for commercial purposes, (3) exploitation of deposits resulting from geothermal activity and (4) development of some geothermal areas as tourism attractions.

Figure 1. The Taupo Volcanic Zone.



There are eight dams on the Waikato River that generate power from the 366 metre fall from Lake Taupo to the Tasman sea. Lakes now occupy many of the narrow river valleys through which the fast flowing Waikato used to flow. The first lake, Lake Arapuni, was filled in 1929 and the most recent Lake Aratiatia was filled in 1964. There are two geothermal power stations in the area, Wairakei, commissioned in 1968 and Ohaaki, commissioned in 1989. These power stations generate 145 MW and 108 MW respectively.

The aquatic biosphere includes the fresh water on the surface of the earth and its biological contents. As described above, there is a large area of the Taupo Volcanic Zone that is covered in fresh water. This provides a medium for numerous organisms as well as a water and a food source for humans.

Known sources of elemental pollution in the aquatic biosphere of the Taupo Volcanic Zone are; (1) elements arising from naturally occurring geothermal activity (Smith, 1985), (2) geothermal bores that release element-rich water into the aquatic biosphere, these include the geothermal power stations, (3) runoff of nutrient-rich fertilisers (Hill, 1975), (4) industrial pollution; *e.g.* the pulp and paper mill at Kinleith and (5) elements added to lakes to control weeds; *e.g.* sodium arsenate added to Lake Rotorua.

Pollution of the aquatic biosphere will affect the ecology of the biota both in the water and in the terrestrial environment. This in turn will affect certain values of the Taupo Volcanic Zone to humans. The most direct effect will be the water value. At present, water from the lakes and rivers of the Taupo Volcanic Zone is used for drinking , irrigation, and for recreational purposes. The lakes and rivers of the area are valued as food sources, providing trout, eels, shellfish and water cress. Pollution may reduce the value of tourism as far as fishing / recreation is concerned. Maori tribes have leased land / waterways to various organisations, and there is a high cultural value placed on the quality of the land.

This study investigates the addition to the aquatic biosphere of any element at a rate that results in higher concentrations of that element than would occur under 'normal' circumstances. 'Normal' is defined as an aquatic environment not influenced by humans or by geothermal activity.It investigates pollution of the aquatic biosphere by making elemental determinations in waters, sediments, plants and animals from various places in the Taupo Volcanic Zone. The study is in three parts: (1) the determination of arsenic and other elements in some geothermal areas in the Taupo Volcanic Zone, (2) investigation of pollution of some natural lakes by arsenic and other elements in the Taupo Volcanic Zone, (3) investigation of pollution of the Waikato River system by arsenic and other elements. Each section is introduced, and the work of other workers is described. The results of each experiment are reported and discussed in relation to pollution of the aquatic biosphere of the area. The study concludes by reviewing the significant results and their implications for the environment, human health and management of the area.

1.2 Sample Collection and Treatment

Water samples were collected in 750 mL polythene bottles *in situ*, and refrigerated. 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 x 150 x 150 mm with a rope attached. This was thrown into the water from which sediment was intended to be collected. The sediment was stored in a sealed polythene bag for transport to the laboratory. Sediment samples were placed on blotting paper and left to dry for at least three weeks, lightly crushed, and then sieved through a -120 mesh polythene screen. Approximately 0.5g (-120 mesh) samples were weighed into 50 mL polypropylene containers. Ten mL of conc. 1:1 HF / HNO_3 were added, and two reagent blanks were prepared. The containers were placed in a water bath at 99 ^{o}C until all the acid had evaporated. Twelve mL of 2M HCl were added, and the sample allowed to dissolve. When the volume had reached *ca.* 10 mL it was measured and the sample allowed to cool. Samples were stored in 25mL polythene sample containers.

Trout samples (*Oncorhynchus mykiss* and *Salmo trutta*) were collected at a fishing competition held in Rotorua. The sex, weight, and lake from which the trout had been caught were recorded. A piece of flesh from behind the head and a section of liver were taken. The samples were stored in polythene bags in a chilly bin. They were subsequently frozen (at -18 ^{o}C) on the evening of the day they were collected. Between 0.5 and 2.5 g fresh weight of muscle or liver were weighed into a boiling tube. Five mL of 70% HNO_3 were added and the sample heated in heating blocks to ca 100 ^{o}C until all the sample dissolved. The solution was transferred to a measuring cylinder and made up to exactly ten mL with distilled water. Samples were stored in 25 mL polythene sample containers.

Shellfish (pipi; *Paphies australis,* cockle; *Austrovenus stutchburyi,* Pacific oyster; *Crassostrea gigas,* mussel *Mytilus canaliculus,* and *Potomopergus sp.*) were collected by hand and kept moist and cool (in a fridge) until they were prepared for analysis. The shellfish remained alive. They were then removed from their shells (except *Potomopergus sp.* which is too small for this to be practical), rinsed in distilled water, weighed (typically the whole animal weighed less than 2g fresh weight) and prepared in the same manner as described for the trout material.

Plant samples (*Ceratophyllum demersum*, *Egeria densa* and *Lagarosiphon major*) that occurred in the river were collected by throwing in a grapple hook and snagging the plants, or by wading in and removing them. Terrestrial / sub - aquatic plants (*Salix sp.*, *Kunzia ericoides*, *Leptospermum scoparium*, *Leucopogon fasiculatum*, *Cyathodes sp.*, *Pteridium esculentum*, *Dracophyllum subulatum*, watercress; *Nasturtium sp.* and *Cytisus scoparius*) were collected by hand. For all plant samples, excess water was allowed to drip off and the plant wrapped in newspaper. Upon return to the laboratory, the plants were placed in a drying cupboard set at 40 ^{o}C until a constant weight was reached. Each plant was ground in a mill and the powder stored in polythene bags. Approximately 0.2 g of plant material was weighed into a boiling tube and prepared in the same manner as for the trout and shellfish.

For each batch of trout, shellfish, plants and sediments, two reagent blanks were prepared.

1.3 Elemental Analysis

The Alkali metals;

The alkali metals were determined by flame emission on a GBC 900 spectrophotometer using an air - acetylene flame with the slit width set at 0.2 µm. The emission lines used (in nanometres) were: lithium 670.8, sodium 589.0, potassium 766.5 and rubidium 780.0.

Magnesium, copper, zinc and cadmium;

These elements were determined by flame atomic absorption on a GBC 900 spectrophotometer with the slit width set at 0.5 µm. Table 1 lists the flame type, lamp current and wavelength used for each element.

Flame atomic absorption was too insensitive for the majority of arsenic, antimony and mercury determinations. These elements were determined by atomic absorption of the hydrides. The development of a hydride generation apparatus for such determinations is described below. Analysis of elements other than those above were carried out by inductively coupled plasma emission spectroscopy (I.C.P.-E.S.) by staff at Ag Research, Palmerston North.

Table 1. Flame types, lamp currents and wavelengths used for some analyses.

Element	Flame Type	Lamp Current (mA)	Wavelength (nm)
Zinc	Air - acetylene	5.0	213.9
Cadmium	Air - acetylene	3.0	228.8
Copper	Nitrous oxide - acetylene	3.0	324.7
Magnesium	Air - acetylene	3.5	285.2

1.4 Development of a Hydride Generation Apparatus for Accurate Arsenic Determinations

1.41 Introduction

A hydride generation technique developed by Holak, in 1969 has become one of the most used methods for arsenic determinations (Narsito and Santosa, 1990). There are several methods of arsine generation and collection and all have the following features in common: (1) a strong reducing agent to generate arsine (2) a heating device that decomposes the hydride, and (3) an atomic absorption measuring device that quantifies the amount of hydride produced. Arsine was originally generated by reaction with a zinc - hydrochloric acid reagent (Thompson and Thomerson, 1974) or other metal - acid systems that produced nascent hydrogen. The reaction time using these reagents was up to ten minutes (Godden and Thomerson, 1980). Thompson and Thomerson (1974) developed a technique using sodium borohydride to produce arsine. This reaction proceeded at a much greater rate and the arsine was liberated within a few seconds. This had two main advantages. The first was that determinations could be carried out at a much faster rate, and the second was that it allowed different methods for determination, such as measurement of arsine concentration rather than total arsine volume.

Firstly As(V) is reduced to As(III) then,

$$4AsO_3^{3-} + 3BH_4^{-} + 15H_3O^{+} \longrightarrow 3H_3BO_3 + 18H_2O + 4AsH_3$$

There are three methods commonly used in the hydride generation technique of arsenic determination. They are: (1) a continuous pump method, whereby a constant flow of sample and sodium borohydride are combined to give a constant absorption (Anderson *et al.*, 1986), (2) an arsine trapping method where the sample is subjected to multiple bursts of sodium borohydride. The arsine gas produced is trapped, either in a U tube cooled in liquid air, a balloon, or some other collection device, then passed into the absorption chamber and, (3) direct introduction. Here a single burst of sodium borohydride is added to the sample, the arsine is directly introduced into the spectrophotometer and the peak height of the arsine absorption curve measured (Godden and Thomerson, 1980).

For the accurate determination of multiple samples in the present study, the direct introduction method was chosen for the following reasons. The continuous pump method was fast but required too much sample (*ca.* 10 mL), used large amounts of sodium borohydride (ca $1 per gram) and the sensitivity was poor. The arsine trapping method gives very accurate results using a small quantity of sodium borohydride, but is too time-consuming for multiple determinations. The direct introduction method, though not as sensitive as the liquid air method, gives good results using a small amount of sample (0.01 to 1 mL) and a small amount of sodium borohydride (ca 5 mL of 12% solution).

The aim of the present experiment was to develop an accurate hydride generation apparatus that could accurately determine arsenic concentrations in a large number of samples, using materials readily available in the laboratory.

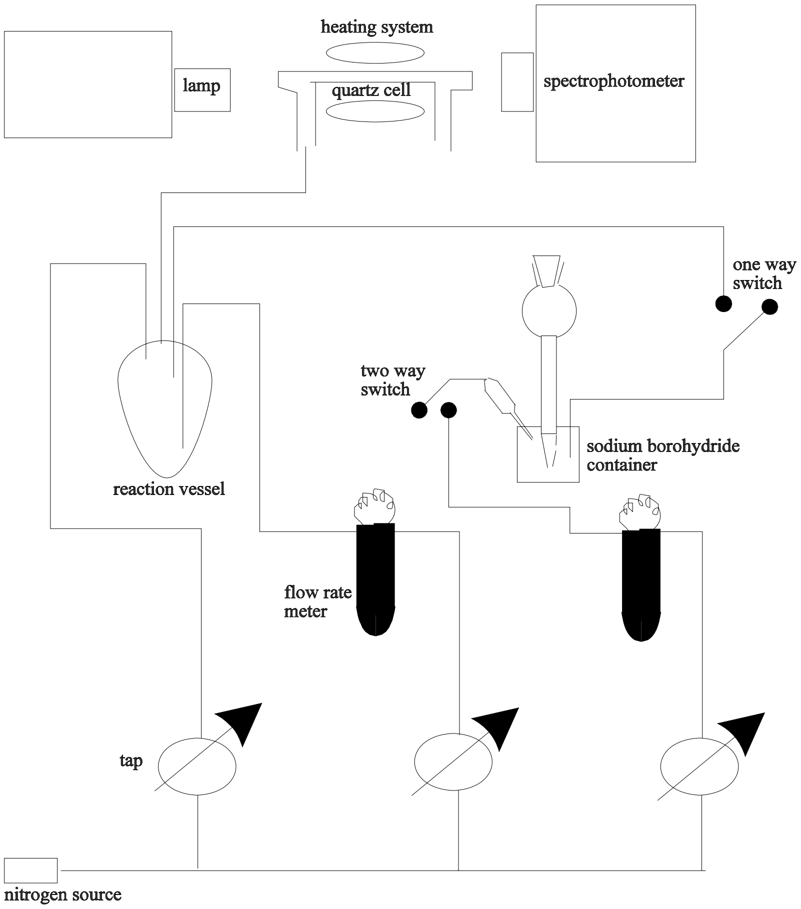
1.42 The Instrument

The apparatus (Fig. 2) basically consisted of a nitrogen source, a series of gas taps, a sodium borohydride container, a reaction vessel and an absorption tube.

Nitrogen was required to blow sodium borohydride into the reaction vessel, to blow the arsine gas through the absorption tube, and to purge oxygen (that absorbs at 193.7 nm) from the absorption tube. The sodium borohydride was contained in an airtight glass container, with a quickfit stopper for refilling ,that was connected in a chicken feeder type arrangement to a small glass flask (ca 40 mL). All bungs in contact with sodium borohydride were either made of teflon or were mechanically secured to the vessels they sealed. This was done because of the strong lubricating action that sodium borohydride has on rubber causing a subsequent blow out of the bung when pressure is exerted. The chicken feeder arrangement was added in an attempt to keep the flow rate of sodium borohydride constant over a large number of samples. The flow rate of sodium borohydride is influenced by the height of the liquid in the container relative to the reaction vessel As the amount of liquid in the container decreased, the flow rate changed. This gave a change in the peak height. A small capacitor was added to minimise fluxes caused by the chicken feeder refilling the container. The capacitor consists of the bulb of a 20 mL pipette connected to the gas input of the borohydride container. A gas switch allows air to pressurise the borohydride container, forcing sodium borohydride into the reaction vessel when in one position , and depressurising the borohydride container (i.e. stopping the flow) in the other position. A second switch allows sodium borohydride to flow into the reaction vessel. Under normal operation the container is pressurised using the first switch, after it has been filled with sodium borohydride, and the second switch is used to control the flow into the reaction vessel. The distance of the sodium borohydride container from the reaction vessel is important. It is best to have the borohydride container just below the level at which it would siphon into the reaction vessel. If the resistance to the flow of sodium borohydride is too great (i.e. the borohydride container is too far away) then it is more difficult to control the increased pressure needed to force sodium borohydride into the reaction vessel.

The reaction vessel was a 75 mL pear-shaped flask. The size and shape of the reaction vessel had a large effect on the performance of the device. Earlier prototypes used a larger (250 mL) round-bottomed flask with three side arms. This vessel gave an erratic flow of arsine to the absorption tube, presumably because of turbulence caused by the side arms. Arsine was also trapped in the side arms and slowly leaked out over subsequent determinations causing errors. A hydride generated in a larger container may also be diluted to a greater extent by the nitrogen already present in the vessel. A smaller vessel (boiling tube) was also tried, but this also gave erratic readings. This may have been due to a longer mixing time, and because sample was splashed up into the exit tube.

Figure 2:
Schematic diagram of the hydride generation apparatus



A teflon bung with four glass tubes inserted, seals the reaction vessel. Of the tubes, the first is shaped into a nozzle and injects sodium borohydride. The rate of flow of sodium borohydride is controlled by the nitrogen pressure, which in turn is controlled by a tap connected to the borohydride container. The second tube carries a slow base flow of nitrogen that bubbles through the sample and carries the arsine through the absorption tube. Again the flow rate is controlled by a nitrogen tap. The third tube carries the purging nitrogen that is blown through the system before the addition of sodium borohydride, to remove oxygen. The other tube carries gas from the reaction vessel to the absorption tube. The bung is held with a clamp and the reaction vessel can be removed for addition of the sample.

Two flow rate meters were used to measure the base flow rate of nitrogen through the system, and to measure the flow rate of sodium borohydride. They were placed in series with the respective nitrogen sources to the reaction vessel and to the sodium borohydride container. Each flow meter consisted of a u-tube 3mm in diameter containing methylene blue. At each end of the U tube there was a T junction, one way leading to the nitrogen entrance / exit and the other connected to a length of plastic capillary tubing. The length and width of this tubing determines the sensitivity of the flow meter. The larger the resistance (i.e. the longer the tube and the smaller the diameter of the tube) the more sensitive the flow meter.

The absorption tube is a closed silica tube with an input tube at one end and an exit at the other.

This type of absorption tube has two advantages over the standard open-ended tube with a single input in the middle: (1) the arsine has a longer residence time in the tube (which improves sensitivity) and (2) excess hydrogen does not ignite because the orifice through which oxygen can enter is relatively small. The tube is heated electrically with a GBC EHG3000 heating system. This allows more control over temperature and gives more uniform heating (Gerdei *et al.*, 1993).

The apparatus was built on a retort stand mounted inside a box. Holes were drilled in the box to mount gas taps, switches, manometers and the reaction vessel outside for easy access. The tubing and sodium borohydride container are contained inside.

The apparatus is connected to a GBC900 atomic absorption spectrophotometer with an ICI arsenic hollow cathode lamp operated at 3 mA.

1.43 Method of Use of the Instrument

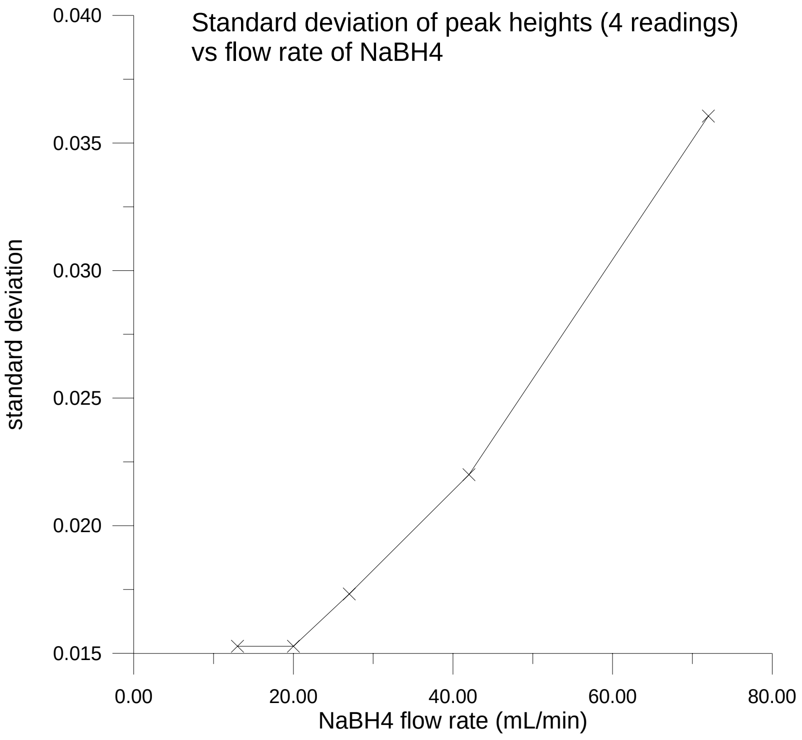
The absorption tube was heated to 950 ^{o}C which gives good atomisation of arsine (Gerdei *et al.* 1993). The GBC900 instrument was set to measure peak height over a period of 12 seconds. The sensitivity was multiplied by a factor of ten. but this can be altered depending on the concentration range being examined.

The sodium borohydride solution used was: 2% $NaBH_4$, 1% KOH.

Samples needed to be in solution. A measured volume was added to the reaction vessel along with ca 7 mL of 0.5 M hydrochloric acid. The reaction vessel was reattached to the apparatus. Nitrogen was blown through the system to remove any oxygen, the presence of which can be detected by the absorption reading on the spectrophotometer. When the oxygen had been removed, the sodium borohydride switch was opened and the recorder was started. The sodium borohydride flow was maintained until the apex of the peak had been reached. The reaction vessel and tubes were then rinsed, and the process repeated for the next sample.

The flow rates of nitrogen and sodium borohydride were critical for the size and shape of the absorption peak. These were controlled using taps controlling the flow of nitrogen and measured using the flow meters. In general, the greater the flow of sodium borohydride, the less accurate the result (Fig. 3). A flow rate of 27 mL / min gave the greatest peak height while still having a relatively low standard deviation. At low flow rates, the arsenic is slower to be reduced because of the lower production of nascent hydrogen. At high flow rates, however, the arsine is diluted by excess hydrogen. The nitrogen flow rate was optimal at 280 to 320 mL/min, this gave the best accuracy and peak height. At very low nitrogen flow rates there is a large standard deviation presumably because of irregularities in arsine production. As the flow rate increases, the standard deviation decreases but so does the sensitivity. Again this is probably because of the hydride being diluted.

Figure 3:



Standard deviation of peak heights (4 readings) vs flow rate of NaBH4

The apparatus may be used in a similar manner for bismuth and mercury determinations as hydrides of these elements can be generated. The optimal sodium borohydride flow rates for these elements is similar to the optimal flow rate for arsenic. The optimal nitrogen flow rates are slightly lower, probably because there is no interference from oxygen.

Other elements that may possibly be determined using this apparatus are: selenium, tellurium, antimony, tin and lead.

1.44 Performance of the Instrument

The instrument can detect as little as 4 ng of arsenic in the reaction vessel (Fig. 4). Up to 5 mL of sample can be added and this gives the maximum sensitivity of 0.8 ng / mL (ppb) arsenic. The standard error over the range 4 - 22 ng is 10% using optimal flow rates. The relative standard deviation decreases as larger concentrations are measured.

The sensitivity of bismuth determinations are similar to that of arsenic. Mercury is about 10 times less sensitive (Fig. 5).

The rate of determination is about one sample every 30 seconds. The cost of manufacture of the instrument was about $75 excluding the quartz cell and heating system.

Figure 4:

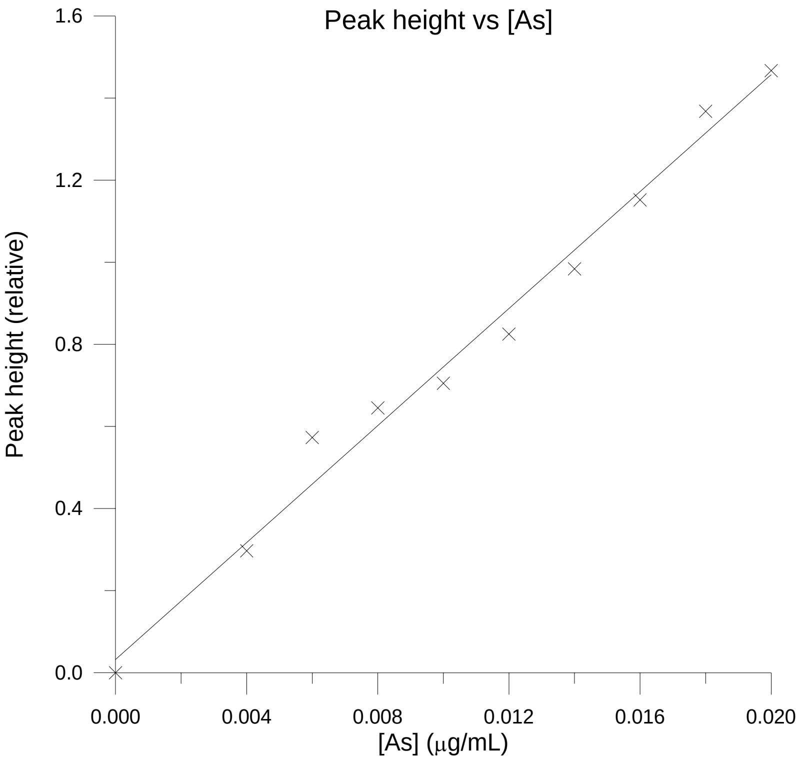
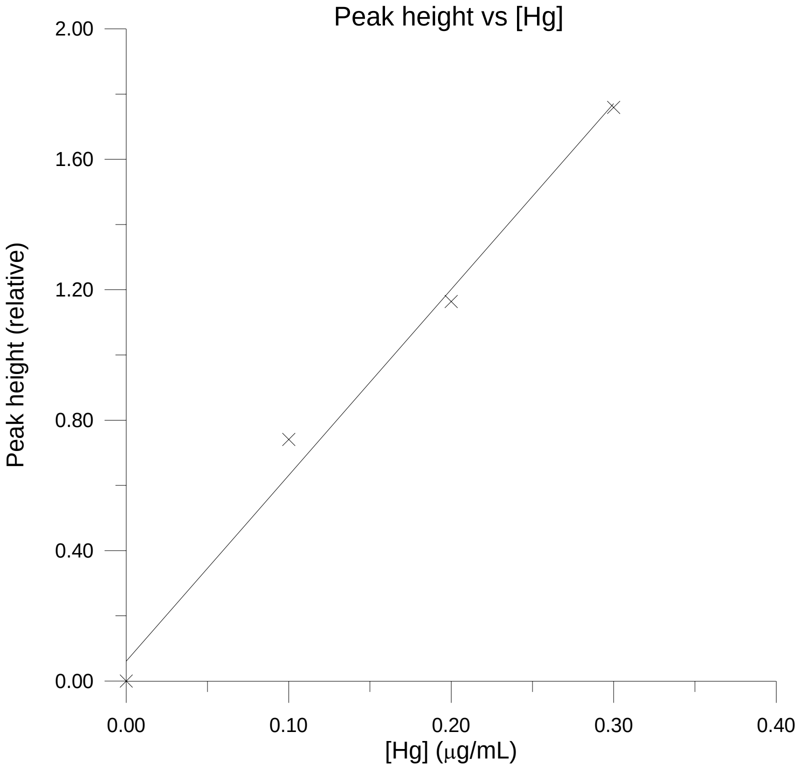


Figure 5:



1.5 Treatment of Data

All data calculations and analyses were done on Microsoft Excel 4.0 for Windows using an IBM 486 compatible computer. The statistical distribution of data was determined by comparing the arithmetic mean and the geometric mean with the median. If the former was closest to the median the data were considered to be normally distributed. If the latter was closest then the data were considered log - normally distributed and all statistical analyses were carried out on the logs of the data. When considering matters of statistical significance the convention of Brookes *et al.* (1966) was used. The criteria for accepting or rejecting the null hypothesis (H) that no relationship existed are shown in Table 2.

Table 2. Conventions used by Brookes *et al.* (1966).

Probability, P	Conclusion	Symbol
P >0.1	Not significant, H accepted	NS
0.1> P >0.05	Possibly significant, some doubt cast on H	PS
0.05> P >0.01	Significant, H rejected	S
0.01> P >0.001	Highly significant, H confidently rejected	S*
P <0.001	Very highly significant, H confidently rejected	S**

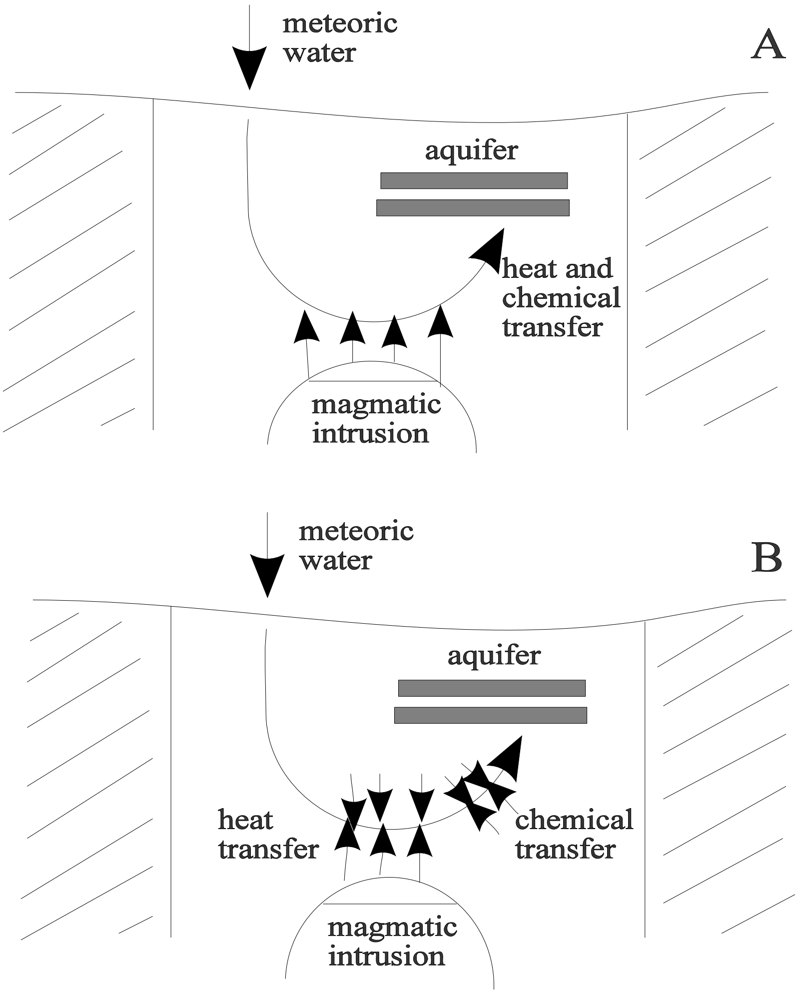
Chapter 2: Arsenic and other Elements in some Geothermal Areas of the Taupo Volcanic Zone.

2.1 Introduction

Much of the reported pollution in the Taupo Volcanic Zone comes from naturally occurring geothermal discharges, largely hydrothermal water. The origins of the hydrothermal waters were once thought to be juvenile waters that have been forced to the surface (Mahon, 1965). Current thinking is that the waters are meteoric in origin and have percolated down through the porous volcanic material to the shallow underlying magma; the subsequent hot water and steam is then forced to the surface. During this passage the water becomes fortified with chemicals. Golding and Speer (1961), and Liddle (1982), discussed two theories that attempt to explain the origin of chemical constituents in geothermal waters. The first theory states that the waters become chemically rich upon contact with the magma and then subsequently some of the chemicals precipitate on the trip to the surface, (Fig. 6 'A'). The second theory argues that the waters are simply heated by the magmatic intrusion and the hot water / steam dissolves chemicals from the rocks on its trip to the surface, (Fig. 6 'B').

The hot surface waters arise either directly from heated subterranean water and/or steam, or are surface waters that have been heated by subterranean steam (Lloyd, 1959; McColl, 1975). The origin of hot surface waters can be distinguished chemically and they are categorised into three groups according to McColl (1975). Depending on the chemical composition of the water, these groups are: (1) neutral chloride waters. These waters contain mainly sodium and potassium chlorides, with lesser amounts of calcium, magnesium, silica, boron, sulphate, and bicarbonate at a pH between 6 and 8.5. They originate at depth and come to the surface unmodified; (2) acid sulphate waters - these waters usually have pH < 3 and result wherever steam containing hydrogen sulphide condenses at the surface. Oxidation of the hydrogen sulphide to sulphurous and sulphuric acid results in the acidification of the water. (3) acidic sulphate chloride waters. These have a chemical composition intermediate between (1) and (2) and arise when hot neutral chloride waters dissolve sulphide minerals at depth or when neutral chloride waters mix with condensed steam as in the formation of acid sulphate waters.

Figure 6:
Two simple models for the origin of heat and chemicals in geothermal waters.



Most of the thermal waters in the Taupo Volcanic Zone are neutral chloride waters or acid sulphate chloride waters. They are rich in the major elements mentioned above but also contain considerable amounts of lithium, rubidium, caesium, arsenic, antimony, fluoride, bromine, phosphorus, and nitrogen as ammonia (McColl, 1975). Golding and Speer (1961) concluded that because of the small differences in caesium / lithium ratios, the waters of the Taupo Volcanic Zone have a similar origin.

The following section investigates previous work done on some specific sites of geothermal outflow as examples of sources of elemental pollution of the aquatic biosphere.

2.11 Tokaanu Hot Springs.

The Tokaanu Hot Springs are located about 1 km from the southern end of Lake Taupo. The springs discharge into a stream, which in turn flows into Lake Taupo.

Mahon and Klyen (1968) reported that approximately 1.98 cubic metres of hot water per minute is discharged from the Tokaanu Hot Springs area. This water flows into Lake Taupo. They reported that the water is of neutral chloride type and contains as much as 0.6% dissolved solids. Their elemental analysis of water from the area showed high mineral contents (Table 3).

Table 3. Data reported from hot spring water in the Tokaanu thermal area by Mahon and Klyen (1968).

Element	Conc. μg/mL	Element	Conc. μg/mL
Lithium	22.6	Iodide	3.0
Sodium	1.1	Sulphate	63
Potassium	168	Arsenic	5.6
Rubidium	0.9	Ammonia	1.2
Caesium	3.3	Carbonate	-
Calcium	32	Bicarbonate	2
Magnesium	0.2	Iron	0.01
Fluoride	1.7	Aluminium	0.01
Chloride	3020	HBO2	364
Bromide	3.3	Silicate	270

This analysis shows that the Tokaanu Hot Springs are releasing a considerable amount of dissolved elements into the aquatic biosphere of the surrounding area.

2.12 Wairakei Hydrothermal System.

The Wairakei field is located 8 km north of Lake Taupo, and covers an area of approximately 20 km^2. The Wairakei geothermal power station, built in 1964, utilises steam from this area for electricity generation. All chemical effluent from the power station is discharged directly into the Waikato River (Axtmann, 1975).

Ellis and Wilson (1960) recorded alkali metal concentrations in bores in the Wairakei hydrothermal system. Typical values were: lithium 12.2 μg/mL, sodium 1130 μg/mL, potassium 146 μg/mL. By using the known ratios of some elements to chloride, they calculated the yearly output of these elements from the Wairakei area (Table 4).

Table 4. Data calculated by Ellis and Wilson (1960) of elemental output from the Wairakei hydrothermal system.

Element	Output from Wairakei g / year
Chlorine	2×10^{10}
Boron	1×10^{9}
Fluorine	8×10^{7}
Lithium	2.5×10^{8}
Caesium	2.5×10^{7}
Arsenic	6×10^{7}

Of the elements shown in Table 4, the high amount of arsenic released is most striking, equating to 1.9 g / sec. As the main drainage system for the area is the Waikato River, presumably that is the final destination of these dissolved elements. Axtmann (1974) calculated the amounts of some elements entering the Waikato River from the Wairakei borefield (Table 5).

Table 5. Data calculated by Axtmann (1975) of elemental discharge into the Waikato from the Wairakei borefield.

Element	Discharge rate (g/sec)	Element	Discharge rate (g/sec)
Chlorine	2640	Calcium	21.5
Sodium	1470	Lithium	16.2
Silicon	798	Fluorine	9.8
Bromine	221	Potassium	245
Boron	34	Arsenic	5.1
Sulphur	31	Mercury	0.0002

Table 5 shows that Wairakei contributes considerable amounts of arsenic into the Waikato River, as well as small amounts of the toxic metal mercury. Axtmann (1975) concluded that only arsenic, mercury, hydrogen sulphide, carbon dioxide and silica appear to produce significant environmental effects. The water from Wairakei contains approximately 4400 μg/mL (0.44%) dissolved solids. When mixed with the Waikato River water, however, this value drops to well below 500 μg/mL (0.05%), the maximum recommended for potable water (Axtmann, 1975). Mahon (1966) showed that the silica content of waters from drill holes in the Wairakei field varied between 315 and 780 μg/mL. A chemical analysis of Wairakei discharge water was carried out by Rothbaum and Middendorf (1987) (Table 6).

Table 6 and other studies show that the Wairakei hydrothermal area is a potentially large source of pollution to the aquatic environments of the area.

Table 6. Chemical Analysis of Wairakei discharge water by Rothbaum and Middendorf (1987).

Element	Concentration (g/ton)	Element	Concentration (g/ton)

Sodium	1200	Silica	560
Potassium	185	Chlorine	2100
Lithium	12	Sulphur dioxide	32
Rubidium	2.5	Boron	28
Caesium	2.5	Arsenic	4.5
Calcium	18	Bicarbonate	18

2.13 Rotokawa Geothermal Field.

Located 9 km east of Wairakei, the Rotokawa field contains numerous hot pools, mud pools and fumaroles. Most of these occur at the northern end of Lake Rotokawa, a small (approximately 6 km^2), acidic (average pH 2.1), highly mineralised lake (Forsyth, 1977). The lake itself will be further discussed in Chapter 4. The hot springs at the north of the lake discharge 5.5 litres per second into the lake (Krupp and Steward, 1987). The lake is drained by the Parariki stream which flows into the Waikato River. The waters are of acid - sulphate - chloride type. Weissberg (1969) carried out analyses of bore waters from Lake Rotokawa. Levels of lithium, sodium, potassium and chloride, were similar to levels discussed for other geothermal sources. Arsenic and mercury levels though not measured in the waters were found to be high in the discharge precipitates indicating high levels in the water.

Table 7. Analysis of discharge precipitates from Rotokawa thermal area by Weissberg (1969).

Element	Conc. (μg/g)	Element	Conc. (μg/g)
Gold	70	Mercury	15
Silver	30	Thallium	0.5%
Arsenic	0.4 %	Lead	50
Antimony	ca 30%	Zinc	100

As shown in Table 7, there are large amounts of toxic heavy metals in the sediments. These values, however, may not reflect values in the water as the solubility / bio availability of the metals can be exceedingly low (Mason and Moore, 1982). Krupp and Steward (1987) produced similar results from a number of precipitates around the area. Ellis and Sewel (1963) reported 45.1 μg/mL boron from a spring at the north end of the lake. Weissberg and Rohde (1978) measured 3.4 and 26 μg / kg mercury in the water and steam of a well near Lake Rotokawa. Thus the Rotokawa geothermal field is probably a source of elemental pollution to the aquatic environment of Lake Rotokawa and the Waikato River.

2.14 Waiotapu.

The Waiotapu geothermal field covers about 18 km^2 and is located at the northern end of the Reporoa valley 23 km SSE of Rotorua (Liddle, 1982). It has been extensively studied and is a major tourist attraction. Hedenquist and Henley (1985) surveyed the sinter around the Champagne Pool. Values for arsenic and antimony were 12000 μg/g and 600 μg/g respectively, there was 90 μg/g mercury in the sinter. Weissberg (1975) measured 2.6 μg/L mercury in the water of the Champagne Pool. Ritchie (1961) determined the arsenic levels in the Postmistress Pool and the Champagne Pool as being 1.1 and 5.5 μg/mL respectively. There was also a measurable amount of antimony, 34 and 115 μg/L respectively. From the above data, it appears that the Waiotapu geothermal field, like the others investigated, is also a potential source of elemental pollution into the aquatic environment.

2.15 General Comment

The above studies show that all the geothermal areas mentioned above have hydrothermal waters that contain high concentrations of certain elements. These waters then become part of the aquatic biosphere of the area. Thus there are reasonable grounds for supposing that some of the waters in the Taupo Volcanic Zone are polluted by natural and human-induced hydrothermal waters. Not all the geothermal fields of the Taupo Volcanic Zone were investigated here. The Waikite, Te Kopia, Orakei Korako, Reporoa, Tauhara, Waihi and Ketetahi geothermal fields were omitted. For information on these areas see Liddle, 1982; Grindley, 1965; Lloyd, 1972; Grindley *et al.*, 1966; Mahon, 1968; and Rennison and Brock, 1981.

Since the earlier work, the Ohaaki geothermal power station has opened. This power station uses a reinjection process to reduce the outflow of heavy metal ions into the environment, but distillates from the cooling tower are piped to holding ponds that then flow into the Waikato River. The water right for the power station allows the release of 3000 tonnes of waste water per day. Depending on the concentration of elements in the waste water, this may affect the aquatic environment of the Waikato. There may also be deterioration of the land leased from the Maori people of the area. Also of interest is the concentration of arsenic in vegetation of some of these areas. Hashem (1993) demonstrated that the fungus *Cladosporium herbarium* showed considerable tolerance to arsenic when grown on a medium containing 200 μg/g of this element. There has been little work done on the effect of arsenic on various seed plants, particularly native plants.

The aims of this study were: (1) to determine elemental concentrations in hydrothermal waters of the area and compare these values with earlier work, (2) to investigate the arsenic concentrations in the vegetation of some areas, and (3) to investigate the elemental content of water released into the Waikato River from the recently opened Ohaaki power station.

2.2 Methods

Water samples were taken from the following areas;

(1) The Tokaanu hot springs and river.
(2) The main drain of the Wairakei power station
(3) Hot springs at the north-western end of Lake Rotokawa.
(4) The two holding ponds adjacent to the Ohaaki power station.
(5) A raw bore in the Ohaaki borefield.
(6) The hot water drain from the Taupo Lucerne plant in the Broadlands field.
(7) The Champagne pool at Waiotapu.

Samples (2) and (7) were collected on 28 / 10 / 93, all other samples were collected on 17 / 1 / 94.

Samples of vegetation (*Kunzia ericoides*, *Leucopogon fasiculatum*, *Leptospermum scoparium*, *Paesia scaberula*, *Cyathodes* spp, *Pteridium esculentum*, *Cytisus scoparius*, and *Dracophyllum subulatum*) around the Rotokawa and Waiotapu geothermal areas were taken and analysed for arsenic. The vegetation was removed from areas immediately adjacent to hydrothermal waters. Secateurs were used to cut off portions of the plants being investigated. The plants were cut *ca.* 300 mm from the apical meristem in plants less than 2 m tall. Samples were taken from the end of a lateral branch in plants over 2 m tall (*Kunzia ericoides*).

All samples were prepared as described in Chapter 1.

2.3 Results

Elemental concentrations in the hydrothermal waters sampled are shown in Table 8. Arsenic, lithium and potassium concentrations in the Tokaanu hot springs were less by about 40% than those reported by Mahon and Klyen (1968). The rubidium concentration, however, was over four times higher. The concentrations were also lower in the main drain of the Wairakei power station than those reported by Rothbaum and Middendorf (1987) except for rubidium, which was higher. The arsenic concentrations measured in the Champagne pool were consistent with those measured by Ritchie (1961).

Table 8. Concentrations (μg/mL) of some elements in hydrothermal waters in the Taupo Volcanic Zone.

Location	Arsenic	Magnesium	Lithium	Sodium	Potassium	Rubidium
Tokaanu	3.0	0.68	7.96	>100	79.91	4.18
Wairakei drain	3.1	0.31	6.58	>100	>100	3.43
Rotokawa spring	0.2	3.5	3.20	>100	38.71	2.49
Ohaaki East Hold	3.3	0.14	7.19	>100	>100	n.d.
Ohaaki Raw Bore	2.7	0.009	7.70	>100	>100	4.8
Lucerne plant drain	3.1	0.054	6.79	>100	>100	6.17
Champagne Pool Waiotapu	6.0	0.032	7.04	>100	>100	6.10

n.d. not determined

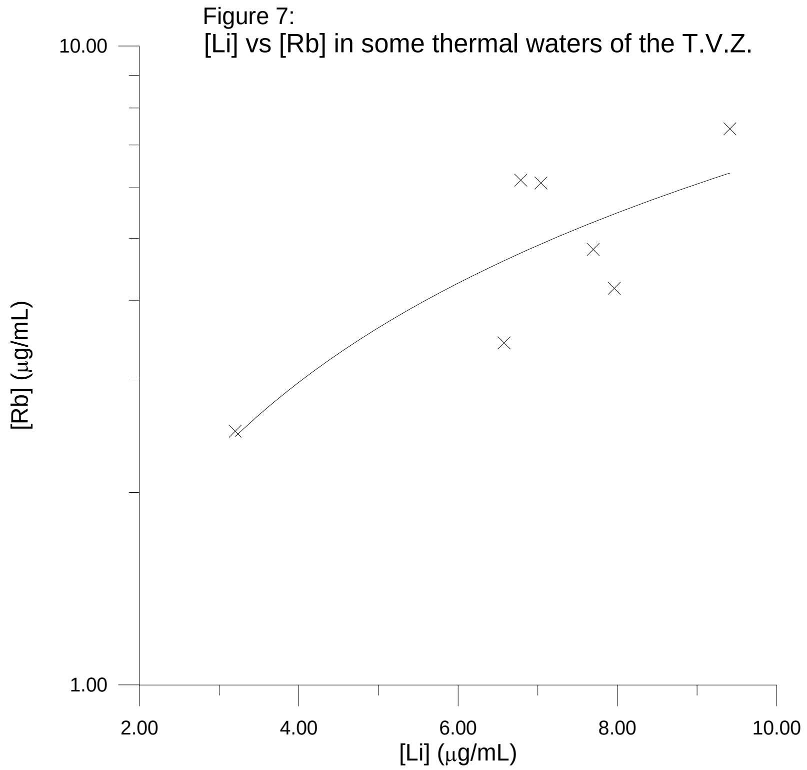


Figure 7:
[Li] vs [Rb] in some thermal waters of the T.V.Z.

The waters measured from the Ohaaki field (*i.e.* East Hold, Lucerne Plant drain and raw bore water) contained similar arsenic concentrations to the others measured which appears to be 'standard' geothermal water.

Lake Rotokawa had an anomalously low amount of arsenic and a relatively high magnesium content.

Table 9. Concentrations (µg/mL) of some elements in water from West Hold, Ohaaki power station.

Element	Concentration	Element	Concentration
Aluminium	0.44	Molybdenum	<0.01
Arsenic	3.6	Sodium	1143
Boron	47.5	Nickel	<0.02
Calcium	9.0	Phosphorus	<0.2
Cadmium	<0.01	Lead	<0.2
Cobalt	<0.02	Sulphur	21.5
Chromium	<0.01	Selenium	<0.3
Copper	<0.03	Silicon	304
Iron	0.07	Tin	<0.03
Potassium	194	Strontium	.12
Magnesium	0.025^{+}	Zinc	<0.02
Manganese	0.004	Lithium	9.413*
Rubidium	7.24*		

* Determined by flame emission. $^{+}$Determined by flame A.A.
All others determined by I.C.P.-E.S.

The results from the West Hold of the Ohaaki power station are shown in Table 9. The water of the west holding pond contains large amounts of arsenic, boron and the alkali metals. The results are lower than would be expected if the water in these ponds is the distillate from the raw bore water. Water from the cooling tower was also analysed for arsenic (Table 10).

Figure 8:
[Mg] vs [Rb] in some thermal water of the T.V.Z.

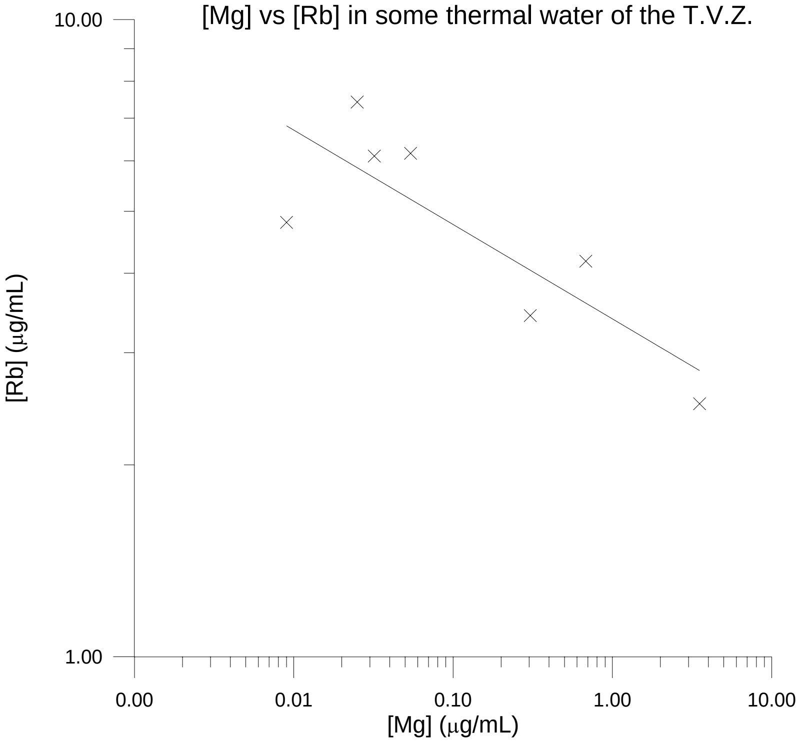


Table 10. Concentration (μg/mL) of some elements from the cooling tower of Ohaaki power station.

Element	Concentration	Element	Concentration
Arsenic	0.0005	Sodium	0.77
Magnesium	0.076	Potassium	0.187
Lithium	<0.01	Rubidium	0.036

Note. At very low concentrations there is a large relative error.

Assuming that the raw bore water is a representation of the hydrothermal water entering the Ohaaki power station, then taking the concentration of a single element in the waters of the raw bore, cooling tower, and holding ponds, it is possible to calculate the relative volumes of the reinjected (cooling tower) waters and the water discharged into the Waikato (holding ponds). Let R, H, and I be the concentrations of rubidium in the raw bore, holding ponds, and reinjection water, respectively. Let x be the percentage of water flowing to the holding ponds, and y be the percentage of water being reinjected. Then x and y may be determined by;

$$x = 100(R - I) / (H - I) \qquad \text{and} \qquad y = 100 - x$$

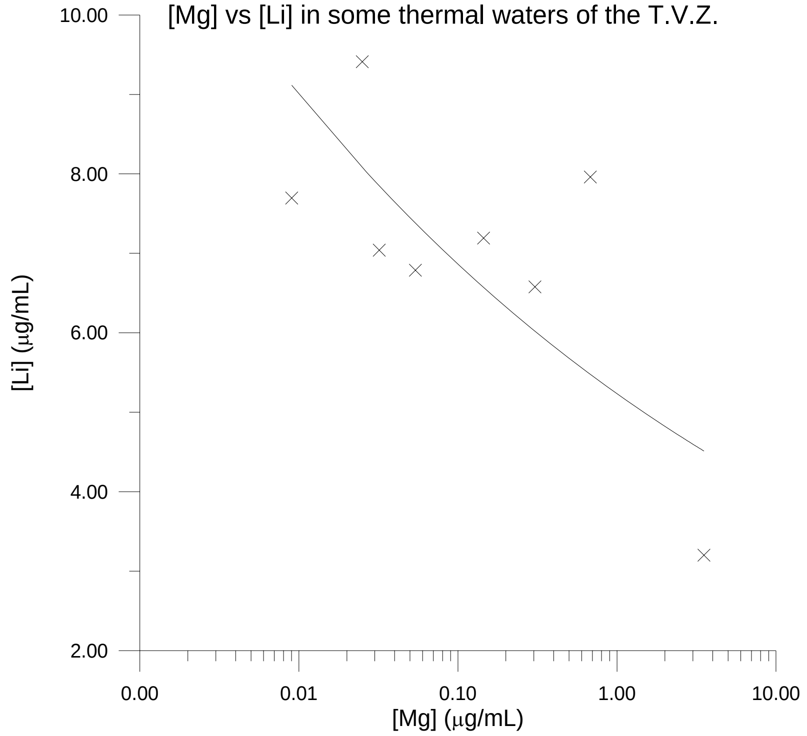


Figure 9:
[Mg] vs [Li] in some thermal waters of the T.V.Z.

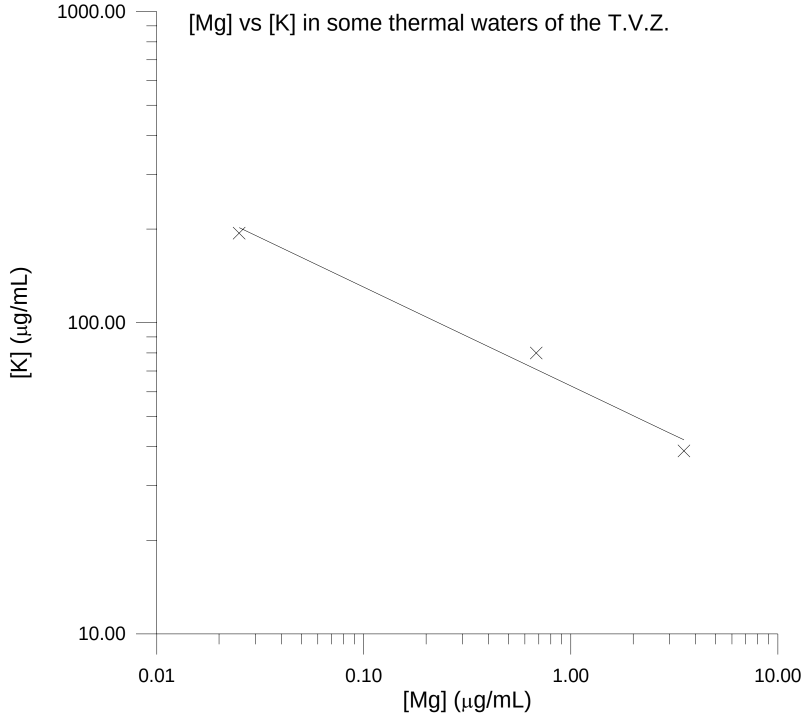


Figure 10:
[Mg] vs [K] in some thermal waters of the T.V.Z.

By substituting the concentrations of rubidium into the equations we find that 34% of the raw bore water is re-injected, while 66% is disposed of into the Waikato River. These calculations make the assumptions that there is no rubidium being lost between the power station and the holding ponds, and that the volume of rainwater entering the system is insignificant compared to the volume of geothermal water.

Table 11. Correlation data (*r*) for arsenic, magnesium and the alkali metals in some geothermal waters in the Taupo Volcanic Zone.

Element	As	Mg	Li	K
Mg	-0.64(NS)			
Li	0.61(NS)	-0.85(S)		
K	0.79(NS)	1(S)	0.85(NS)	
Rb	0.64(NS)	-0.77(PS)	0.84(S)	1(S*)

There were some significant correlations between concentrations of some elements found in geothermal waters. The alkali metals were all positively correlated with each other and negatively correlated with magnesium (Table 11,Figs. 7 - 10). Arsenic showed no significant correlation with any of the other elements tested.

An analysis was made on the water from the Tokaanu stream that flows into Lake Taupo (Table 12).

Table 12. Concentrations (µg/mL) of some elements in the water from the Tokaanu stream.

Element	Concentration	Element	Concentration
Arsenic	0.058	Sodium	12.5
Magnesium	2.4	Potassium	3.1
Lithium	0.15	Rubidium	0.04

Table 12 shows that water from the Tokaanu stream has an elevated arsenic concentration relative to the background level for fresh water (1.7 ng/mL). The arsenic concentration in the water of the Tokaanu stream is above the World Health Organisation (WHO) limit for arsenic in drinking water (0.05 µg/mL). This indicates that geothermal activity is capable of contributing environmentally significant amounts of arsenic to a fresh water system.

Considerable amounts of arsenic were found in some of the plants taken from the hot pools around Lake Rotokawa and the Champagne springs (Tables 13 and 14).

Table 13. Arsenic concentrations (µg/g dry weight) in some plants around a hot pool at Lake Rotokawa.

Species	Part	Conc.	Species	Part	Conc.
Kunzia ericoides	Stems	1.1	L. scoparium	Roots	75.6
K. ericoides	Leaves	0.5	Paesia scaberula	fronds	20.7
Leucopogon fasiculatum	Stems	3.6	Cyathodes	steams	1.4
L. fasiculatum	Leaves	10.3	Cyathodes	leaves	0.8
Leptospermum scoparium	Stems	17.1	Pteridium esculentum	fronds	38.7
L. scoparium	Leaves	54.3	Cytisus scoparius	stems + leaves	9.6
			Dracophyllum subulatum	stems + leaves	0.8

Table 14. Arsenic concentrations (µg/g dry weight) in some plants around the Champagne pool at Waiotapu.

Species	Part	Conc.	Species	Part	Conc.
Kunzia ericoides	Stems	0.9	Leucopogon fasiculatum	Stems	0.6
K. ericoides	Leaves	0.7	L. fasiculatum	Leaves	14.6

These data show that some of the common plants growing around hot springs contain considerable amounts of arsenic. Because of the small amount of samples taken, however, and because the arsenic concentrations in the soil around the plants were not measured, no quantitative statements can be made about the plants' uptake abilities or tolerances.

2.4 Discussion

The data obtained for the geothermal waters examined in this experiment are consistent with results that previous authors have found in other geothermal waters. The possible exception to this is the arsenic content of the hot pool at Lake Rotokawa. The low arsenic and alkali metal content of these waters may be due to the fact that the waters around Lake Rotokawa are of acid - sulphate - chloride type, as reported by McColl (1975). Acidic conditions may favour the formation of an insoluble precipitate. This would explain the high levels of arsenic found in the sediments by Weissberg (1969) and Krupp and Steward (1987). Timperley and Vigor-Brown (1986) showed that in geothermal steam (which leads to the formation of acid sulphate waters) there are very low concentrations of arsenic and alkali metals relative to geothermal water. If the acid - sulphate - chloride waters in the Rotokawa area arise by mixing of acid sulphate and neutral chloride, a high ratio of acid sulphate to neutral chloride waters may be the cause of the low arsenic content.

Possible sources of error in the measurements of the geothermal waters include: (1) localised dilution of the sampling site by surface waters, (2) seasonal variation in the mineral content of the spring due to seasonality or anomalies in rainfall. (3) precipitation of some chemicals in the water between the spring and the sampling site.

The Ohaaki power station has a water right for disposing of 3000 tonnes of water per day into the Waikato River. This is far less than the Wairakei power station which releases 5400 tons per hour. Assuming that the Ohaaki power station uses a similar amount of geothermal water / steam as the Wairakei station, then using the calculated 66% : 33% waste water / reinjection ratio, the power station should release more than the 3000 tonnes waste water per day into the Waikato. The calculation will be incorrect, however, if some rubidium (the element used in the calculations) is lost from the water before it reaches the holding ponds where the sample was taken, or large amounts of rain water enter the holding ponds. More data are needed to accurately assess the situation.

All the alkali metals in the geothermal waters had a positively significant mutual correlation. This may be an artefact because some of the waters in the Broadlands field (Raw Bore, West Hold, and East Hold) are related, *i.e.* come from the same source. There is still a clear relationship, however, when these data are removed from the graphs. This relationship may occur because: (1) for any sample taken, the geothermal water source (which may contain fixed alkali metal ratios) may be diluted to differing degrees, by surface waters (which contain very few alkali metal ions), (2) the alkali metal ions may be concentrated by differing degrees of evaporation in separate sources, (3) some of the alkali metals are removed from the water between the geothermal outlet and the collection site. The latter is unlikely because all the alkali metals are very soluble and organisms usually uptake alkali metal ions at different rates.

Some of the alkali metals measured have a significant negative correlation with magnesium. This relationship supports (1) above, and makes (2) very unlikely. If (2) were correct, it would be expected that magnesium would be positively correlated with the alkali metals. Reason (1) above could explain the relationship if the surface waters were higher in magnesium than geothermal water. Support for reason (1) also comes from Mahon (1965) whose magnesium determinations in geothermal waters from deep drill holes (>300 m) in three geothermal areas (Wairakei, Waiotapu and Kawerau) showed that the majority of waters contained < 0.090 μg/mL magnesium. Because at this depth contamination by surface waters is unlikely, and assuming that the geothermal water does not subsequently pass through sedimentary rock (which is high in magnesium), the results may give a good indication of the magnesium concentration in the hypothetical 'pure' geothermal water (Table 15). The higher magnesium values found in hydrothermal waters, may be coming from mixing with surface waters. This implies that water from the raw bore in the Ohaaki field, the Champagne pool at Waiotapu and the Lucerne Plant drain (containing 0.009 μg/mL Mg) are good models of 'pure' geothermal water, largely undiluted by surface waters (as would be expected coming from a bore). The Tokaanu hot springs, the hot pool near Lake Rotokawa, and the main drain from the Wairakei power station have probably undergone mixing with surface waters to varying degrees.

Table 15. The chemical composition (μg/mL) of hypothetical 'pure' geothermal water.

Element	Concentration	Element	Concentration
Arsenic	3.9	Sodium	>100
Magnesium	0.032	Potassium	>100
Lithium	7.2	Rubidium	5.7

The negative relationship between magnesium and the alkali metals may also be explained if there is a chemical or biological synergism between the two, *i.e.* the concentration of one, directly affects the concentration of the other, either chemically or in the uptake / release of the elements from biological tissue.

Arsenic determinations of the vegetation showed that some of the plants, particularly *Leptospermum scoparium,* contained considerable amounts of arsenic. It was noted that the results cannot be used quantitatively for reasons mentioned above. The levels found in some plants cause growth inhibition in *Allium cepa* (Pepper *et al.*, 1987) and barley (Benson, 1952; Asher and Reay, 1979). Arsenic tolerance may be advantageous for plants growing close to geothermal sources. Arsenic accumulation may also be advantageous to terrestrial plants in that it may have the effect of deterring grazing and / or parasitism.

To conclude, geothermal areas appear to be sources of some elements to the aquatic biosphere. Arsenic is present in particularly high concentrations and being a semicumulative toxin may significantly affect the biota of the aquatic environment. Much arsenic remains unaccounted for in the Ohaaki field from the geothermal power station. This arsenic may be entering the aquatic environment. Some terrestrial plants found near geothermal areas take up arsenic.

Further work on the geothermal waters entering / exiting the Ohaaki power station is needed to assess the arsenic burden that the station places on the Waikato River. A full study could be conducted on the vegetation around the geothermal pools with respect to the effect of arsenic and other elements and the plants ecology / physiology / biochemistry.

Chapter 3: Arsenic in the Environment

As shown in Chapter 2, of all the elements coming from geothermal sources, arsenic is likely to have the greatest environmental impact. Arsenic has been known since antiquity and was described by Theophrastus *ca*. 300 B.C. The element was first prepared in around 1250 A.D. by Albertus Magnus and described as a "bastard metal" (which translates to metalloid) (Boyle and Jonasson, 1973).

Humans have used arsenic compounds as: insecticides, vermicides, fungicides, herbicides, and to kill other humans, both covertly (food laced with arsenious oxide) and overtly (the war gas lewisite). At present arsenic is only used in some herbicides, the other roles being filled by more effective agents (Penrose, 1974).

The global crustal abundance of chalcophile arsenic is 1.8 μg/g (Mason and Moore, 1982) and it is ubiquitous in distribution. In nature, arsenic is present in four oxidation states; (-III), (0), (III), and (V). The element is most commonly associated with sulphur, though it is associated with many elements in natural deposits including; Cu, Ag, Au, Zn, Cd, Hg, U, Sn, Pb, P, Sb, Bi, S, Se, Te, Mo, W, Fe, Ni, and Co (Boyle and Jonasson, 1973).

Arsenic is a non-essential element in plants and animals, but it has an affinity for biological material, and can be detected in trace amounts in virtually all living organisms. At low concentrations arsenic is tolerated by most organisms. As the concentration increases, the element becomes toxic and eventually lethal. Arsenic forms kinetically stable bonds to sulphur and carbon in organic molecules. The reaction of As (III) with sulfhydryl groups of cystine in proteins causing enzyme inactivation may be the primary mode of arsenic toxicity (Ferguson and Gavis, 1972).

Arsenic poisoning in humans can be either chronic or acute, depending on rate of intake of the element. The effects of acute arsenic poisoning are a latent period followed by rapid collapse, shock and sudden death. Chronic arsenic poisoning leads to progressive symptoms; disturbances in peripheral circulation, polyneuritus (numbness and loss of reflexes), mental disturbances, liver cirrhosis, hyperkeratosis and pigmentation of the skin, kidney damage and changes in heart rhythm (Penrose, 1974).

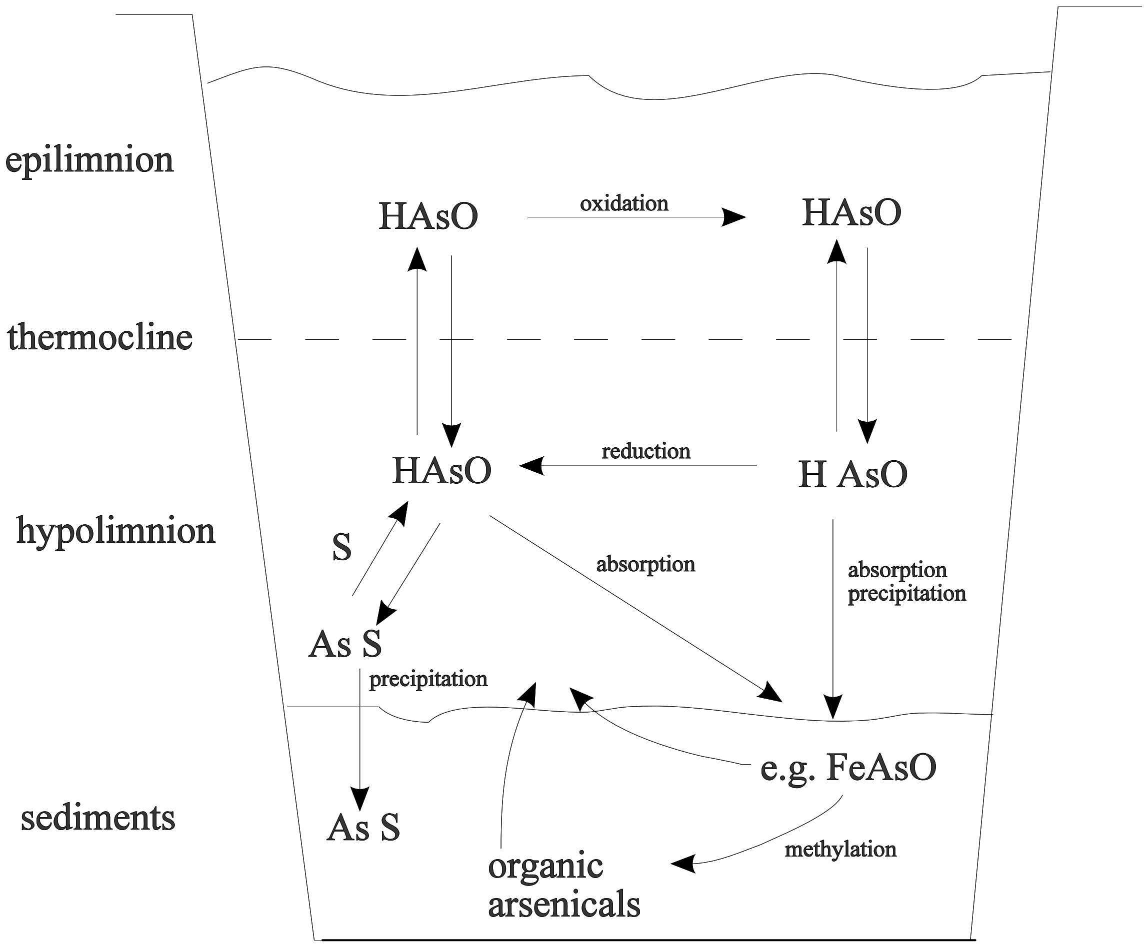
The oxidation state and chemical combination of arsenic dramatically affects its toxicity. In humans As(III) is about 60 times more toxic than As(V) (Ferguson and

Gavis, 1972) and inorganic arsenic is more toxic than when it is organically combined. Woolson *et al.* (1973) showed that high levels of phosphorus lessen the effects of high levels of arsenic in soils and possibly in organisms in general. This may be because phosphorus competes with the binding sites of arsenic.

The background level of arsenic in the aquatic environment is 1.7 ng/g (Boyle and Jonasson, 1973). Ground waters tend to have higher arsenic concentrations than surface waters. The arsenic contents of rocks in an area has a large bearing on the arsenic concentrations in the waters and sediments of nearby lakes and rivers. Ferguson and Gavis (1972) gave a model of the behaviour of arsenic in a stratified lake (Fig. 11).

There are some organisms in aquatic environments that accumulate or change the form of arsenic, including several species of bacteria that reduce As(V) to the more toxic As(III). Some aquatic macrophytes accumulate the element and may act as a sink for arsenic in the aquatic environment. Arsenic in the aquatic environment may be transported to the terrestrial and marine environments and vice-versa by a number of mechanisms. These include; flooding, leaching / runoff, irrigation, biotic transport, and flowing into the sea.

Figure 11:
Local cycle of arsenic in a stratified lake



Chapter 4: Pollution of the Natural Lakes in the Taupo Volcanic Zone by Arsenic and other Elements.

4.1 Introduction

The Taupo Volcanic Zone contains over 32 lakes. Many of these are associated with geothermal activity (McColl, 1975), having geothermal waters either flowing into the lake, or upwelling in the lake itself. As shown in the present and numerous other studies, geothermal waters contain large amounts of certain elements (particularly arsenic) that may affect the biota of any aquatic environment they enter. Some lakes have large amounts of sodium arsenate added in an attempt to control invasive aquatic macrophytes (Liddle, 1982; Rutherford, 1984; Tanner and Clayton, 1990). Tanner and Clayton (1990) showed there were still large amounts of arsenic in Lake Rotoroa near Hamilton 24 years after the application of a sodium arsenate herbicide. The lake has no geothermal inflows.

Arsenic accumulates in the sediments of lakes (Aggett and O'Brien, 1985; Aggett and Kriegman, 1987). Aggett and O'Brien (1985) gave a mechanism of water - sediment arsenic interactions. The cycle is dominated by inorganic processes, despite considerable amounts of organic matter present in some lakes. Ferric and ferrous ions interact with arsenic during its precipitation and mobilisation from sediments. It was shown that arsenic was liberated from the sediments under anoxic conditions as As(III) and that over 90% of arsenic present in the hypolimnion and interstitial water was present as As(III). Thus the arsenic levels in the waters of lakes decrease after turnover when the water becomes oxygenated, and then slowly increase again until the next turnover.

Gifford *et al.* (1993) showed that the water, sediments and trout of Lake Rotorua had concentrations of arsenic up to 130 µg/L, 68µg/g and 6.8 µg/g dry weight (D.W.) respectively, in some areas. Freshwater mussels in Lake Rotorua contained as much as 73.3 µg/g D.W. arsenic. These values are of some concern to public health as they are above the World Health Organisation (WHO) limits for arsenic in drinking water (50 µg/L) and food (2 µg/g). The arsenic concentrations in the living organisms would be much less, however, if they were analysed on a fresh weight instead of a dry weight basis. Little is known about the arsenic content of other lakes in the area or the (human) food sources that they contain. Based on the work of Aggett and Aspell

(1978), trout may not be expected to contain large arsenic concentrations . Trout caught from Lake Taupo and from the Waikato near Broadlands, had flesh arsenic concentrations of the same order of magnitude as the water. Tanner and Clayton (1990) showed that rudd, perch, catfish and eel caught from Lake Rotoroa had arsenic concentrations of between 0.3 and 0.5 μg/g though the level of arsenic in the water was less than 0.01 μg/mL.

Mercury is known to occur in some thermal waters in the Taupo Volcanic Zone (Weissberg, 1975; Liddle, 1982) although the concentrations in natural waters are usually undetectable (<0.001 μg/mL). Mercury shows a strong cumulative pattern in biological systems (much more so than arsenic) so although the basal concentration is low, organisms near the top of the food chain may show appreciable concentrations. Trout are the top predators in the lakes of the Taupo Volcanic Zone. Brooks *et al.* (1976) showed that detectable amounts of mercury were present in trout taken from many of the lakes in the region. Trout from Lakes Rotorua, Rotoiti and Rotomahana had average mercury concentrations above 0.5 μg/g (which is the WHO limit for mercury in foodstuffs). There was a positive correlation between fish size and mercury concentration. Also measured by Brooks *et al.* (1976) were cadmium, copper, zinc, iron and manganese. These elements were found to be 'unlikely to cause problems in public health'. Gifford, 1993 found up to 0.47 μg/g mercury in the sediments in Lake Rotorua and up to 2.0 μg/g D.W. in the trout of the lake. From these two studies it appears that there is a massive amplification of mercury in the higher organisms of the aquatic environment in the Taupo Volcanic Zone.

The chemistry of the waters of lakes that have geothermal inputs is usually rock dominated (McColl, 1975). The chemical inputs to the lakes, both geothermal and non-geothermal, are strongly influenced by the rhyolitic strata which dominate most lake catchments (Timperley and Vigor - Brown, 1986). This being so, and the fact that sedimentary rocks are scarce in this region, means that the concentrations of sodium and potassium, often exceed the concentrations of calcium and magnesium. Lakes with geothermal inputs usually have much higher concentrations of dissolved elements and usually have a different flora and fauna than lakes without geothermal inputs (McColl, 1975). Lake Rotokawa, with relatively high concentrations of dissolved elements, situated *ca.* 10 km north of Taupo, has an aquatic flora limited to a few species of algae and bacteria (Forsyth, 1977).

The aims of this study were: (1) to investigate the concentrations of arsenic and some elements in the waters and sediments of selected lakes in the Taupo Volcanic Zone, (2) To investigate the levels of arsenic and mercury in trout and fresh water mussels from selected lakes in the region.

4.2 Methods

Water, sediment and fish samples (flesh and liver), using methods described in section 2, were taken from the following lakes; Taupo, Rotorua, Rotokakahi, Okareka, Rotoiti, Rotoma, Tarawera, Okataina, Rotoehu, Rerewhakaaitu, Rotomahana, Rotokawa, and Blue Lake. Fresh water mussels were taken from Lakes Rotorua and Tarawera and the soft portions analysed. The trout samples were collected during a fishing competition held on the 25 of November, 1993.

All samples were analysed for arsenic and mercury. Water samples were also analysed for magnesium and the alkali metals.

4.3 Results

Analysis of the water samples gave the results shown in Table 16.

Table 16. Concentrations (μg/mL) of some elements in waters taken from lakes in the Taupo Volcanic Zone.

Lake	As	Mg	Li	Na	K	Rb
Taupo*	0.019	2.6	0.04	9.7	1.7	0.03
Rotorua*	0.007	2.0	0.10	16.1	4.4	0.03
Rotokakahi	0.005	1.2	0.01	5.9	1.9	<0.01
Okareka	0.003	2.5	0.01	6.3	1.7	<0.01
Rotoiti*	0.007	1.8	0.10	15.9	3.7	0.07
Rotoma*	0.002	1.8	0.19	>100	3.5	0.05
Tarawera*	0.048	9.4	0.45	63.9	8.6	0.13
Okataina	0.023	1.3	0.04	9.9	2.0	<0.01
Rotoehu*	0.062	8.3	0.77	17.5	12.7	0.10
Rerewhakaaitu	0.001	1.5	<0.01	5.6	0.7	0.02
Rotomahana*	0.475	8.7	1.71	>100	21.6	0.57
Blue Lake	<0.001	0.4	<0.01	2.4	0.2	<0.01
Rotokawa*	0.173	2.0	1.72	>100	23.2	1.09

* Hot springs enter the lake.

The concentration of mercury in all the waters was below the detection limit for the apparatus (0.001 μg/mL). The above results show that there is a wide variation in the concentrations of the elements measured in different lakes in the Taupo Volcanic Zone. The lakes appear to fall into two distinct groups concerning the concentrations of the elements measured. Members of the first group contain arsenic concentrations below 0.08 μg/mL and include all the lakes without geothermal inputs together with Rotorua, Rotoiti, and Rotoma. For the second group, arsenic concentrations were above 0.19 μg/mL, all these lakes have geothermal inputs. Three of the lakes in the second group had arsenic levels well in excess of the WHO limit for arsenic in drinking water (0.05 μg/mL). These lakes were: Rotoehu, Rotomahana, and Rotokawa.

Table 17. Correlation data (*r*) for arsenic, magnesium and the alkali metals in water and sediments of the lakes in the Taupo Volcanic Zone.

Element	As	Mg	Li	Na	K	Rb
Mg	0.64(S)					
Li	0.77(S*)	0.62(S)				
Na	0.67(S)	0.85(S*)	0.84(S*)			
K	0.85(S**)	0.79(S*)	0.95(S**)	0.88(S**)		
Rb	0.85(S**)	0.42(NS)	0.90(S**)	0.85(S*)	0.89(S**)	
Sed. As	0.78(S)	0.39(NS)	0.80(S*)	0.80(S*)	0.81(S*)	0.91(S**)

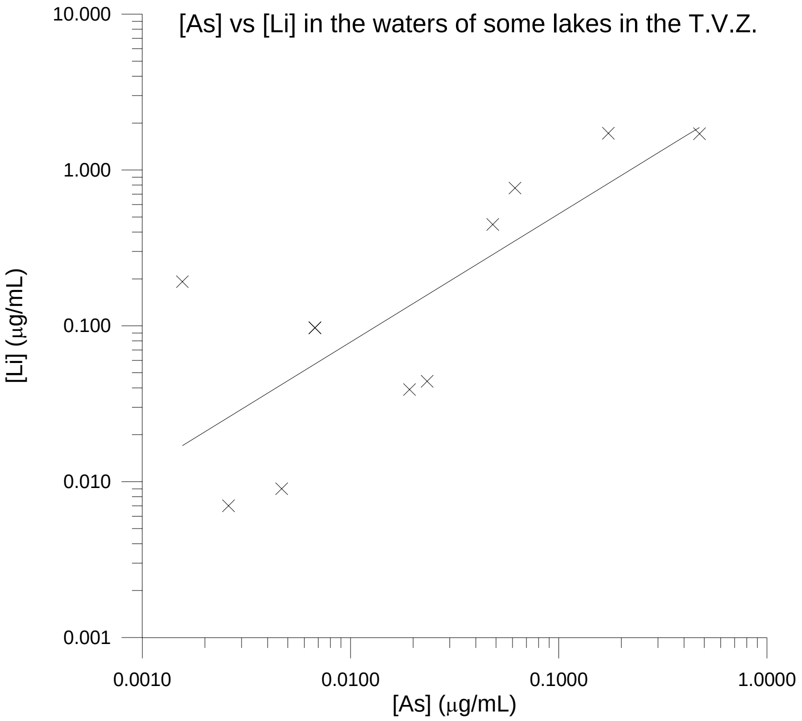
There were significant positive correlations between arsenic and the alkali metals of the lakes (Table 17, Figs 12 - 14) and significant to highly significant positive correlations between the alkali metals (Table 17, Fig. 15). Unlike the geothermal waters investigated in the first study, there were positive correlations between the alkali metals and magnesium (Fig. 16) as well as a positive correlation between arsenic and magnesium (Table 17).

Table 18. Concentration (μg/mL) of arsenic in sediments from some lakes in the Taupo Volcanic Zone.

Lake	Arsenic Conc.	Lake	Arsenic Conc.
Taupo	-	Okataina	0.8
Rotorua	14.1	Rotoehu	-
Rotokakahi	-	Rerewhakaaitu	5.5
Okareka	4.3	Rotomahana	87.7
Rotoiti	-	Blue Lake	8.3
Rotoma	0.7	Rotokawa	443.4
Tarawera	1.0		

Figure 12:

[As] vs [Li] in the waters of some lakes in the T.V.Z.



The arsenic concentrations in the sediments (Table 18) were significantly positively correlated with the concentration of arsenic in the waters (Tables 17 & Fig. 17). The results are low compared with determinations made by Gifford *et al.* (1993) for Lake Rotorua.

Arsenic determinations made on trout from the lakes listed above revealed that the concentration of arsenic in the flesh for all trout tested was very low, close to 0.01 μg/g (fresh weight) F.W. The liver of the trout contained even less arsenic *ca.* 0.005 μg/g F.W. Because of the sample preparation technique used (see Section 1.2) the arsenic in the sample solution was barely detectable and consequently there was a large relative error. Surprisingly, trout from lakes with the highest arsenic levels in the waters *i.e.* Lakes Rotomahana and Rotoma, had flesh arsenic levels below the detection limits. The other lakes with relatively high water arsenic levels (Lakes Tarawera and Okataina, Table 19) had measurable amounts of arsenic in the flesh of the trout.

Table 19. Levels of arsenic (μg/g fresh weight) in the flesh of trout from Lakes Tarawera and Okataina.

Lake	Tarawera	Okataina
Number of samples with measurable arsenic	11	12
Average arsenic concentration	0.031	0.014
Standard deviation	0.020	0.012
Range	<0.007 to 0.075	<0.002 to 0.047

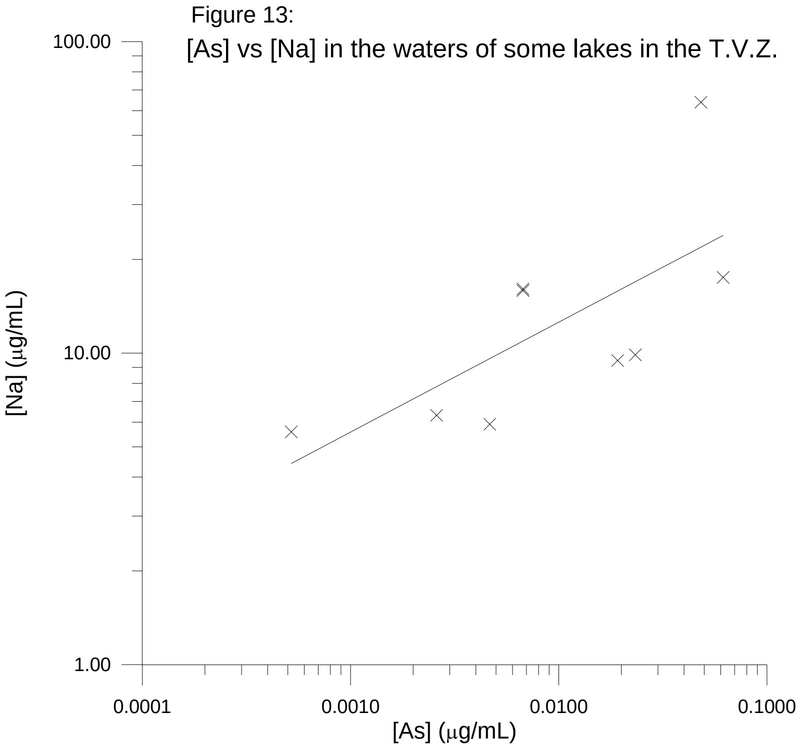


Figure 13:
[As] vs [Na] in the waters of some lakes in the T.V.Z.

Table 20. Levels of mercury in flesh and livers of trout from some lakes in the Taupo Volcanic Zone.

Lake	**Rotorua**	**Tarawera**	**Okataina**	**Rotoiti**	**Rotoma**	**Rotoehu**
# of samples	20	20	20	23	7	17
Av. fish wt.	1.43 kg	1.98 kg	2.11 kg	1.93 kg	1.31 kg	1.26 kg
Av. flesh [Hg]	0.611	0.114	0.064	1.26	0.104	0.125
Flesh S.D.	0.58	0.084	0.053	0.70	0.074	0.069
Flesh [Hg] range	0.24 to 2.07	0.045 to 0.345	0.022 to 0.234	0.257 to 3.83	0.020 to 0.216	0.08 to 1.63
Av. liver [Hg]	1.17	0.196	0.305	1.71	0.229	0.156
Liver S.D.	1.48	0.25	0.958	1.44	0.337	0.068
Lake	**Rotomahana**	**Aniwhenua**	**Galatea**	**Ohakure**	**Rerewhakaaitu**	**Taupo**
# of samples	15	1	6	1	2	7
Av. fish wt.	1.42 kg	3.03 kg	3.21 kg	0.73 kg	1.85 kg	1.4 kg
Av. flesh [Hg]	1.27	0.058	0.070	0.136	0.15	0.073
Flesh S.D.	0.322	-	0.067	-	-	0.043
Flesh [Hg] range	0.937 to 2.156	-	0.01 to 0.165	-	0.13 to 0.17	0.035 to 0.16
Av. liver [Hg]	2.82	0.044	-	0.424	-	-
Liver S.D.	1.47	-	-	-	-	-

These results are well below the WHO limit for arsenic in foodstuffs (2 μg/g) and so the trout are fit to eat so far as arsenic levels are concerned. The arsenic levels in the flesh are actually 30% lower than the values measured in the water, but as mentioned above, there is a large analytical error at these concentrations. There was no correlation between the body weight of the fish and its the concentration of arsenic in its flesh.

Trout from all the lakes had measurable amounts of mercury in their flesh and livers (Table 20). There were four lakes where fish had mercury concentrations in their flesh above the WHO limit for mercury. They were Lakes Rotorua, Rotoiti, Rotomahana and Rotoehu. In the first three lakes mentioned, the average fish contained more than 0.5 μg/g mercury. This was significantly greater than any of the other lakes (Table 21). There was generally no significant difference in the flesh mercury concentrations of trout from lakes with an average flesh mercury concentration of below 0.5 μg/g. The livers of the trout had higher mercury concentrations than the flesh, in some cases up to three times higher. The relative standard deviation of mercury in the livers was also higher.

Table 21. T -Tests (values of P) for differences in trout flesh mercury concentrations for trout from different natural lakes in the Taupo Volcanic Zone.

Lake	R.rua	Tarawera	Okatai.	R.iti	R.ma	R.ehu	R.mah.
Taraw.	0.00(S**)						
Okatai.	0.00(S**)	0.02(S*)					
R.iti	0.00(S**)	0.00(S**)	0.00(S**)				
R.ma	0.01(S)	0.35(NS)	0.21(NS)	0.00(S**)			
R.ehu	0.00(S**)	0.21(NS)	0.01(S*)	0.00(S**)	0.25(NS)		
R.mah	0.00(S**)	0.00(S**)	0.00(S**)	0.02(S)	0.00(S*)	0.00(S**)	
Galatea	0.00(S**)	0.07(PS)	0.27(NS)	0.00(S**)	0.10(NS)	0.06(PS)	0.00(S**)
Taupo	0.00(S**)	0.06(PS)	0.27(NS)	0.00(S**)	0.25(NS)	0.03(S)	0.00(S**)

N.B. Values of P<0.01 are shown as 0.00. *R.=Roto. Galatea - Taupo P=0.18 (NS)

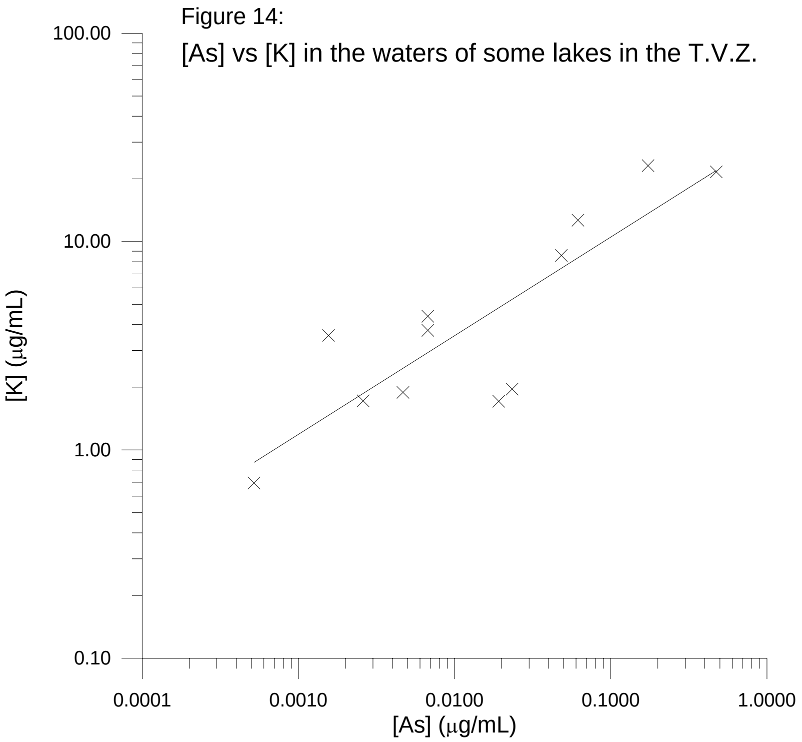
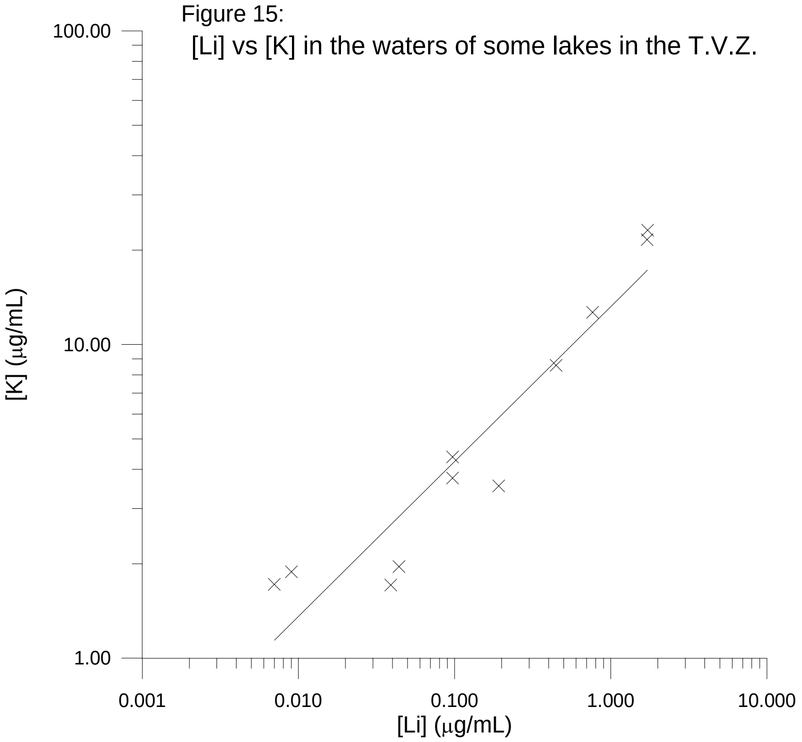


Figure 14:
[As] vs [K] in the waters of some lakes in the T.V.Z.

Figure 15:

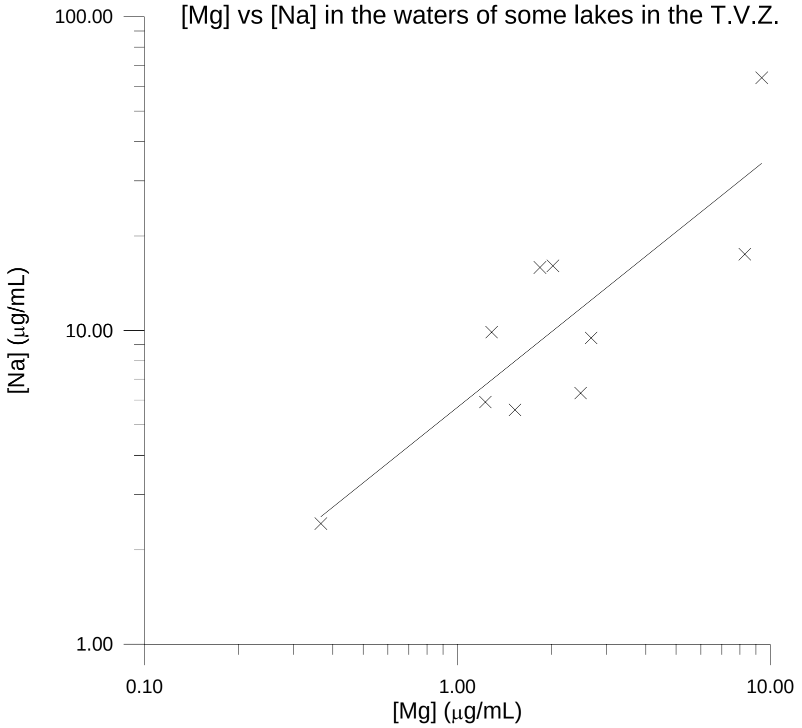
[Li] vs [K] in the waters of some lakes in the T.V.Z.



Lakes containing fish with an average flesh mercury concentration greater than 0.12 μg/g, had fish with significant to highly significant positive correlations between liver and flesh mercury concentrations. In lakes containing fish with an average flesh mercury concentration less than 0.12 μg/g, there was no correlation between liver and flesh mercury concentrations.

Figure 16:

[Mg] vs [Na] in the waters of some lakes in the T.V.Z.



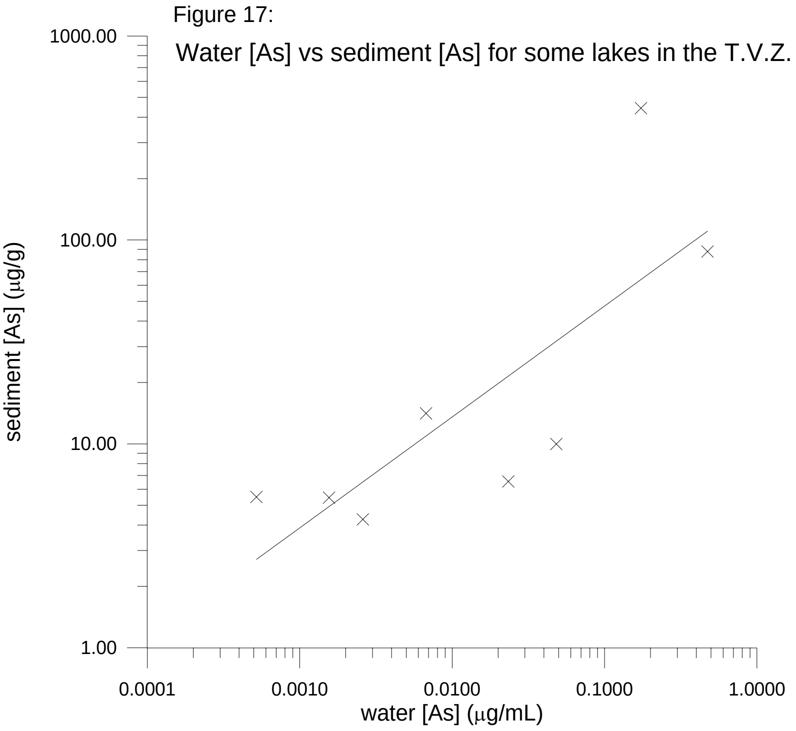


Figure 17:

Water [As] vs sediment [As] for some lakes in the T.V.Z.

There were highly significant positive correlations between the weight of fish and the mercury concentration in the flesh for fish from Lakes Rotorua and Rotomahana (Figs. 18 and 19). This shows that as the fish grows older it accumulates more mercury in the liver and flesh. This should be taken into account when consuming fish from lakes with high mercury levels. There was a possibly significant negative correlation between the size of the fish and mercury concentration in the flesh for trout from Lake Taupo (Table 22). There was no correlation between the mercury concentration in the liver and the weight of the fish in any of the lakes.

Table 22. Correlation data (*r*) for trout in lakes of Taupo Volcanic Zone.

Lake	flesh [Hg] – weight	liver [Hg] - weight	flesh [Hg] liver [Hg]
Rotorua	0.664(S*)	0.118(NS)	0.916(S**)
Tarawera	-0.158(NS)	0.294(NS)	0.109(NS)
Okataina	0.194(NS)	0.185(NS)	0.006(NS)
Rotoiti	0.114(NS)	0.213(NS)	0.991(S**)
Rotoma	-0.231(NS)	-	-
Rotoehu	0.248(NS)	0.100(NS)	0.614(S*)
Rotomahana	0.713(S*)	0.506(PS)	0.771(S**)
Galatea	-0.501(NS)	-	-
Taupo	-0.740(PS)	-	-

Figure 18:

Body weight vs flesh [Hg] for trout in lake Rotorua

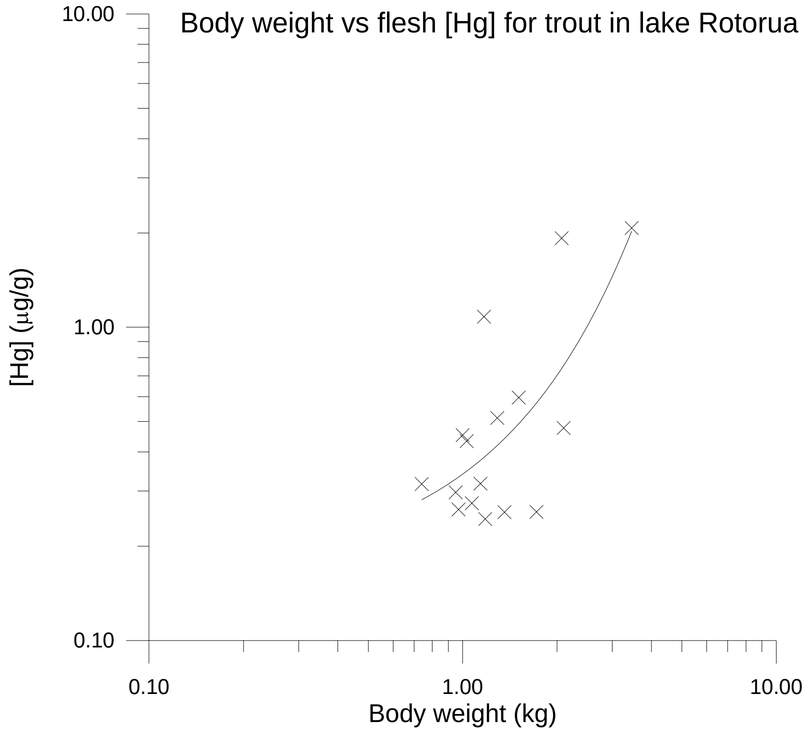
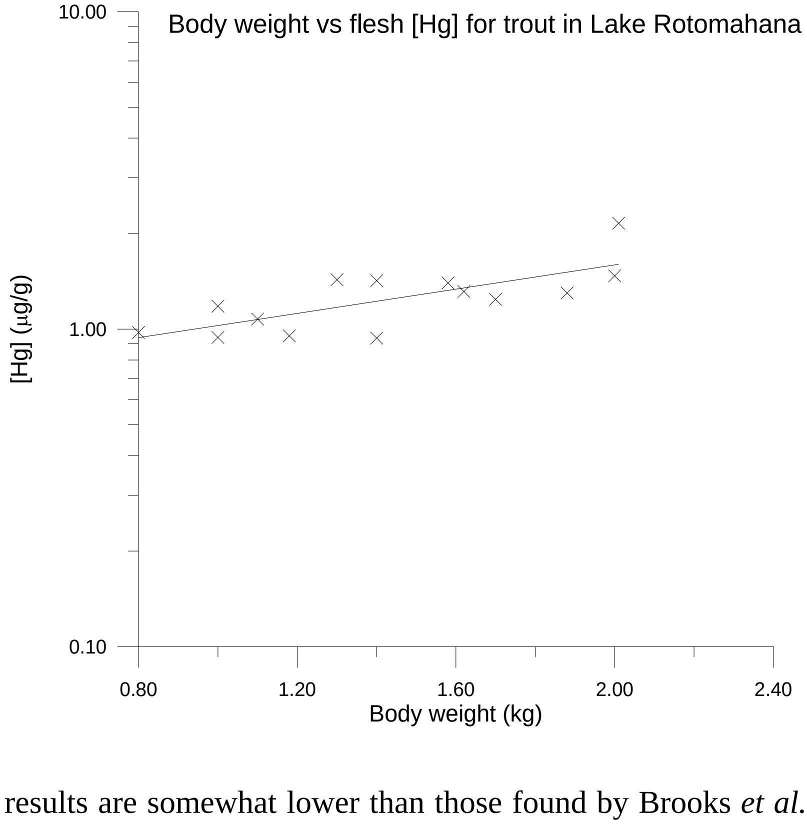


Figure 19:

Body weight vs flesh [Hg] for trout in Lake Rotomahana



The results are somewhat lower than those found by Brooks *et al.* (1976) and the average weight of the fish is heavier. The mercury concentrations in fish from Lakes Rotorua and Tarawera Rotomahana are similar to methylmercury concentrations reported by Kim (1994) for these lakes.

Fresh water mussels from Lakes Rotorua and Tarawera were analysed for mercury and arsenic (Table 23).

Table 23. Mercury and arsenic concentrations (µg/g) of the soft portions of some fresh water mussels from Lakes Rotorua and Tarawera.

Lake	Rotorua	Tarawera
Mean fresh weight (excluding shell)	7.20	7.91
Number of samples	5	12
Mean [As]	3.68	4.30
Standard dev.	0.78	1.42
Mean [Hg]	0.14	0.03
Standard dev.	0.09	0.02

Table 23 shows that mussels from both Lake Rotorua and Tarawera contain arsenic concentrations above the WHO limit for arsenic in food stuffs. The mercury levels were well below WHO limits.

4.4 Discussion

None of the waters from any lakes had measurable amounts of mercury. This was expected, however, based on the data of Weissberg (1975) which show that the major contributor of mercury to the area (geothermal waters) had barely measurable amounts of this element.

Waters from three of the lakes measured had arsenic concentrations above the WHO limit for arsenic in drinking water, a fourth had an arsenic concentration marginally lower than the WHO limit. There are two probable sources for this arsenic: (1) geothermal activity and (2) residual arsenic from sodium arsenate added as an aquatic herbicide. The arsenic concentrations of the lake waters fell into two groups - those with <0.08 µg/mL As and those with greater than 0.19 µg/mL As. The lakes without geothermal input fell into the first group as well as three lakes (Rotorua, Rotoiti and Rotoma) with associated geothermal activity. All the lakes in the latter group have known geothermal activity. This indicates that if the a lake does not have geothermal activity, its arsenic content is likely to be low, and that geothermal activity may be the major source of arsenic in the lakes. The fact that some lakes with a known high geothermal input had low levels of arsenic may be explained by sampling error. Gifford *et al.*, 1993 recorded a large variation (0.11 µg/mL) in arsenic concentrations from different regions in Lake Rotorua. This implies the sampling error of the waters from the lakes in this study is large, as only one sample was taken from each lake. The arsenic content of the water may also change depending on season and rainfall. During periods of high rainfall, the arsenic level would be expected to drop as the lakes become diluted by rainwater and / or runoff containing no arsenic. Sediments absorb - release arsenic at different rates depending on the time since turnover (see below).

Aggett and Aspell (1978) showed that with the occasional exception of a few summer months, over 90 percent of the arsenic in water of the Waikato River and dams was present as As(V). It is thus likely that the majority of arsenic in the lakes of the Taupo Volcanic Zone is also in this oxidation state. Rutherford (1984) noted that there have been occasional algal blooms in lake Rotoroa, involving species of the cyanobacterium *Anabaena.* It was demonstrated by Freeman (1985) that *Anabaena oscillaroides* can reduce considerable amounts of As(V) to As(III) which is over 60 times more toxic (Ferguson and Gavis, 1972). The quality of the water pertaining to arsenic toxicity should be reassessed during and shortly after any algal blooms. Algal blooms may arise spontaneously or as the result of eutrophication of the lake (discussed below).

The concentrations of certain alkali metal ions in the water may show the degree of geothermal input into the lake. In the first study, it was hypothesised that all geothermal water had approximately the same chemical concentrations and that the variations in alkali metals measured were due to dilution by surface waters. The amount of magnesium, alkali metal ions and arsenic in a hypothetical 'pure' geothermal water was calculated. As lithium and rubidium are virtually restricted to waters of geothermal origin (Liddle, 1982), it may be possible to estimate the percent geothermal input into the lake. The calculations assume that (a) all the element in the lake is of geothermal origin and (b) none of the element is being removed from the water in the lake. Arsenic, lithium and rubidium are three elements that are rare in surface waters but rich in geothermal waters. Arsenic determination is extremely sensitive and the element can be accurately determined at low concentrations in water. It is readily removed, however, from the lake water by precipitation into sediments and uptake into aquatic macrophytes. This would give an artificially low reading. Lithium and rubidium are not removed in quantity from lake water by any known mechanism, however, there is a large analytical error when measuring them at very low concentrations. Lithium also occurs in small amounts in some surface waters, this would give an artificially high reading.

Table 24. Calculations using lithium, rubidium, and arsenic, of amount of the geothermal water entering some lakes in the Taupo Volcanic Zone as a percentage of total water entering the lake.

Lake	% using Li	% using Rb	% using As
Taupo	0.56	0.53	0.49
Rotorua	1.39	0.53	0.18
Rotokakahi	0.14	<0.2	0.13
Okareka	0.14	<0.2	0.08
Rotoiti	1.39	1.23	0.18
Rotoma	2.64	0.88	0.05
Tarawera	6.25	2.28	1.23
Okataina	0.56	<0.2	0.59
Rotoehu	10.69	1.75	1.59
Rerewhakaaitu	<0.1	0.35	0.03
Rotomahana	23.75	10	12.18
Blue Lake	<0.1	<0.2	<0.01
Rotokawa	23.89	19.12	4.43
AVERAGE	6.49	4.07	1.76

It is to be noted that these calculations only apply to the water in the part of the lake sampled, not the entire lake.

The calculations show that, as predicted, lithium gave the highest results (possibly because of the presence of non - geothermal lithium) and arsenic gave the lowest results (because arsenic is being removed from the water). The lower the calculated percentage geothermal water, the higher the relative error because of the increasing analytical error at low concentrations. The calculations based on rubidium may well be the best measure of percent geothermal water entering the lakes. This is supported by the fact that with the exception of Lake Rerewhakaaitu, none of the lakes listed as having no geothermal input by McColl (1975) had any measurable rubidium content.

The values shown in Table 24 imply that the major source of arsenic in the lakes of the Taupo Volcanic Zone results from geothermal activity. This is because there is a highly significant positive correlation between the amount of rubidium (and calculated percent of geothermal water entering the lake) and arsenic.

Typically, sodium and potassium concentrations exceeded magnesium concentrations contrary to most natural waters (Forstner and Wittmann, 1983; Mason and Moore, 1982). This is consistent with observations made by Timperley and Vigor-Brown, 1987, and explained by the dominance of rhyolitic rocks in the area.

The amount of magnesium in the lake waters was positively correlated with the alkali metals and with arsenic (Table 17). This is somewhat surprising as magnesium showed a significantly negative correlation with the alkali metals in the hydrothermal waters of the area. The magnesium content of the waters was also an order of magnitude higher in the lakes than in the hydrothermal waters. A possible explanation for the magnesium - alkali metal relationship in lakes is that warm / hot water from geothermal areas gains magnesium as it passes over surface material in or on its way to the lake. This could be tested by measuring the magnesium content of a geothermally heated stream at various points along its length.

The sediments of most of the lakes in the Taupo Volcanic Zone typically had arsenic values of the order of 10 μg/g. There was a highly significant correlation between the arsenic concentrations in the sediments and the arsenic concentrations in the water of the lakes. It would be expected that the amount of arsenic in the sediments will change depending on the degree of oxygenation of the water. Thus there might be a variation in the arsenic levels in the waters and sediments depending on the time since turnover (season). Addition of nitrogen and phosphorus wastes to lakes results in a proliferation of the aquatic flora and fauna. Its subsequent decay results in a lowering of the oxygen content of the water due to microbial respiration. This process, known as eutrophication has occurred in some lakes in the Taupo Volcanic Zone, most notably Lake Rotorua. This may affect the arsenic levels in the waters of the lake as arsenic is liberated from sediments under the anoxic conditions brought about by microbial action. Thus disposing of wastes into the lakes of the area may indirectly cause an increase in the arsenic levels of the water and subsequent increase in the biota of the lake.

Levels of arsenic in the flesh and liver of trout were very low, of the same order of magnitude as the concentration in the water. This is consistent with the study done by Aggett and Aspell (1978). It thus appears that either arsenic does not accumulate strongly up the food chain or that trout have an excretion mechanism for the poisonous element. Wagemann *et al.* (1978) noted that the growth of rainbow trout was adversely affected at concentrations of 1 μg/mL arsenic and above. The arsenic concentrations in the water and the fish were generally an order of magnitude less than this value and so it is unlikely the arsenic in the lake waters is going to affect trout. Levels in flesh were well below the WHO limit for foodstuffs (2 μg/g) so there should be no health problems caused by arsenic from eating trout.

Unlike arsenic, all trout had measurable amounts of mercury. Some lakes had trout that had mercury concentrations in the flesh of greater than the WHO limit of 0.5 μg/g. It would appear that there is a strong accumulation of mercury up the food chain, as none of the waters from any lake had any measurable amounts of mercury. Strong positive correlations between the body weight and mercury concentrations in the flesh of the trout suggest that mercury is not excreted in appreciable quantities and accumulates during the life of the fish. Bache *et al.* (1971) showed a strong positive correlation between the age of the trout (*Salvelinus namaycush*) and mercury content of the flesh. Livers of the trout generally contained more mercury than the flesh. This is probably because the liver intercepts the products of digestion before they are laid down in flesh tissue and thus bind some of the mercury from all food items ingested.

Following the lead of Brooks *et al.* (1976) the maximum daily consumption of trout flesh from various lakes has been calculated using the *acceptable daily intake* of mercury set at 30 μg for an adult by Grimstone (1972). The calculations make the assumption that all the mercury in the trout is in the methyl form. Weissberg and Zobel (1973) and Kim (1994) showed that virtually all the mercury in trout sampled by them was in the methyl form.

Table 25. Maximum allowable daily consumption of trout flesh by adult humans to keep within an acceptable daily intake of 30 μg of mercury. All units are grams (fresh weight).

Lake	A.D.I.	Lake	A.D.I.
Rotorua	49	Rotomahana	24
Tarawera	263	Aniwhenua	508
Okataina	462	Galatea	429
Rotoiti	24	Ohakure	221
Rotoma	286	Rerewhakaaitu	200
Rotoehu	242	Taupo	411

For all but three of the lakes (Rotorua, Rotoiti and Rotomahana), it is extremely unlikely that an individual could maintain a consumption rate above the acceptable daily intake of flesh (Table 25). The three lakes listed are unlikely to cause problems unless trout makes up a large proportion of an individual's diet. Kim (1994) showed that the flesh methylmercury concentration of a fish decreases posteriorly by about 20%. As flesh samples in this study were taken from behind the head of the fish, the average mercury concentration for the whole fish may be slightly lower, and the consequent ADI value may be slightly higher. The ADI values in this study are higher than those calculated by Brooks *et al.* (1976), because the average mercury concentration in the flesh of the trout was approximately 30% less for many of the lakes. The differences may have been due to: (a) different analytical techniques, (b) a decrease of mercury concentration in some of the lakes or (c) seasonal variation in the fish. A decrease in the mercury concentrations in the water of the lakes is likely to be caused if there is a decrease in geothermal input into the lakes or if there has been a cessation of mercury pollution from a human source. Geothermal sources are known to change over time (Henley, 1985). Drilling of bores for steam / hot water may also change the rate of geothermal activity in the area. This occurred when the Wairakei power station opened in 1967, and several geysers at the 'craters of the moon' park disappeared (Henley, 1985). There may be seasonal variation in the mercury concentration in trout. A possible explanation for this may be that after a fish has gone through a stage of rapid growth, the newly grown flesh will not have accumulated much mercury and thus have a low concentration. Mercury will accumulate in the flesh that has had no considerable growth for a period and consequently the fish will have a higher mercury concentration in its flesh.

Fresh water mussels from Lakes Rotorua and Tarawera contained very little mercury. This is probably because mussels are low in the 'food chain', being filter feeders consuming macromolecules and micro organisms. Mercury therefore does not accumulate in them as strongly as in animals such as trout near the top of the food chain.

The average arsenic levels in mussels from both lakes is above the WHO limit of 2 μg/g. Mussels being benthic animals may be exposed to much higher water arsenic levels than the concentrations measured in the surface waters of the lake. As discussed above, Aggett and O'Brien (1985) and Aggett and Kriegman (1987) showed that there were large amounts of arsenic in the sediments, interstitial water and hypolimnion of lakes relative to surface waters.

To conclude, three of the lakes studied, Rotokawa, Rotomahana and Rotoehu had arsenic concentrations above the WHO recommendations for drinking water. These lakes should not be used as a water supply. The concentration of the alkali metals and magnesium showed strong positive correlations with the concentration of arsenic in lake water. Thus easy-to-quantify alkali metals and magnesium may be used as an indicators of the level of arsenic in a given lake. Rubidium, because it is almost exclusively geothermal in origin, may be used to calculate the percentage water entering the lake that is geothermal in origin. Rubidium like the other alkali metals is strongly positively correlated to arsenic and this implies that the majority of arsenic in the lakes of the Taupo Volcanic Zone is geothermal in origin. Trout from the lakes had flesh arsenic concentrations similar to the water of the lakes they were in and consequently pose no health risk as far as arsenic is concerned. Mercury concentrations in trout were all elevated relative to the lake water (which had mercury concentrations below detection limits 0.001 μg/mL). Most trout from Lakes Rotorua, Rotoiti and Rotomahana had flesh mercury concentrations above the WHO recommendations and should not form a large part of an individual's diet. The mercury concentrations in the flesh of the trout were positively correlated with body weight. Fresh water mussels sampled from Lakes Rotorua and Tarawera had arsenic levels in excess of WHO limits and should not be eaten.

There is potential for further study on the distribution, and seasonal variation of arsenic in the various Lakes of the Taupo Volcanic Zone. Future arsenic analysis of the sediments of the various lakes could be made to determine if the sediments are accumulating arsenic over time. Other food sources from the lakes *e.g.* water cress and fresh water crayfish (koura) should also be analysed for arsenic and mercury.

Chapter 5: Pollution of the Waikato River system by Arsenic and other Elements.

5.1 Introduction

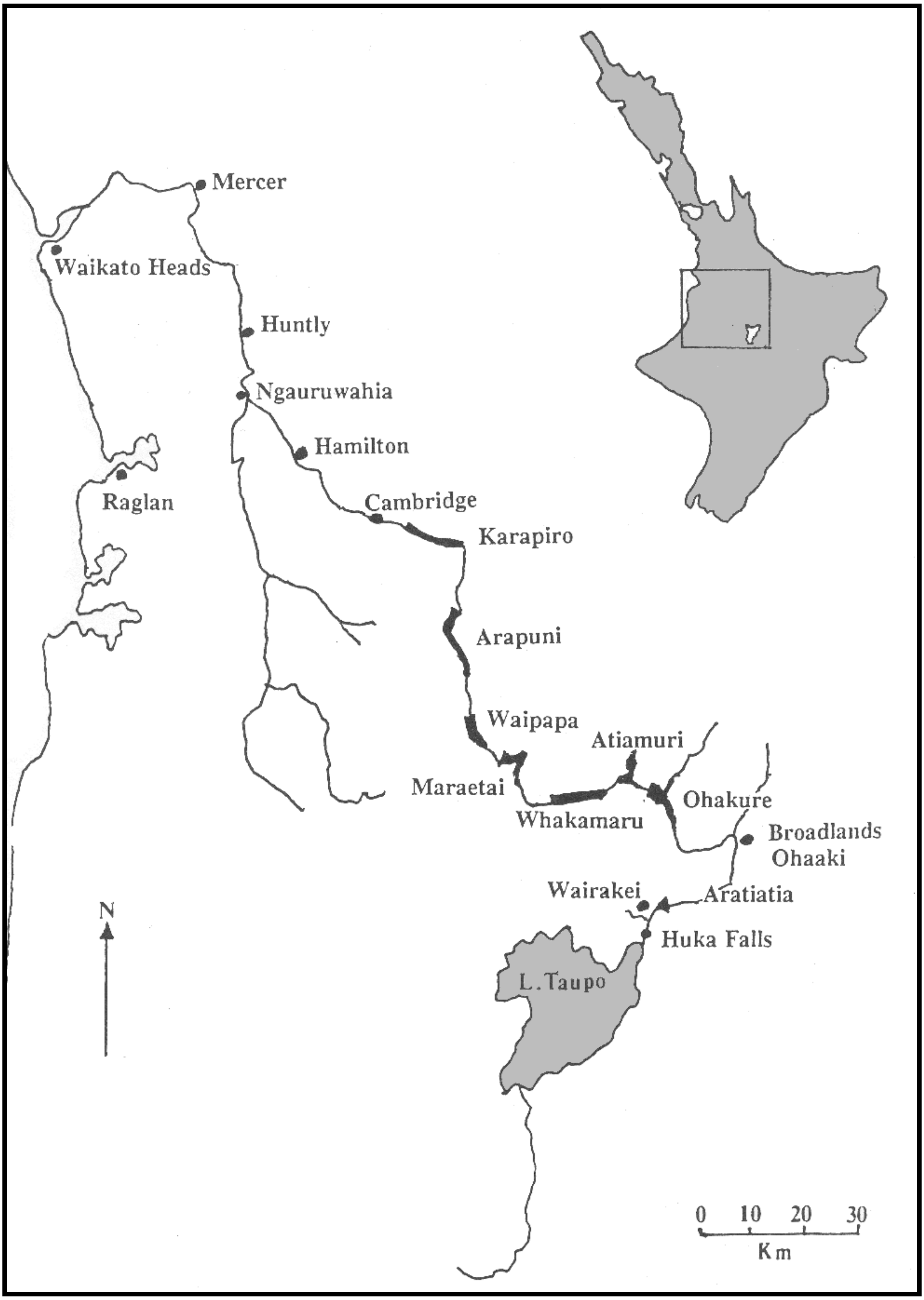
The Waikato River (Fig. 20), at 425 km, is the longest river in New Zealand. It drains the largest lake in the country, Lake Taupo. From Lake Taupo, the river flows in a north-westerly direction through an incised channel near Tokoroa, and on to the flat, often swampy lowlands from Cambridge to Mercer. Northward from Mercer, the river narrows and finally discharges into the Tasman sea at Port Waikato *via* a large estuary. The Waikato drains a total catchment area of 14,000 km^2 (Liddle, 1982). The 366 metre fall of the river from Lake Taupo to the sea, has been exploited by the strategic placement of eight hydro electric power stations. These occur in narrow valleys through the plateau lands near Tokoroa.

At its upper reaches, the Waikato River flows through four geothermal fields, Wairakei, Broadlands, Orakei Korako and Atiamuri. Also, there are several geothermal fields in the catchment area of the river namely; Tokaanu, Waihi, Rotokawa, Mokai, and Te Kopia. Both the Wairakei and Ohaaki geothermal power stations release geothermal effluents into the Waikato River, though some of the waste water from the Ohaaki power station is re-injected. Chapter 2 showed that the hydrothermal waters discharged from the power stations and some geothermal areas contain relatively large amounts of some elements. The toxic element arsenic is present in particularly large amounts. It might thus be expected that the Waikato River contains elevated levels of arsenic as well as other elements of geothermal origin. Reay (1973) estimated the amounts of arsenic entering the Waikato River from various geothermal sources (Table 26).

Table 26. Estimates of the arsenic inputs into the Waikato River from geothermal areas by Reay (1973).

Natural Source	Tonnes per annum
Lake Taupo	30
Wairakei field	22
Ohaaki pool	0.5
Orakei Korako	8 - 13
Waiotapu – Repora valley	1 - 2
Total Natural As	61 - 67
Geothermal development	
Wairakei power station	190

Figure 20. Map of the Waikato River.



Other sources of pollutants in the Waikato River include phosphate run-off from farms using phosphate fertilisers and effluents from various industrial plants along the river such as the pulp and paper mill at Kinleith. Liddle (1982) reported that the Kinleith pulp and paper mill releases effluent containing 0.05 µg/mL arsenic.

Aggett and Aspell (1978) determined the levels of arsenic in water samples taken at various points on the Waikato River at different times of the year in 1976. Values tended to be slightly higher in summer though there was fluctuation throughout the year. Typically, the arsenic concentrations increased from 11 µg/L at Tuakau to 62 µg/L at Lake Aratiatia then decreased to 8 µg/g at Lake Taupo. Of the arsenic measured over 90% was As(V). Liddle (1982) reported similar results. Freeman (1985) reported that in the spring and summer months the more toxic As(III) species was the predominant form of the arsenic in the water of the Waikato. This was attributed to the action of the cyanobacterium *Anabaena oscillaroides.* It was demonstrated this bacterium could take up As(V) and reduce it to As(III) at a rate of 12ng As per 10^6 cells per day. Some of the waters in the Waikato River had greater than 50 µg/L, the WHO limit for arsenic in drinking water, but water with greater than 50 µg/L, namely Lake Aratiatia, is not used as a drinking water supply.

Arsenic concentrations have been determined in some sediments in the Waikato River by Aggett and Aspell (1978), Aggett and O'Brien (1985) and Aggett and Kriegman (1987). In general, these reports find that: deep water sediments have higher arsenic concentrations than shallow water sediments, there is a large variation in the arsenic concentrations of sediments from the same lake, and that sediments may contain up to 400 µg/g As. It is clear that arsenic accumulates in sediments over time. Mechanisms for water - sediment arsenic interactions were given Aggett and O'Brien (1985), and these were discussed in Chapter 4.

Some of the biota of the Waikato River, such as aquatic macrophytes, have been reported to contain large amounts of arsenic (Table 27). Reay (1971) found large amounts in some aquatic macrophytes in the river. He estimated that aquatic macrophytes may account for 3% of the total arsenic in the river system at any one time.

Aggett and Aspell (1978) and Liddle (1982) have also reported high levels of arsenic in some aquatic macrophytes in the Waikato River. Lancaster *et al.*, (1971) tested some of the aquatic macrophytes suitability as a stock feed, which may provide an incentive for the weeds to be removed from the river. It was found that sheep, after three weeks eating the lake weed, had a flesh arsenic concentration of 1.13 μg/g. The arsenic in the flesh virtually disappeared four weeks after stopping consumption of the weeds. There were no health problems reported in the sheep.

Table 27. Average arsenic concentrations (μg/g D.W.) of some aquatic macrophytes from the Waikato River as reported by Reay (1971).

Plant	Arsenic concentration
Ceratophyllum demersum	650
Lagarosiphon major	251
Elodea canadensis	307
Potamopergon sp.	178
Lemna sp.	30
Nitella hookeri	182

The trout of the Waikato River have arsenic concentrations of the same order of magnitude as the water in which they live (Aggett and Aspell, 1978, Aggett and Aspell, 1980). This is concurrent with the results of arsenic determinations made on the flesh of trout from the lakes of the Taupo Volcanic Zone in Chapter 4. Trout from the Waikato River are safe to eat as far as arsenic is concerned. Brooks *et al.* (1976) showed that trout caught from Lake Maraetai had an average flesh mercury concentration of 1.4 μg/g, well above the WHO limit for mercury.

Bower and Timperley (1988) found up to 0.6 μg/mL Li and 0.7 μg/mL Rb in the river. Other than this, elements of geothermal origin in the Waikato River have had little attention.

Aside from geothermal fluids, the chemistry of the water of the Waikato River is influenced primarily by Lake Taupo, whose composition is determined mostly by weathering of superficial volcanic rocks (Bower and Timperley, 1988). Like the lakes in the region the Waikato River has relatively low concentrations of calcium and magnesium.

The Waikato River has a large and diverse range of values to humans, and these will be affected to varying degrees by pollution of the river. The values can be categorised into three groups; (1) physical values, (2) biological values and (3) cultural values. The most obvious physical value of the Waikato River is its power generation potential which has been extensively exploited by humans in the form of hydro-electric power stations. About twenty towns and settlements have a water supply from, or are supplemented by, the Waikato River or its tributaries (Liddle, 1982). There are now plans to supplement the water supply for Auckland with water from the Waikato. Many rural districts use water from the Waikato for irrigation. River water is used for commercial operations in several industrial plants near the river for example washing, grading, and cooling.

The biological values of the Waikato River system include all native flora and fauna in the river. This has been much reduced since humans introduced exotic predators and competitors such as trout and exotic lake weeds which now comprise the bulk of the biomass in the river. Some exotic water weeds (*Egeria densa, Lagarosiphon major, Ceratophyllum demersum, Elodea canadensis*) are now considered noxious. The Waikato River affects the biota of the surrounding terrestrial flora and fauna, providing a habitat / food and water source for some organisms at various stages in their life cycles.

The Waikato River has many cultural values to people living in the vicinity of the river as well as people visiting the region. The river provides many tourist / recreational features including; fishing, swimming, water skiing, rowing / kayaking, and sight seeing. Most of these activities bring revenue into the area. The river is a food source to local people providing them with trout, eels, shell fish, koura, and water cress. The Waikato is culturally important to the Maori tribes of the region.

The aims of this study were (1) to investigate the concentrations of arsenic and some other elements in the waters, sediments, aquatic macrophytes and some other organisms in / near the Waikato River, (2) to investigate the arsenic and mercury concentrations of shellfish and mullet taken from the mouth of the Waikato.

5.2 Methods

Samples were collected and prepared using the methods described in Section 1.2 from numerous sites along the Waikato River on three separate occasions. Water, weed and sediment samples as well as shellfish and mullet were collected between 29th October and 1st November 1993. A second sample of water, weeds and sediments were collected between the 1st and 5th of February 1994. Water cress (*Nasturtium sp.),* willow (*Salix sp.), Potomogeton sp., Spirodela sp.* and snails were collected in April 1994.

Rainbow trout (*Oncorhynchus mykiss*) and brown trout (*Salmo trutta*) were collected from Lakes Maraetai and Atiamuri and surrounding streams.

The sampling sites stretched from Lake Taupo to Port Waikato (Fig. 20)

All samples were analysed for arsenic, magnesium and the alkali metals. In addition plants were analysed for zinc and antimony, and fish were analysed for mercury.

5.3 Results

The arsenic concentrations in water samples collected in November 1993 increased from 0.003 μg/mL at Ngarawahia to 0.121 μg/mL at Lake Aratiatia (Fig. 21). The concentration of arsenic in water taken from Huka falls was 0.006 μg/mL. Water samples collected in February 1994 had arsenic concentrations 15 - 25% higher than the 1993 samples and showed a different distribution pattern, with a maximum arsenic concentration at Broadlands rather than Lake Aratiatia (Fig. 22). This shows that the arsenic concentration in the water changes over time.

Some of the water samples taken up stream from Lake Atiamuri had arsenic concentrations in excess of the WHO limit for arsenic in drinking water. The arsenic concentrations found in the waters of the Waikato River in this study are slightly higher than those reported by Aggett and Aspell (1978) and Liddle (1982) for the same time of year.

The concentration of mercury in all the waters was below the detection limit for the apparatus (0.001 μg/mL).

Table 28. Table of correlations (*r*) of distance down stream and the concentrations of some elements in water samples from the Waikato River.

	Dist. dn. str.	As	Mg	Li	Na	K
As	-0.64(S**)					
Mg	-0.56(S*)	-0.07(NS)				
Li	-0.51(S*)	0.85(S**)	0.07(NS)			
Na	-0.28(NS)	0.78(S**)	-0.02(NS)	0.96(S**)		
K	0.05(NS)	0.65(S**)	-0.13(NS)	0.87(S**)	0.96(S**)	
Rb	0.66(S**)	-0.17(NS)	-0.24(NS)	0.07(NS)	0.43(S)	0.58(S*)

There were significant to very highly significant negative correlations between the concentration of lithium and magnesium and distance down stream from the Wairakei drain (Table 28). There were also strong positive correlations between sodium and lithium and arsenic (Table 28, Figs 23 and 24). This indicates that the sources of the majority of arsenic in the Waikato River are the geothermal areas between Wairakei and Broadlands. As shown in Chapter 2, water of geothermal origin has large alkali metal concentrations, this implies that the arsenic in the Waikato River is of geothermal origin. The concentration of potassium and sodium in water samples showed no correlation with the distance from the Wairakei drain whereas rubidium showed a very highly significant positive correlation with the distance down stream from the Wairakei drain. There were no significant differences in the alkali metal or magnesium concentrations between samples taken in November 1993 and February 1994 (Table 29).

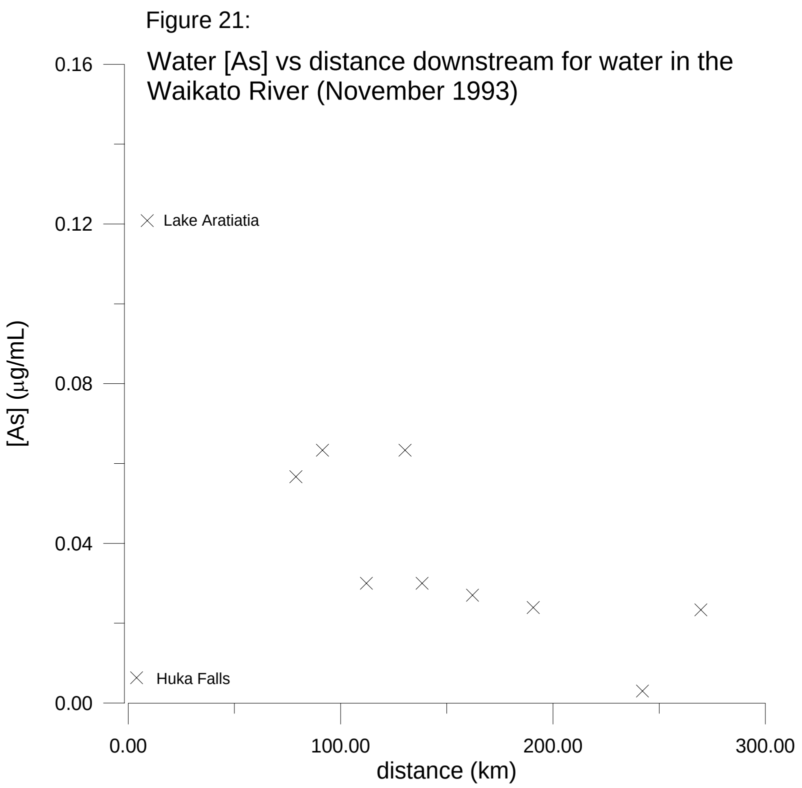


Figure 21:
Water [As] vs distance downstream for water in the Waikato River (November 1993)

Figure 22:

Water [As] vs distance downstream for water in the Waikato River (February 1994)

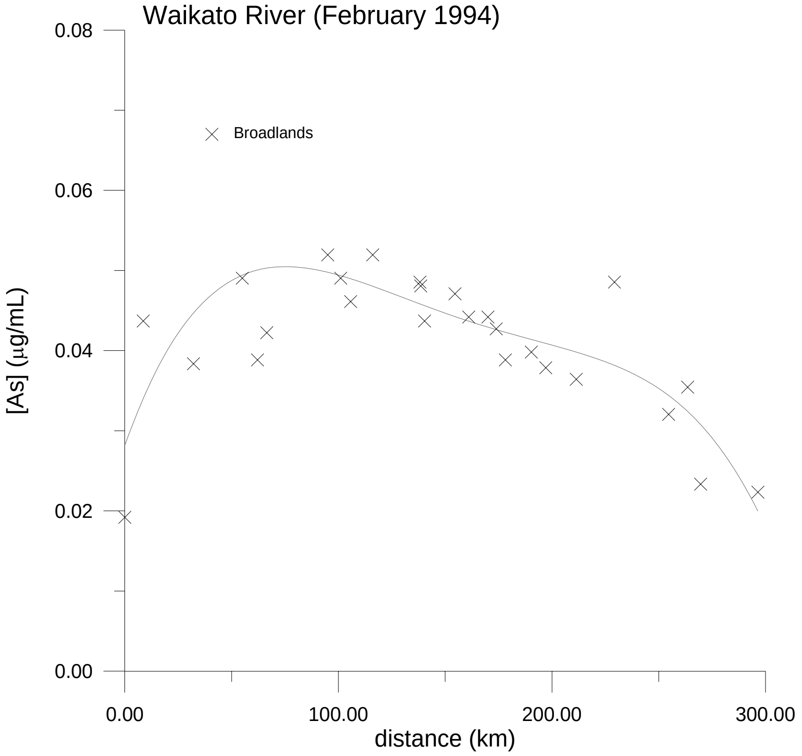


Table 29. Concentration (µg/mL) of arsenic, magnesium and the alkali metals in water samples from the Waikato River.

	(11 / 93)		(2 / 94)	
Element	Median	Range	Median	Range
Arsenic	0.03	0.003 - 0.121	0.044	0.019 - 0.067
Magnesium	2.1	1.8 - 2.6	2.2	1.9 - 2.7
Lithium	0.15	0.01 - 0.22	0.13	0.04 - 0.23
Sodium	17.5	2.2 - 20.7	15.5	9.5 - 22.0
Potassium	3.9	1.9 - 6.1	3.4	1.7 - 5.0
Rubidium	0.07	0.03 - 0.09	0.12	0 - 0.46

Water taken from the river at Broadlands in 1994 was analysed for various elements by I.C.P.-E.S. (Table 30).

Table 30. Concentrations (µg/mL) of some elements in water from the Waikato River at Broadlands.

Element	Concentration	Element	Concentration
Aluminium	<0.20	Molybdenum	<0.010
Arsenic$^+$	0.093	Sodium	31.0
Boron	0.85	Nickel	<0.02
Calcium	8.1	Phosphorus	<0.02
Cadmium	<0.10	Lead	<0.02
Cobalt	<0.02	Sulphur	5.2
Chromium	<0.01	Selenium	<0.30
Copper	<0.03	Silicon	17.7
Iron	<0.03	Tin	<0.03
Potassium	3.9	Strontium	<0.04
Magnesium	3.4	Zinc	<0.010
Manganese	<0.03	Lithium*	0.326
Rubidium*	0.274		

* Determined by flame emission. $^+$ Determined by hydride generation AA.

Figure 23:
[As] vs [Li] along the length of the Waikato River.

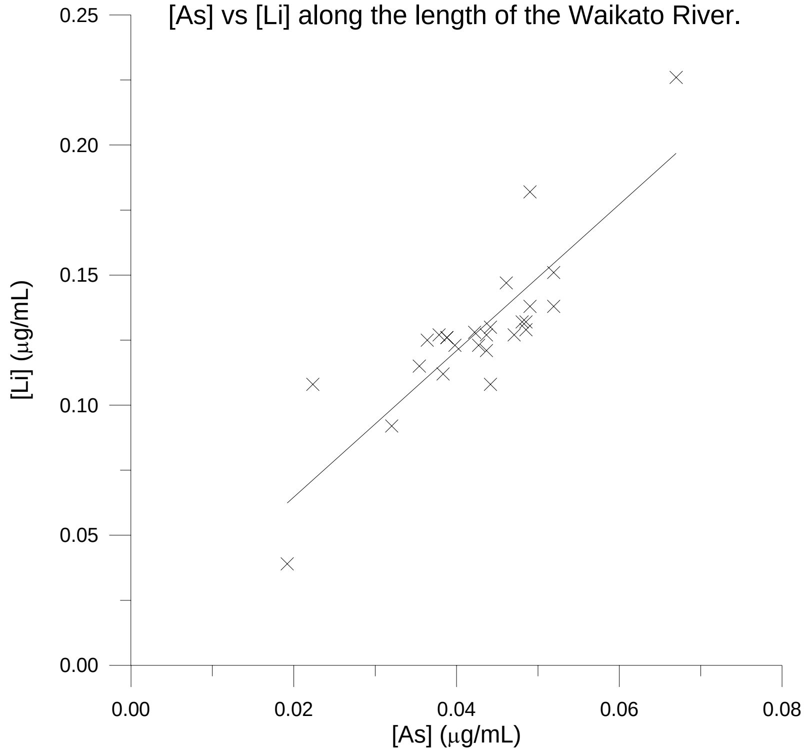


Table 30 shows that at Broadlands, of the common elements, only arsenic is present in sufficient quantities to significantly affect the aquatic environment.

The sediments taken from various parts of the Waikato River had arsenic concentrations ranging from 9 μg/g at Huka falls to 156 μg/g at Lake Maraetai (Table 31). There was no significant difference (P=0.12) in the arsenic concentration of sediments taken from the lakes along the river, and those taken from the river bed. The average concentration was 35 μg/g. Sediment from the Wairakei main drain had an arsenic concentration of 532 μg/g. There was no significant correlation (0.19 NS) between the arsenic concentration of the sediments and distance down stream or the arsenic concentration in the water from which they were taken. There was a significant positive correlation (0.72 S) between the copper concentration in the sediments (which ranged from 4 to 27 μg/g) and distance down stream.

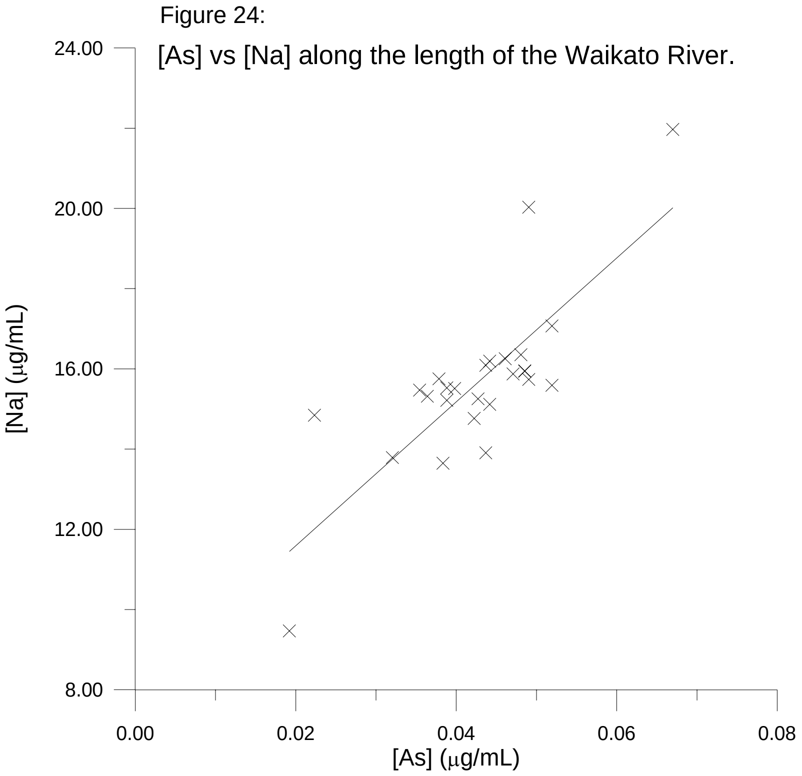


Figure 24:
[As] vs [Na] along the length of the Waikato River.

Table 31. Concentrations (μg/g) of some elements in sediments from selected locations along the Waikato River.

Location	[As]	[Cu]	Location	[As]	[Cu]
Raglan	12.1	27.9	Maraetai	28.4	7.0
Port Waikato	27.3	16.7	Whakamaru	31.4	8.8
Rangariri	57.1	14.8	Atiamuri	37.1	18.6
Ngaruwahia	19.6	12.6	Ohakuri	27.3	5.8
Karapiro	41.7	-	Aratiatia	30.5	4.7
Arapuni	27 .6	16.8	Wairakei drain	531.9	9.2
Waipapa	156.1	9.6	Huka falls	8.7	-

Trout taken from the Waikato river had flesh arsenic concentrations similar to the water from which they were taken (Table 32). This is concurrent with the flesh arsenic levels reported in fish from the natural lakes of the Taupo Volcanic Zone (Chapter 4). There was no significant correlation between flesh arsenic concentration and the length of the fish (Table 33). The average mercury content of fish from all locations was less than 0.3 μg/g, and none of the rainbow trout had mercury concentrations above the WHO limit of 0.5 μg/g. The brown trout from Puwheto had significantly higher (Table 33) flesh mercury concentrations than rainbow trout taken from the same area, some of the larger fish had flesh mercury concentrations above the WHO limit. The mercury content of the fish was highly significantly correlated with the length and head width of the fish. This implies that the flesh mercury concentration may be increasing with the age of the fish. This is consistent with the findings in Chapter 4.

Table 32. Arsenic and mercury concentrations (μg/g) in trout taken from the Waikato River and nearby streams.

Species	rainbow	rainbow	rainbow	rainbow	rainbow	rainbow	brown
Location	Kawhiti	Maraetai	Atiamuri	Mangrun	Mangstr	Puwheto	Puwheto
No. samp.	9	7	2	7	10	22	11
g.m. [As]	0.017	0.033	0.02	0.036	0.046	0.053	0.054
sd. range	0.006 - 0.049	0.017 - 0.062	-	0.018 - 0.072	0.019 - 0.072	0.031 - 0.092	0.028 - 0.103
g.m. [Hg]	0.16	0.14	0.32	0.14	0.16	0.14	0.28
sd. range	0.10 - 0.27	0.09 - 0.21	-	0.11 - 0.19	0.11 - 0.22	0.05 - 0.37	0.11 - 0.70

Three species of aquatic macrophytes (*Egeria densa*, *Ceratophyllum demersum* and *Lagarosiphon major)* from the river were analysed for various elements (Table 35). *C. demersum* occurred from Lake Aratiatia north ward. *L. major* occurred between Lake Taupo and Broadlands whereupon it was 'replaced' with *E. densa*. All species had arsenic concentrations up to 1200 μg/g D.W. *E. densa* and_*C. demersum* had arsenic concentrations that were highly significantly negatively correlated (-0.86 S** and -0.76 S** respectively) with the distance of the plant down stream (Figs. 25 and 26). The results show that the aquatic macrophytes listed above actively extract arsenic from the water in which they grow.

Table 33. Table of correlations (*r*) of arsenic, mercury, length of fish and head width for trout taken from the Waikato River.

	Length	Head width	[Hg] μg/g
Head Width	0.67(S**)		
[Hg] μg/g	0.55(S**)	0.40(S**)	
[As] μg/g	0.18(NS)	0.02(NS)	0.04(NS)

L. major from Huka falls and Lake Aratiatia had arsenic concentrations of 11 and 300 μg/g respectively. The arsenic concentration of *C. demersum* showed a highly significant (0.65 S*) correlation with the water from which it was taken. The arsenic concentration in this plant was 10000 +/- 2000 times the arsenic concentration in the surrounding water. The arsenic concentration in *E. densa* showed no significant correlation (0.41 NS) with the water from which it was taken.

Table 34. T -Tests (values of P) for differences in mercury concentrations in brown and rainbow trout from different locations in the Waikato River.

	Kawhiti	Maraetai	Atiamuri	Mangrun	Mangstrm	Puwhito R.
Maraetai	0.20(NS)					
Atiamuri	0.03(S)	0.00(S*)				
Mangrun	0.20(PS)	0.42(NS)	0.04(S)			
Mangstrm	0.36(NS)	0.25(NS)	0.01(S*)	0.27(NS)		
Puwhito R.	0.20(NS)	0.43(NS)	0.01(S*)	0.48(NS)	0.20(NS)	
Puwhito B.	0.22(NS)	0.02(S)	0.29(NS)	0.02(S)	0.04(S)	0.00(S*)

N.B. values of P<0.01 are shown as 0.00.

The macrophytes also contained measurable amounts of the metals antimony, zinc and copper. It is likely that the plants also accumulate these elements as the concentrations in the river water were below detection limits (0.001, 0.1 and 0.01 μg/mL respectively).

Table 35. Concentrations (μg/g D.W.) of arsenic, antimony, zinc and copper in some aquatic macrophytes from the Waikato River.

	Ceratophyllum		*Egeria*	
Element	**Median**	**Range**	**Median**	**Range**
Arsenic	378	44 - 1160	488	94 - 1120
Antimony	0.31	0.14 - 1.54	0.48	0.16 - 0.97
Zinc	58	22 - 153	36	21 - 120
Copper	17	8 - 72	21	10 - 111

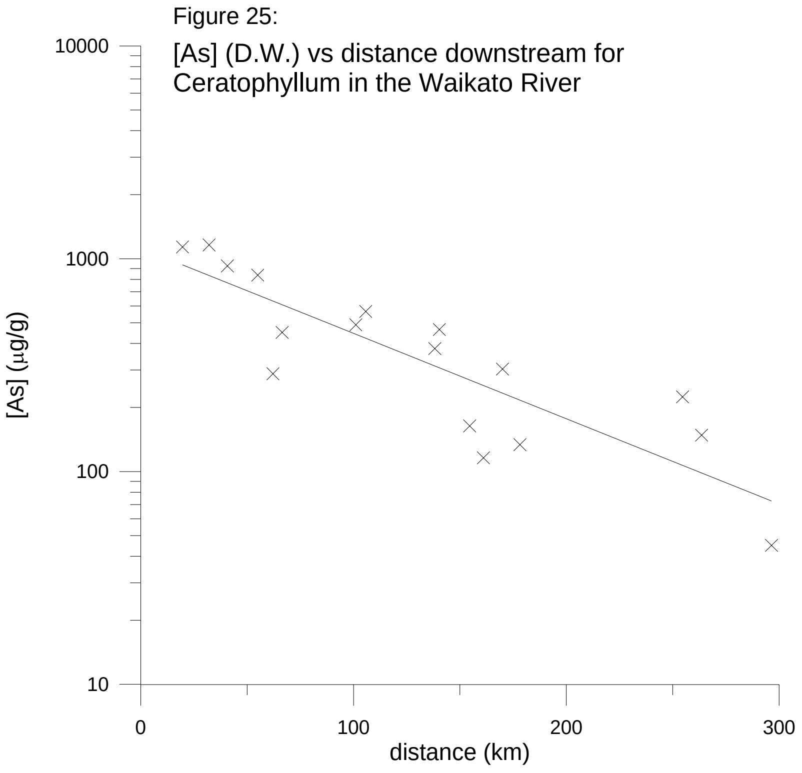
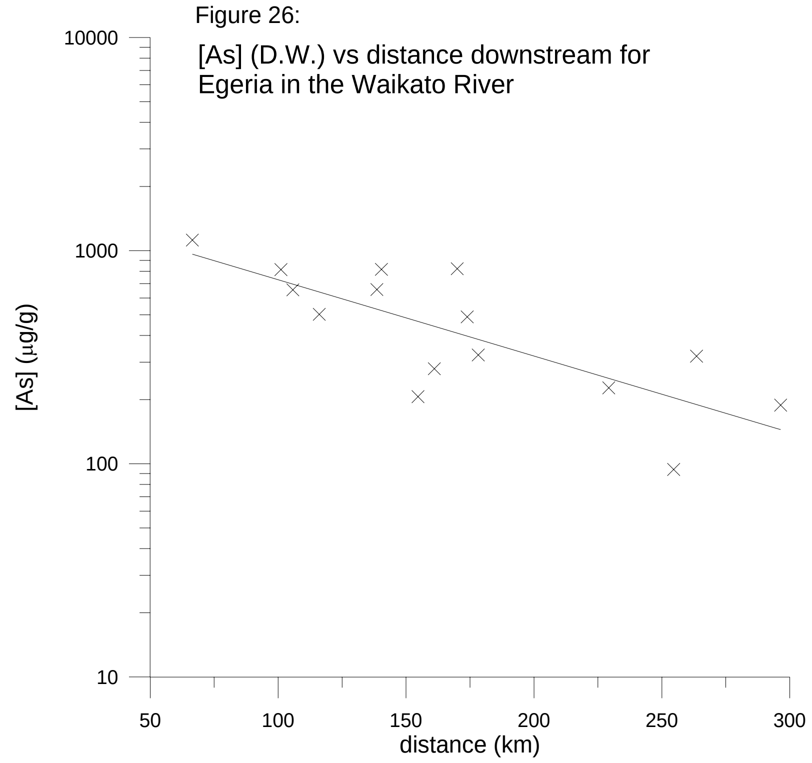


Figure 25:
[As] (D.W.) vs distance downstream for Ceratophyllum in the Waikato River



Water cress collected in late February 1994 from Broadlands was found to contain 306 μg/g D.W. arsenic. Two more samples from the same site collected in April 1994 contained 273 and 659 μg/g D.W. As respectively. A sample collected from Lake Ohakuri contained 30 μg/g D.W. As. The amount of arsenic in the water cress from the Waikato River is well in excess of the WHO limit for arsenic in food stuffs (2 μg/g F.W.). A sample taken as a control from Turatea stream near Massey University had less than 0.001 μg/g D.W. As.

Table 36. Average arsenic concentrations (μg/g) of some organisms in / near the Waikato River.

Organism	Arsenic concentration	Number of samples
Potomopergus sp.	10	3
Salix sp. Leaves	0.3	3
Stems	2.2	3
Duck weed (Spirodela spp)	52	1
Potomogeton sp.	316.9	2
Grass (Agrostis sp.)	2	1

Table 36 shows that arsenic is ubiquitous in the aquatic environment of the Waikato River, with every organism measured containing detectable amounts of arsenic. It also shows there is a large variation in arsenic concentrations between different organisms.

Shell fish and mullet taken from the estuary at the mouth of the Waikato River were analysed for arsenic and mercury. The results were compared with analysis for shellfish taken from an estuary near Raglan (Table 37)

Table 37. Concentrations (μg/g) of arsenic and mercury in mullet, and shellfish from the mouth of the Waikato River and an estuary near Raglan.

	Species	Oyster	Pipi	Cockle	Spiral	Mussel	Mullet
Waikato [As]	average	0.69	1.01	1.24	0.64	1.10	0.11
	S.D.	0.22	0.21	0.39	0.29	0.75	0.06
	# of samp.	10	10	10	10	10	4
Raglan [As]	average	0.32	-	1.11	-	0.28	-
	S.D.	0.13	-	0.77	-	0.05	-
	# of samp.	10	-	10	-	10	-
Waikato [Hg]	geomean	0.005	0.002	0.003	0.010	0.003	0.035
	S.D. range	0.001 - 0.027	0.001 - 0.006	0.002 - 0.006	0.005 - 0.020	0.002 - 0.005	0.047
	# of samp.	10	10	10	10	10	4
Raglan [Hg]	geomean	0.003	-	0.006	-	0.009	-
	S.D. range	0.001 - 0.009	-	0.001 - 0.032	-	0.005 - 0.014	-
	# of samp.	10	-	10	-	10	-

No pipis or spirals could be found at Raglan. Of the comparable species (oysters, cockles and mussels), those collected from the mouth of the Waikato River had higher arsenic concentrations than those collected from Raglan but only oysters ($P=6x10^{-5}$) and mussels ($P=6x10^{-5}$) were significantly higher. None of the animals had flesh arsenic concentrations above 2 μg/g, the WHO limit for arsenic. The mercury concentration of all the animals tested was extremely low (<0.01 μg/g) and there were no significant differences between the two locations.

5.4 Discussion

The arsenic concentrations in water samples taken from the Waikato River varied between 0.003 and 0.121 μg/mL. These values are well above the background level of arsenic (1.7 ng/mL) in aquatic systems (Boyle and Jonasson, 1973). These higher values are indicative of additional arsenic entering the aquatic system. Based on previous reports (Sarbutt, 1964; Reay, 1973; Axtmann, 1975; Aggett and Aspell, 1978; Liddle, 1982) and the results found in Chapter 2, it is reasonable to assume that the majority of the arsenic in the river is of geothermal origin, either naturally occurring, or effluent from power stations.

There are two possible sources of variation / error in the arsenic concentration of water samples. The first are localised factors that may cause a water sample to be non - representative of the area from which it was taken, these include: (1) the presence of an arsenic source such as a hot spring or drain from a bore close to the sampling site, giving an anomalously high concentration, (2) the presence of a water source containing no / low arsenic, diluting the water of the sampling site giving an anomalously low concentration, (3) areas of low flow, such as the side arm of a lake may have arsenic removed from / added to the water by growing / decaying vegetation or water - sediment interactions. The effect of the presence of an arsenic rich or freshwater source will be amplified in areas of low flow. (4) if the lake or river was highly stratified then water taken from the surface may not be representative of the area, though Aggett and Aspell (1980) showed that the effect of depth was small. An attempt to minimise the first source of variation was made by collecting a large number of samples from the river, thus averaging out most of the variability.

The second source of variations in the arsenic concentrations of water samples are temporal variations of various factors. These include changes in rainfall, geothermal activity, and human controls on the river such as control gates on dams and variations in the rate of effluent release.

The arsenic concentrations of the water samples in this study were slightly higher than those reported by Aggett and Aspell (1978) and Liddle (1982) at similar times of the year. This may be the result of; (a) differences in rainfall or natural geothermal activity between the time of this study and the time of the aforementioned studies, or (b) an increase in the amount of arsenic entering the river. The recently (1989) opened power station at Ohaaki may be responsible for some of the increase.

The water arsenic concentration increased between the samples taken in late October and those taken in February. This is probably accounted for by one or more of the temporal variations mentioned above. For example a decrease in rainfall would cause less dilution of the geothermal waters entering the river, thus increasing the arsenic concentration in the river water.

Between Whakamaru and Lake Aratiatia, there were water samples with arsenic concentrations of greater than 0.05 μg/mL, the WHO limit for arsenic in drinking water. From Whakamaru to Finley, there were water samples with arsenic concentrations between 0.04 and 0.05 μg/mL, which may in a period of dry weather, also exceed the WHO limit. The arsenic concentration in the water of all places north of Lake Aratiatia will probably fall below the WHO limit in winter. The arsenic concentration of the water should be taken into consideration when using river water for drinking water at the above areas.

The arsenic concentration in the water increases upstream from the Tasman sea to the Ohaaki / Lake Aratiatia region, then drops to a lower level from Lake Aratiatia to Lake Taupo. This is consistent with other evidence suggesting that the two power stations and geothermal springs around the Wairakei and Broadlands geothermal fields are responsible for the majority of arsenic in the river. The decrease in water arsenic concentration downstream from this area may be caused by; (1) dilution of the arsenic by rain and low arsenic tributaries to the Waikato, (2) precipitation of the arsenic into the sediments of the dams and river bed, (3) removal of arsenic by biological mechanisms *e.g.* arsenic uptake by aquatic macrophytes. The fate of arsenic bound in aquatic macrophytes may be one of the following: (1) return to the river upon the decomposition of the plant, (2) deposition in the sediment upon decomposition of the plant, (3) transfer to another organism in the river system such as a herbivore or decomposer or (4) removal from the river system. Weeds may be removed from the river system by floating into the sea, being deposited onto the land by floods or humans, or consumed by terrestrial herbivores such as cattle.

The concentration of lithium in the water samples was strongly positively correlated to the arsenic concentration in the water samples and negatively correlated with the distance down stream where they were taken. Chapter 2 showed that 'typical' geothermal waters contained 7.2 μg/mL Li. The distribution patterns of lithium may be accounted for by the same mechanisms that govern the distribution of arsenic.

The concentrations of sodium and potassium showed no correlation with the distance down stream from which the sample was taken. The rubidium concentration in the water increased down stream. If the source of sodium, potassium and rubidium was mainly geothermal, then it would be expected that these three elements would have similar distribution patterns to lithium and arsenic. Other possible sources of potassium and rubidium are: (1) weathering of volcanic rocks, (2) human pollution and (3) sea water. The rhyolitic rocks of the Taupo Volcanic Zone are a major source of sodium and potassium into the lakes of the area (Timperley and Vigor - Brown, 1987). It is thus probable that the weathering of volcanic rocks accounts for considerable amounts of these elements in the Waikato River.

Bower and Timperley (1988) stated that rubidium was more common in rocks than lithium. This statement was not supported by the results of Chapter 3 which showed that only lakes with geothermal inputs had measurable amounts of rubidium whereas lithium was found in some lakes with no geothermal input. It is thus unlikely that the increasing rubidium down stream in the river is due to the weathering of the substrate rocks, though weathering may contribute some potassium to the river. There are no factories near the Waikato River that use rubidium so human pollution is also unlikely to explain the rubidium distribution.

Sodium, potassium and rubidium are found in sea water at concentrations of 11000, 390 and 0.12 μg/mL respectively (Mason and Moore, 1982) so it is plausible that tidal influences may be responsible for large amounts of these elements in the lower Waikato River. This could explain the increase of rubidium in the waters down stream as rubidium from geothermal sources can account for a maximum of 0.06 μg/mL in the Waikato River.

The sediments of the Waikato River had arsenic concentrations between 9 and 156 μg/g. with an average value of 35 μg/g. The results were an order of magnitude higher than the arsenic concentrations reported by Aggett and Aspell (1978) for the shallow water sediments of Lake Karapiro (3.6 and 10.3 μg/g) and Lake Aratiatia (4.7 μg/g). This finding may not be significant as there was large variation in the arsenic content of the sediments and no correlation with the water arsenic level or distance downstream where the samples were taken.

The arsenic concentration of the sediments increases with increasing depth (Aggett and Kriegman, 1987). As the sediments collected in this study were collected at depths < 2.5 m, the amount of arsenic in the samples will be less than the average arsenic content of sediments in the entire lake. The arsenic concentration of the sediments fluctuates over time, with arsenic being released when the levels of oxygen in the water are low (Aggett and O'Brien, 1985).

Despite the large variations in the arsenic concentration of the sediments, it appears that the sediments may be a major sink for arsenic in the Waikato River. Arsenic may be accumulating in the sediments over time. If the rate of arsenic fixation in the sediments is/becomes greater than the rate in which sediments are deposited, a time may be reached where the sediments become 'saturated' with arsenic. In this event, there would be a large increase in the arsenic concentration of the waters of the river thus affecting the quality of the water to the biota of the river and to humans.

The sediments contained between 4 and 27 μg/g copper. This was significantly positively correlated with the distance down stream where the samples were taken. Chapter 2 showed that geothermal water contains less than 0.03 μg/mL copper, so the copper in the sediments is unlikely to be of geothermal origin.

Similar to the results in 4 and the findings of previous studies (Aggett and Aspell, 1978), trout taken from the Waikato River had flesh arsenic concentrations similar to the water from which they were taken. This indicates that either arsenic does not accumulate strongly up the food chain or that trout are able to excrete the element.

Flesh mercury concentrations of the rainbow trout taken from the Waikato river were on average 0.1 to 0.2 μg/g. No rainbow trout exceeded the WHO limit of 0.5 μg/g. There were strong positive correlations (Table 33) between the flesh mercury concentration and the length and head width of the fish. This supports the age - mercury concentration relationship discussed in Chapter 4. The mercury concentrations were significantly (P=0.0008 S**) lower in Waikato trout than in trout from the natural lakes of the Taupo Volcanic Zone. This is somewhat surprising as the Waikato River has water arsenic concentrations equal to or above most of the natural lakes in the Taupo Volcanic Zone, indicating similar geothermal inputs and hence similar water mercury concentrations. The majority (75%) of geothermal effluent entering the Waikato river system comes from geothermal power stations, while hot springs contribute the majority of effluent to the natural lakes of the Taupo Volcanic Zone. It is possible that the effluent released by the power stations contains less mercury than natural geothermal waters. Other possible explanations for the differences in trout mercury concentrations are: (1) differences in the removal of mercury from a river environment compared to a lake environment, and (2) Differences in trout diet.

Brown trout taken from Puwheto had significantly higher (Table 34) flesh mercury concentrations than rainbow trout taken from the same area. Some of the larger brown trout had flesh mercury concentrations above the WHO limit. This may be caused by differences in the trout's ability to excrete mercury, or more likely, differences in the trout's diet.

The aquatic macrophytes *Ceratophyllum demersum, Egeria densa* and *Lagarosiphon major* from the Waikato River, all contained large amounts of arsenic, approximately 10 000 times the arsenic concentration of the water in which they grew. This suggests that the aquatic macrophytes actively accumulate the poisonous element and appear to act as a sink for arsenic in the Waikato River. High concentrations of arsenic in aquatic macrophytes may have the effect of deterring grazing animals from consuming the plant. This would provide a selection pressure favouring individuals with an ability to uptake arsenic, and thus a mechanism for the evolution of arsenic accumulation in plants. For this process to occur, the weeds needed to have evolved in waters with relatively high arsenic concentrations. It is unlikely that *E. densa* (native of south America), *L. major* (native of South Africa) and *C. demersum* (tropical in origin) all evolved in areas with high water arsenic concentrations. As the weeds have been in New Zealand for less than a century, and because reproduction is vegetative (as only one sex of each species was introduced) the development of ecotypy in New Zealand seems unlikely.

The high concentrations of arsenic in the weeds may be the result of the element being taken up by the same process as the uptake of an essential element. Arsenic has some chemical similarities with phosphorus, which is an essential plant macro nutrient. Accumulation of arsenic may be incidental to phosphorus uptake. This possibility is supported by the observation that nearly all the plants tested that grow in waters with elevated arsenic levels, accumulate arsenic to some degree.

The concentration of phosphorus in the water may affect the amount of arsenic accumulated by the plant, this may in turn affect the amount of arsenic in the river water. Benson (1953) showed that increasing levels of phosphorus decreases the toxicity of arsenic to barley plants, possibly competing for the binding sites of the poisonous element. It is normal farming practice to apply 400 kg/ha phosphate fertiliser to pumice soils (Hill, 1975) and some of the phosphorus ends up in the waterways of the area. The amount of phosphorus applied to farms around the Waikato may directly affect the amount of arsenic accumulated by plants, which will affect the arsenic concentration in the waters of the Waikato River.

Weed eradication programmes that involve the use of herbicides need to take into account the amount of arsenic released into the water as the weeds decay. Obviously arsenic herbicides will be ineffective in combating the waterweeds. The performance of carp and other herbivorous fish introduced in an attempt to control the weeds will be affected by the arsenic concentration of weeds in the Taupo Volcanic Zone. Arsenic in weeds may be toxic and / or unpalatable to the fish.

The concentration of arsenic in the water plants may give a good indication of the average concentration of arsenic in the water, they thus may be used as a bio - indicator for the arsenic pollution in an area. The weeds may also have a use as detoxification agents in water ways with high levels of arsenic. Arsenic may be removed from a body of water by growing and periodically removing the macrophytes in a particular area. Lakes such as Lake Rotoroa, which still contains large amounts of arsenic from a weed eradication programme 25 years ago, may be detoxified in this manner.

The average concentration of antimony in the plants was 0.31 μg/g. This is many times greater than the antimony concentration of the water (<0.001 μg/mL). Antimony, having similar chemical properties to arsenic, may be accumulated by the same mechanism. The negative correlation of the concentration of antimony in *E. densa* with the distance down stream from which it was taken, indicates that geothermal sources contribute some antimony to the Waikato River.

Water cress samples taken from Broadlands and Lake Ohakuri averaged 300 and 30 μg/g arsenic respectively. This is in excess of the WHO limit and health problems will arise in individuals eating the water cress. The water cress is not harvested until a month after the samples were taken, and the arsenic content of the plant may change as the plant matures. It is somewhat surprising that humans consuming the water cress that contained 300 μg/g have not already developed health problems. The plants taken from Broadlands are near to the recently opened Ohaaki power station. It is possible that this power station is responsible for the increase in the arsenic concentration of the river in the area, resulting in increased arsenic levels in the water cress. Since the power station has only been open since 1989, this may explain why people consuming the water cress from the area have not yet developed health problems.

Other organisms in / near the Waikato River such as periphyton, duck weed, willow, *Potomopergus* snails and nearby grass, all contained elevated levels of arsenic. Organisms that were in the water, such as the periphyton, snails and the duckweed contained over 50 μg/g arsenic while nearby organisms such as grass and willow contained 1 - 2 μg/g arsenic. The level of arsenic in the pasture should not affect sheep or cattle (Aggett and Aspell, 1978).

Periphyton is one of the most important primary producers in the New Zealand aquatic ecosystem (Marples, 1962). Presumably the high arsenic concentration of the periphyton will affect most of the heterotrophic life forms in the water. *Potomopergus* snails, which graze on periphyton, also had high arsenic concentrations. Arsenic, although apparently biophilic, does not seem to accumulate in the food chain the way other heavy metals do. Organisms at the top of the food chain, *i.e.* trout and eels have arsenic concentrations similar to the water in which they live. In an aquatic system such as the Waikato River, arsenic appears to be accumulated in the aquatic plants and algae, then excreted by animal life as it travels up the food chain.

Shellfish taken from the mouth of the Waikato River had significantly higher arsenic concentrations than shellfish from Raglan. The Waikato shellfish also contained more arsenic than shellfish from the Makety Estuary as reported by Park (1992). None of the shellfish had arsenic concentrations above the WHO limit. This indicates that arsenic entering the Waikato River in the Taupo Volcanic Zone, persists the entire length of the river and affects some marine life. The molluscs at the mouth of the river and along its length may be a good indicator of the metals entering / in the aquatic environment. Kennedy (1986) discussed the use of marine molluscs for monitoring trace metals in the marine environment. Mud from the estuary where the shellfish were taken contained 27 μg/g arsenic compared to the 12 μg/g arsenic in mud from Raglan. Mullet from the mouth of the Waikato River, although herbivorous, contained arsenic levels below 0.04 μg/g.

To conclude, arsenic is a ubiquitous pollutant in the aquatic environment of the Waikato River. During the summer months parts of the upper Waikato River have arsenic concentrations in the water greater than the WHO limit. A large part of the river has arsenic concentrations in the water slightly below the WHO limit. Any new developments that release arsenic into the Waikato River may make the majority of the river unusable as drinking water in the summer months. Arsenic accumulates in the sediments and aquatic macrophytes of the river. If the rate of arsenic accumulation in the sediments is greater than the amount of sediment deposition, then a time may come when the sediments become saturated with arsenic thus inducing a corresponding increase in water arsenic levels. Rainbow trout from the Waikato River pose no health threat as far as arsenic or mercury is concerned. Some of the larger brown trout have mercury concentrations above the WHO limit and should not make up a large proportion of an individuals diet. Destruction of aquatic macrophytes may cause an increase in water arsenic levels as the plants decay. Some of the aquatic macrophytes may be used as detoxification agents for bodies of water containing arsenic. The water cress in the Waikato River appears to behave similarly to other aquatic or semi-aquatic macrophytes in that it accumulates arsenic. Water cress should not be consumed from the Waikato River until further studies have been carried out. Some other organisms in the Waikato River accumulate arsenic. These appear to be mainly aquatic plants and algae. Some animals lower in the food chain have high arsenic concentrations. It is thought that arsenic is accumulated by the autotrophic organisms in the ecosystem, then excreted as it moves up the food chain. Shellfish at the mouth of the Waikato River have elevated arsenic levels but are still below WHO limits. There appear to be no other elements, with the exception of mercury in trout, that will significantly affect the environment of the area or its value to humans.

Further work is necessary on the water cress of the Waikato, such as complete sampling along the length of the river and arsenic uptake experiments. Any future developments that release arsenic into the river need to be carefully investigated.

Chapter 6: The Uptake of Arsenic by Water Cress

6.1 Introduction

Water cress taken from the Waikato River in the summer of 1993 - 94 was found to contain up to 400 µg/g (D.W.) arsenic. Water cress, unlike the aquatic macrophytes previously reported to be high in arsenic, is consumed by humans. As the WHO limit for arsenic in foodstuffs is 2 µg/g, the level found in the plant is of obvious concern to public health.

It is widely known that some aquatic macrophytes contain high concentrations of arsenic. Reay (1971) reported that some aquatic macrophytes had an average arsenic concentration of over 600 µg/g D.W. (see Table 23 Chapter 5). Aggett and Aspell (1978) reported similar results, and mentioned that the predominant form of arsenic in the lake weeds was the more toxic As(III) species. Liddle (1982) conducted experiments involving the uptake of arsenic by *Ceratophyllum demersum*. It was found that plants grown in arsenic solutions containing below 0.1 µg/mL As (III or V) reached equilibrium in one or two days, while plants in greater than 0.5 µ g/mL took up to a week to reach equilibrium. Plants grown in more concentrated solutions had higher arsenic concentrations. The arsenic concentration of plants grown in arsenic solutions contained far less arsenic than plants taken from water with similar concentrations in the Waikato River and Lakes in the Taupo Volcanic Zone. A plant grown in a 0.5 µg/g As solution reached equilibrium 66.9 µg/g As. It was noted that the majority of the arsenic in the plant was stored in the leaves.

More work has been done on the interactions of terrestrial plants with arsenic. Pepper *et al.* (1987) showed that root growth in *Allium cepa* could be adversely affected by soil arsenic concentrations below 1 µg/g, and suggested that the effect of arsenic on plants may be an inhibitory effect on cellular proliferation and elongation. Arsenic in the As (III) form is considerably more toxic to plants than As (V) (Asher and Reay, 1979). The tolerance of arsenic by plants is achieved by one of two mechanisms: (1) the exclusion of arsenic from the plant (Macnair and Cumbes 1987) or (2) Biochemical tolerance and/or inactivation of the arsenic by storage or chemical combination. The aquatic plants studied fall into the latter category on account of their high arsenic concentration.

The uptake of arsenic may be analogous to phosphorus uptake *i.e.* arsenic behaves as a phosphorus analogue. Evidence for this includes: (1) arsenic shows some chemical similarities to phosphorus (both in group VB), (2) arsenate (AsO_4^{3-}), an analogue of the plant nutrient phosphate (PO_4^{3-}), is taken up by the plant over three times faster than arsenite (AsO_2^-) (Asher and Reay, 1979) and (3) The uptake of arsenate is strongly inhibited by the addition of phosphorus (Benson, 1953) where as the uptake of arsenite is little affected (Asher and Reay, 1979).

Arsenic uptake is strongly affected by temperature. The uptake of arsenate by barley at 20.5 °C is over ten times higher than at 2.5 °C (Asher and Reay, 1979).

The water cress samples analysed in Chapter 5, were taken from two sites along the Waikato River. Water cress from one of those sites had an average arsenic concentration of 400 μg/g D.W., cress from the other site had an arsenic content of only 30 μg/g D.W. The arsenic in these samples may have been the result of localised contamination or freak individuals that accumulate arsenic. The aim of this experiment was to determine the extent, and rate, of arsenic accumulation by water cress grown in solutions containing small amounts of arsenic.

6.2 Methods

Water cress was collected from a stream near Newbery line, Palmerston north. Plants were removed by hand with care being taken to keep them intact. The plants were transported to the laboratory in a plastic bag filled with water from the stream. One plant was immediately prepared for analysis using methods described below.

Plants used in the experiments had excess water removed, and weighed. They were placed in 1 L beakers along with 600 mL of arsenic solution. Each beaker had a bubbler placed in it. The experiment was conducted near the biology building at Massey University from the 19th to the 25th of August, 1994. The plants were out of direct sunlight. Average temperature of the water during the day was approximately 17° C.

The arsenic solutions were prepared by taking a measured amount of 1000 μg/mL sodium arsenite standard and making the volume up to 600 mL with distilled water. Plants were grown in solutions containing approximately 0.02, 0.1 and 0.5 μg/mL arsenic. There were four replicates of each treatment. Two replicates were started on the 19th of August while two were started on the 22nd of August. All plants were harvested on 25th of August. A beaker was set up with 600 mLs of 0.5 µg/mL As solution and a bubbler, but no plant. Aliquots of approximately 5 mLs of solution were taken from each beaker initially at 3:30 pm, then once every twenty four hours until the end of the experiment. The Aliquots were analysed using the procedures described in Section 1.2.

At the end of the experiment, the plants were removed from their beakers, rinsed in distilled water, and dried at 40^{o} C. Plants were ground up in using a mortar and pestle, then dissolved in HNO_3 and analysed using methods described in Section 1.2.

6.3 Results

The arsenic concentration in the plants at the end of the experiment ranged from 1 µg/g D.W. to 92 µg/g D.W. (Table 38). These were all elevated relative to the control plant not put in an arsenic solution, which had an arsenic concentration below detection limits (> 0.05 µg/g D.W.). The arsenic concentrations in the plants were strongly positively correlated to the arsenic concentrations of the bathing solutions. The average water content of the plants was 96.2% with a standard deviation of 0.4%. Using this value, the arsenic concentrations of the fresh plants were calculated. Table 38 shows that with the exception of plant C, all plants in the experiment had fresh weight arsenic concentrations between 2.3 and 11.7 times the concentration of the bathing solution. At the end of the experiment, it was noticed that plant C was broken at the base of the stem. The concentration of arsenic in the plants relative to the concentration of arsenic in the solutions at equilibrium (see below), was 1 to 2 orders of magnitude lower in this experiment than ratios calculated for water cress in the Waikato River.

All solutions that the plants were in had a decrease in arsenic concentration corresponding to the increase of arsenic in the plants. No arsenic was removed from the solution in the control, the slight increase measured was probably due to evaporation.

The rate of uptake was dependent on the arsenic concentration of the solution. Plants in solutions with arsenic concentrations below 0.05 µg/mL appeared to reach equilibrium within 36 hours, but the decrease in concentration in the solution was so slight that it was difficult to measure. Plants in solutions between 0.05 and 0.15

μg/mL As reached equilibrium after 3 days (Fig. 27) and plants in solutions >0.5 μg/mL as took 4 days to reach equilibrium (Fig. 28). The arsenic concentrations of the solutions (plants) decreased (increased) logarithmically until equilibrium was reached.

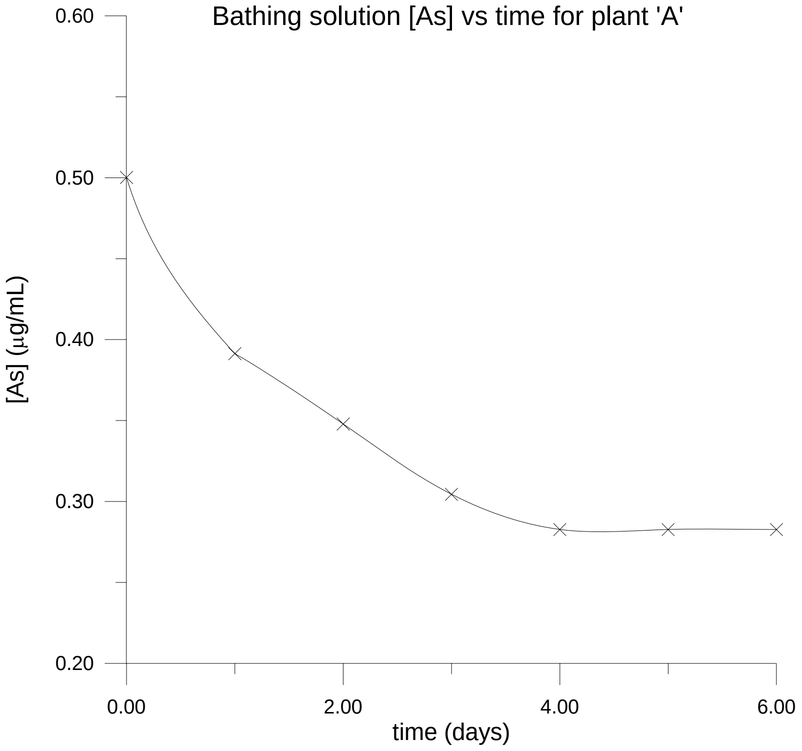
Table 38. Plant weights, and arsenic concentrations of plants (μg/g) and solutions (μg/mL) in experiment.

Code	Fresh weight (g)	[As] dry weight	Calc. [As] fresh weight	Initial solution [As]	Final solution [As]	EqR+
A	23	92.4	3.29	0.50	0.28	11.7
B	13	28.0	1.02	0.14	0.10	10.4
C	13	1.0	0.04	0.03	0.03	1.2
D	34	57.2	2.24	0.61	0.35	6.4
E	20	11.9	0.38	0.10	0.08	4.9
F	35	3.4	0.12	0.03	0.03	4.1
G*	14	79.1	3.35	0.76	0.63	5.3
H*	11	18.5	0.66	0.11	0.09	7.6
I*	24	1.7	0.06	0.03	0.03	2.3
J*	20			0.78	0.50	
K*	17	17.6	0.68	0.12	0.10	6.4
L*	33	2.8	0.12		0.03	3.5
Cont.	-	-	-	0.58	0.59	-

*Started on 22/8/94, all others started on 19/8/94. It is to be noted that plants G and J have not reached equilibrium so would normally have a higher equilibrium ratio.

+Equilibrium ratio of the arsenic concentration in the plant (Fresh Weight) and the final concentration of the solution at the end of the experiment.

Figure 27:



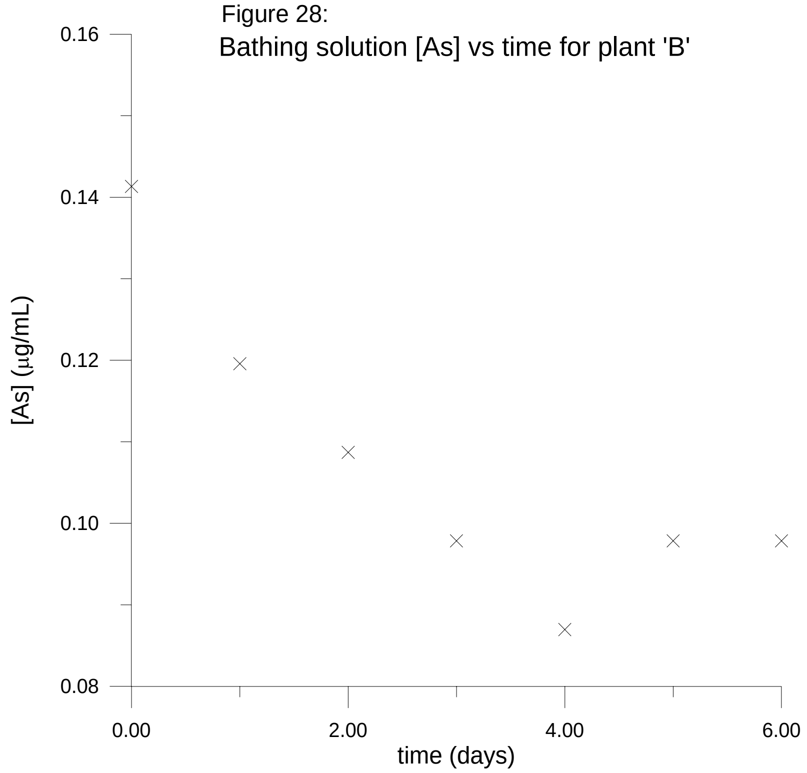


Figure 28:
Bathing solution [As] vs time for plant 'B'

6.4 Discussion

All the plants in arsenic solutions accumulated arsenic. At equilibrium, the arsenic concentrations in the plants in this experiment were an order of magnitude less than plants taken from the Waikato River, though both were in arsenic solutions of similar concentrations. This is similar to the findings of Liddle (1982) for *Ceratophyllum demersum*. Possible reasons for these differences are: (1) the ratio of arsenite to arsenate may have been higher in the solutions of this experiment than in the waters of the Waikato River. It has been shown that arsenate is taken up over three times faster than arsenite by barley plants (Asher and Reay, 1978). At equilibrium, arsenite may not be as concentrated in the plant as arsenate. (2) The water cress from the Waikato River was collected in early autumn (March 1994), when temperatures were higher than the temperatures in this experiment. This may result in decreased arsenic uptake. (3) There were no other solutes in the water besides arsenic in this experiment whereas there are traces of nitrogen, phosphorus, alkali metals, halides and other plant nutrients in the Waikato River. This may affect arsenic uptake. It is well known that phosphorus decreases arsenic uptake, but the effect of other plant nutrients is unknown. (4) The water cress in this experiment was free floating, whereas in the river it is rooted to the sediment layer. Sediments from the Waikato River have been found to contain on average 35 µg/g As. If this is a major source of arsenic to the plant, then it would be expected that the plants growing in a high arsenic sediment would have a higher arsenic content. (5) Other factors which may have been different such as light intensity and seasonal growth of the plant.

The predominant form of arsenic in the environment is As(V), As(III) being oxidised by atmospheric oxygen (Pepper *et al.*, 1987). For much of the year, over 90% of the arsenic in the Waikato River is present as As(V) (Aggett and Aspell, 1978), but in summer months As(III) predominates, probably because of bacterial action (Freeman, 1985). In this experiment, As(III) was used. During the experiment, this will have been oxidised (mainly by the bubblers) to As(V). The uptake of As(III) is 3 to 4 times slower than As(V), thus the time taken for the plants to reach equilibrium in this experiment, depending on the rate of oxidation, may be longer than plants in the Waikato River.

To conclude, water cress actively absorbs arsenic. The time the plant takes to reach equilibrium is dependent on the concentration of the solution, but for solutions of <0.75 μg/mL As equilibrium is reached within 4 days. Typically the average arsenic concentration in the fresh plant is 4 to 10 times the concentration of the solution. The accumulation of arsenic by water cress is of concern to human health. The plants in this experiment did not concentrate arsenic to the same extent as plants from the Waikato River. This may be accounted for by one or more of the aforementioned reasons. Until these have been investigated, it should be recommended that water cress growing in water that at any time has greater than 0.05 μg/mL arsenic, should not be consumed.

Chapter 7: Concluding summary

The majority of polluting elements entering the aquatic biosphere of the Taupo Volcanic Zone are geothermal in origin, either from natural sources, or from geothermal power stations. Geothermal waters in the Taupo Volcanic Zone contain elevated levels of some elements relative to the background level for surface waters. These elements are; the alkali metals, the halogens, boron, sulphur, antimony, arsenic, and mercury. Of these elements, only arsenic and mercury are present in sufficient quantities to be toxic. Some terrestrial plants growing near geothermal sources were found to contain large amounts of arsenic.

Water from the Waikato River between Lake Aratiatia and Whakamaru as well as Lakes Rotokawa, Rotomahana and Rotoehu contain arsenic concentrations above the WHO limit when they were sampled (concentrations will decrease in winter). Water from these areas should not be consumed. Lakes Tarawera and Okataina as well as the lower Waikato River have elevated levels of arsenic and need to be monitored for arsenic in the future. The arsenic in the lakes of the Taupo Volcanic Zone appears to be from natural geothermal sources whereas the majority of the arsenic in the Waikato River comes from the Wairakei and Ohaaki power stations. Any future geothermal developments should not be permitted to release any extra arsenic into the Waikato River or aforementioned lakes.

Sediments appear to be a major sink for arsenic in the Taupo Volcanic Zone. Arsenic is released from sediments under anoxic conditions. The eutrophication of waterways caused by pollution decreases the oxygen content of the water and may increase the arsenic concentration.

Trout from the Taupo Volcanic Zone all contained low levels of arsenic, of the same order of magnitude as the water from which they were taken. Trout from lakes Rotorua, Rotoiti and Rotomahana had flesh mercury concentrations above the WHO limit for mercury. Trout from these lakes should not make up a large proportion of an individual's diet. Occasional consumption should cause no problems. Trout from lake Maraetai and nearby streams have on average, flesh mercury concentrations below the WHO limit. Fish further up stream are likely to have higher flesh mercury concentrations. There was a strong positive correlation between body weight and flesh mercury concentration in areas with trout that had flesh mercury concentrations above 0.1 μg/g.

Freshwater mussels from the aforementioned lakes and probably from the Waikato River, have arsenic concentrations well in excess of the WHO limit and should not be consumed. Shellfish from the mouth of the Waikato River have elevated arsenic levels compared to shellfish at Raglan but are safe to consume.

The aquatic macrophytes in the lakes of the area and Waikato River have very high arsenic concentrations. Arsenic herbicides will probably be ineffective in combating these weeds. Any weed control programme that involves killing the weeds but not removing them, needs to take into account that there may be a temporary increase in the arsenic concentration of the water as the weeds decay. Some macrophytes might possibly be used to detoxify arsenic polluted waterways by growing then removing them. Further work needs to be carried out to investigate this possibility.

Two water cress samples taken from the Waikato River had enormously high arsenic concentrations. No water cress from the Waikato (and probably from the lakes with high arsenic levels) should be consumed until a full investigation has been carried out.

References

Aggett J. and Aspell A.C., 1976. The Determination of Arsenic(III) and Total Arsenic by Atomic-absorption Spectroscopy. Analyst. 101: 341 - 347.

Aggett J. and Aspell A.C., 1978. Release of Arsenic from Geothermal Sources. New Zealand research and development committee. No. 35.

Aggett J. and Aspell A.C., 1980. Arsenic from geothermal sources in the Waikato catchment. New Zealand Journal of Science 23: 77 - 82.

Aggett J. and Kriegman M., 1987. The extent of formation of arsenic(III) in sediment interstitial waters and its release to hypolimnetic waters in Lake Ohakuri. Water Research 22: No 4. 407 - 411.

Aggett J. and O'Brien, 1985. Detailed Model for the Mobility of Arsenic in Lacustrine Sediments Based on Measurements in Lake Ohakuri. Environmental Science and Technology. 19: (3). 231 - 238.

Agterdenbos J., Bussink R.W., and Bax D., 1990. Role of pH in the stripping of gaseous selenium hydride from reaction mixture in hydride generation atomic absorption spectrometry. Analytica Chimica Acta. 21: 405 - 407.

Anderson R.K., Thompson M., and Culbard E., 1986. Selective Reduction of Arsenic Species by Continuos Hydride Generation. Analyst. 111: 1143 - 1158.

Asher C.J. and Reay P.F., 1969. Arsenic Uptake by Barley Seedlings. Australian Journal of Plant Physiology. 6: 459 - 66.

Axtmann R.C., 1975. Environmental Impact of a Geothermal Power Plant. Science. 187: 795 - 803.

Bache C.A., Gutemann W.H. and Lisk D.J., 1971. Residues of total mercury and methylmercuric salts lake trout as a function of age. Science. 172: 951 - 952.

Benson N.R., 1953. Effect of season, phosphate and acidity on plant growth in arsenic toxic soils. Soil Science. 76: 215 - 224.

Boyle R.W. and Jonasson I.R., 1973. The geochemistry of arsenic and its use as an indicator element in geochemical prospecting. Journal of Geochemical Exploration. 2: 251 - 296.

Bower J.E. and Timperley M.H., 1988. Lithium and rubidium in the Waikato River, New Zealand. New Zealand Journal of Marine and Fresh Water Research 22: 201 - 204.

Brookes C.J., Bettely I.G., and Loxston S.M., 1966. Mathematics and Statistics. Wiley, London. pp 285.

Brooks R.R., Lewis J.R., and Reeves R.D., 1976. Mercury and other heavy metals in trout of the central North Island, New Zealand. New Zealand Journal of Marine and Fresh Water Research. 10 (2): 233 - 244.

Brooks R.R., Ryan D.E. and Zhang H., 1981. Atomic absorption spectrometry and other instrumental methods for quantitative measurements of arsenic. Analytica Chimica Acta. 1 - 16.

Costa E.W.B.D., 1972. Variation in the Toxicity of Arsenic Compounds To Microorganisms and the Suppression of the Inhibitory Effects by Phosphate. Applied Microbiology. 23(1): 46 - 53.

Coulter G.W., 1977. The Ecological Impact on the Waikato River of untreated effluent from the proposed Broadlands Geothermal Power Station. New Zealand energy research and development committee. Report No 26.

Ebdon L., Hill S., Walton A.P., and Ward R.W., 1988. Coupled Chromatography - Atomic Spectrometry for Arsenic Speciation - a Comparative Study. Analyst 113: 1159 - 1165.

Ellis A.J. and Anderson D.W., 1961. The geochemistry of bromine and iodine in New Zealand thermal waters. New Zealand Journal of Science. 4: 415 - 430.

Ellis A.J. and Sewell J.R., 1963. Boron in waters and rocks of New Zealand hydrothermal areas. New Zealand Journal of Science. 6: 589 - 606.

Ellis A.J. and Wilson S.H., 1960. The geochemistry of alkali metal ions in the Wairakei hydrothermal system. New Zealand Journal of Geology and Geophysics. 3: 593 - 617.

Ferguson J.F. and Gavis J., 1972. A review of the arsenic cycle in natural waters. Water Research. 6: 1259 - 1274.

Fish G.R., 1963. Observations on excessive weed growth in two lakes in New Zealand. New Zealand Journal of Botany. 1: 410 - 418.

Forseyth D.J., 1977. Limnology of Lake Rotokawa and its outlet stream. New Zealand Journal of Marine and Freshwater Research. 11(3): 525 - 539.

Forstner U. and Wittmann G.T.W., 1983. Metal Pollution in the Aquatic Environment. Springer - Verlag. New York.

Freeman M.C., 1985. The reduction of arsenate to arsenite by an *Anabaena* bacteria assemblage isolated from the Waikato River. New Zealand Journal of Marine and Freshwater Research. 19: 277 - 282.

Gerdei T., Gill R. and Wallis N., 1993. A Comparison between Flame-Heating and Electrical-Heating Trace-Level Hydride Analysis. GBC AA Applications.

Gifford J.S., Hannus I.M., Judd M.C., McFarlane P.N., Anderson S.M., and Amoamo D.H., 1993. Assessment of chemical contaminants in the Lake Rotorua catchment. FRI report.

Godden R.G. and Thomerson D.R., 1980. Generation of Covalent Hydrides in Atomic absorption Spectroscopy. The Analyst. 105: 1137 - 1156.

Golding R.M. and Speer M.G., 1961. Alkali ion analysis of thermal waters in New Zealand. New Zealand Journal of Science. 4: 203 - 213.

Grimstone, G., 1972. Mercury in British fish. Chemistry in Britain. 8: 244 - 247.

Grindley G.W., 1965. Subsurface Geology of the Orakei Korako and Te Kopia Geothermal Fields. Geological Geothermal Report No. 3.

Grindley G.W., Rishwork D.E., and Watters W.A., 1966. Geology of the Tauhara Geothermal Field. Geological Geothermal Report No. 4, NZGS.

Hashem A.R., 1993. Effect of arsenic on the growth of *Cladosporium herbarum*. Cryptogramic Botany. 3: 307 - 309.

Hedenquist J.W. and Henley R.W., 1985. Hydrothermal Eruptions in the Waiotapu Geothermal System, New Zealand: Their Origin, Associated Breccias, and Relation to Precious Metal Mineralisation. Economic Geology. 80: 1640 - 1668.

Henley R.W., 1985. Applied chemistry in the exploration and development of New Zealand geothermal systems. New Zealand Journal of Technology 1: 207 - 221.

Hill C.F., 1975. *Impounded Lakes of the Waikato River.* in "New Zealand Lakes" edited by V.H. Jolly and J.M.A. Brown. Auckland University Press. Auckland.

Jackson L.L., Baedecker P.A., Fries T.L., and Lamothe P.J., 1993. Geological and Inorganic Materials. Analytical Chemistry. 65: 12R - 28R.

Jackson K.W., and Qiao H., 1992. Atomic Absorption, Atomic Emission and Flame Emission Spectrometry. Analytical Chemistry. 64: 50R - 66R.

Kennedy P.C., 1986. The use of molluscs for monitoring trace elements in the marine environment in New Zealand. New Zealand Journal of Marine and Freshwater Research. 20: 627 - 640.

Kim J., 1994. Methylmercury in Rainbow Trout (*Oncorhyncus mykiss*) from Lakes Okareka, Okaro, Rotomahana, Rotorua and Tarawera, North Island, New Zealand. Science of the Total Environment.

Krupp R.E. and Seward T.M., 1987. The Rotokawa Geothermal System, New Zealand: An active Epithermal Gold - Depositing Environment. Economic Geology. 82(5): 1109 - 1129.

Lancaster R.J., Coup M.R., and Hughes J.W., 1971. Toxicity of arsenic present in Lakeweed. New Zealand Veterinary Journal. 19: 141 - 145.

Liddle J.R., 1982. Arsenic and Other Elements of Geothermal Origin in the Taupo Volcanic Zone. Unpublished PhD thesis. Massey university.

Lloyd E.F., 1959. The hot springs and hydrothermal eruptions at Waiotapu. New Zealand Journal of Geology and Geophysics. 2: 141 - 176.

Lloyd E.F., 1972. Geology and Hot Springs of Orakei Korako. NZGS Bulletin 85, DSIR Wellington.

MacNair M.R. and Cumbes Q., 1987. Evidence that arsenic tolerance in *Holcus lanathus* is caused by an altered phosphate uptake system. The New Phytologist. 107: 387 - 394.

Mahon W.A.J., 1965. Calcium and magnesium in the natural thermal waters of New Zealand. New Zealand Journal of Science. 8: 66 - 78.

Mahon W.A.J., 1966. Silica in hot water discharged from drill holes at Wairakei, New Zealand. New Zealand Journal of Science 9: 135 - 144.

Mahon W.A.J. and Klyen L.E., 1968. Chemistry of the Tokaanu - Waihi hydrothermal area. New Zealand Journal of Science. 11: 140 - 158.

Marples B.J., 1962. An Introduction to Freshwater Life in New Zealand. Whitcombe and Tombes ltd. Christchurch.

Mason B., and Moore C.B., 1982. Principals of Geochemistry. John Wiley and Sons. Brisbane.

McColl R.H.S., 1975. *Chemical and biological conditions in lakes of the volcanic plateau.* in "New Zealand Lakes" edited by V.H. Jolly and J.M.A. Brown. Auckland University Press. Auckland.

Modriniak N. and Studt F.E., 1959. Geological structure and volcanism of the Taupo - Tarawera district. New Zealand Journal of Geology and Geophysics. 2: 654 - 684.

Narsito, Agterdenbos J., and Santosa S.J., 1990. Study of the process in the hydride generation atomic absorption spectrometry of antimony, arsenic and selenium. Analytica Chimica Acta. 237: 189 - 199.

Park S., 1992. Bay of Plenty Regional Council Maketu Estuary Environmental Baseline Monitoring Project 1990/91. Bay of Plenty Regional Council Technical Report Number 20.

Penrose W.R., 1974. Arsenic in the marine and aquatic environments: Analysis, occurrence, and significance. CRC Critical Reviews in Environmental Control. 465 - 482.

Pepper I., Galanti N., Sans J., and Lopez-saez J.F., 1987. Reversible inhibition of root growth and cell proliferation by pentavalent arsenic in *Allium cepa*. Environmental and Experimental Botany. 28(1): 9 - 18.

Rennison G. and Brock J.L., 1981. A survey of the Ketetahi Hot Springs. New Zealand Journal of Science 24: 161 - 177.

Ritchie J.A., 1961. Arsenic and antimony in some New Zealand thermal waters. New Zealand Journal of Science. 4: 218 - 229.

Robertson D.E., Crecelius E.A., Fruchter J.S., and Ludwick J.D., 1977. Mercury Emissions from Geothermal Power Plants. Science. 196: 1094 - 1097.

Rothbaum H.P. and Middendorf K., 1987. Lithium extraction from Wairakei geothermal waters. New Zealand Journal of Technology. 2: 231 - 235.

Rutherford J.C., 1984. Trends in Lake Rotorua water quality. New Zealand Journal of Marine and Freshwater Research. 18: 355 - 365.

Sarbutt J.V., 1964. A chemical survey of the hot spring and drillhole waters of the Taupo borough. New Zealand Journal of Science. 7: 491 - 505.

Smith D., 1985. Sources of heavy metals in the aquatic environment. New Zealand Environment. 45: 18 - 23.

Tanner C.C., and Clayton J.S., 1990. Persistence of arsenic 24 years after sodium arsenite herbicide application to Lake Rotoroa, Hamilton, New Zealand. New Zealand Journal of Marine and Fresh Water Research 24: 173 - 179.

Thompson K.C. and Thomerson D.R., 1974. Atomic - absorption Studies on the Determination of Antimony, Arsenic, Bismuth, Germanium, Lead, Selenium, Tellurium and Tin by Utilising the Generation of Covalent Hydrides. Analyst 99: 595 - 601.

Thornton J., 1985. Field Guide to New Zealand Geology. Heinemann Reed. Auckland.

Timperley M.H., 1979. Metals in the Waikato River, New Zealand. New Zealand Journal of Science. 22: 273 - 279.

Timperley M.H., and Vigor-Brown R.J., 1986. Water chemistry of Lakes in the Taupo Volcanic Zone, New Zealand. New Zealand Journal of Marine and Freshwater Research. 20: 173 - 183.

Wagemann R., Snow N.B., Rosenberg, D.M. and Lutz A., 1978. Arsenic in sediments, water and aquatic biota from lakes in the vicinity of Yellowknife, North West Territories, Canada. Archives of environmental contamination and toxicology 7: 169 - 191.

Weissberg B.G., 1969. Gold-Silver Ore-Grade Precipitates from New Zealand Thermal Waters. Economic Geology. 64: 95 - 108.

Weissberg B.G., 1975. Mercury in some New Zealand Waters. New Zealand Journal of Science. 18: 195 - 203.

Weissberg B.G. and Rohde A.G., 1978. Mercury in some New Zealand geothermal discharges. New Zealand Journal of Science. 21: 365 - 369.

Weissberg B.G. and Zobel M.G.R., 1973. Geothermal mercury pollution in New Zealand. Bulletin of Environmental Contamination and Toxicology. 9: 148 - 155.

Wells R.D.S. and Clayton J.S., 1991. Submerged vegetation and spread of *Egeria densa* Planchon in Lake Rotorua, central North Island, New Zealand. New Zealand Journal of Marine and Freshwater Research. 25: 63 - 70.

Welz B. and Melcher M., 1981. Mutual interactions of elements in the hydride technique in atomic absorption spectrometry. Analytica Chimica Acta. 16: 17 - 25.

Woolson E.A., Axley J.H., and Kearney P.C., 1973. The Chemistry and Phytotoxisity of Arsenic in Soil. Soil Science American Proceeding. 37: 254 - 249.