

The distribution and fate of arsenic in the Waikato River system, North Island, New Zealand

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ABSTRACT

Arsenic levels were determined in waters, sediments, aquatic macrophytes and other organisms taken from the Waikato River system, North Island, New Zealand. All water samples contained elevated levels of arsenic relative to $0.0017 \mu\text{g g}^{-1}$, the background level for arsenic in aquatic systems. Most water samples taken between Lakes Aratiatia and Whakamaru had arsenic levels above the World Health Organization (WHO) limit for arsenic in drinking water ($0.01 \mu\text{g mL}^{-1}$). Arsenic levels in the water of the river decreased downstream from the Wairakei and Ohaaki geothermal power stations, indicating that these are major sources of arsenic to the river. The arsenic concentration of the sediments was typically around $30 \mu\text{g g}^{-1}$, though there was a large variation. Sediments appear to be a sink for arsenic. Some aquatic macrophytes (*Ceratophyllum demersum* and *Egeria densa*) had arsenic concentrations up to $1,000 \mu\text{g g}^{-1}$, (0.1%) in dried tissue. These plants may be used as bioindicators of arsenic pollution in aquatic systems. Water cress taken near Broadlands (Ohaaki) contained around $300 \mu\text{g g}^{-1}$, (dry weight) arsenic, and should not be consumed. Shellfish taken from the mouth of the Waikato river had significantly higher arsenic concentrations than the same species taken further down the coast at Raglan.

Keywords: Arsenic in aquatics systems, New Zealand.

INTRODUCTION

The Waikato River (Figure 1), at 425 km, is the longest river in New Zealand. It drains the largest lake in the country, Lake Taupo, from which the river flows in a northwesterly 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 $14,000 \text{ km}^2$ (Liddle 1982). The 366-metre fall of the river from Lake Taupo to the sea, has been exploited by the strategic emplacement of eight hydroelectric power stations. These occur in narrow valleys through the plateau lands near Tokoroa.

In 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 at Tokaanu, Waihi, Rotokawa, Mokai, and Te Kopia. Both the Wairakei and Ohaaki geothermal power stations release geothermal effluent into the Waikato River, though some of the waste water from the Ohaaki power station is re-injected. It is well documented (Ritchie, 1961; Aggett and Aspell, 1978; Liddle, 1982) that hydrothermal waters discharged from the power stations and some geothermal areas contain relatively large amounts of the toxic element arsenic. It might thus be expected that the Waikato River contains elevated levels of arsenic. Reay (1973) has given an estimate of the amounts of arsenic entering the Waikato River from various geothermal sources (Table 1).

Arsenic may also be entering the Waikato river from industrial sources. Liddle (1982) reported that the Kinleith

pulp and paper mill releases effluent containing $0.05 \mu\text{g mL}^{-1}$ 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 $0.011 \mu\text{g mL}^{-1}$ at Tuakau to $0.062 \mu\text{g mL}^{-1}$ at Lake Aratiatia then decreased to $0.008 \mu\text{g mL}^{-1}$ at Lake Taupo. Over 90% of the measured arsenic was as 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 that this bacterium could take up As(V) and reduce it to As(III) at a rate of 12 ng As per 10^6 cells per day. Most of the waters in the Waikato River had greater than $0.01 \mu\text{g mL}^{-1}$ arsenic, the WHO limit for drinking water. However, much of this is

Table 1 Estimates of arsenic inputs (tonnes yr^{-1}) into the Waikato River from geothermal areas

Geothermal source	Input
Lake Taupo	30
Wairakei field	22
Ohaaki Pool	0.5
Orakei Korako	8–13
Waiotapu/Reporoa Valley	1–2
Total natural sources	61–67
Wairakei Power Station	190

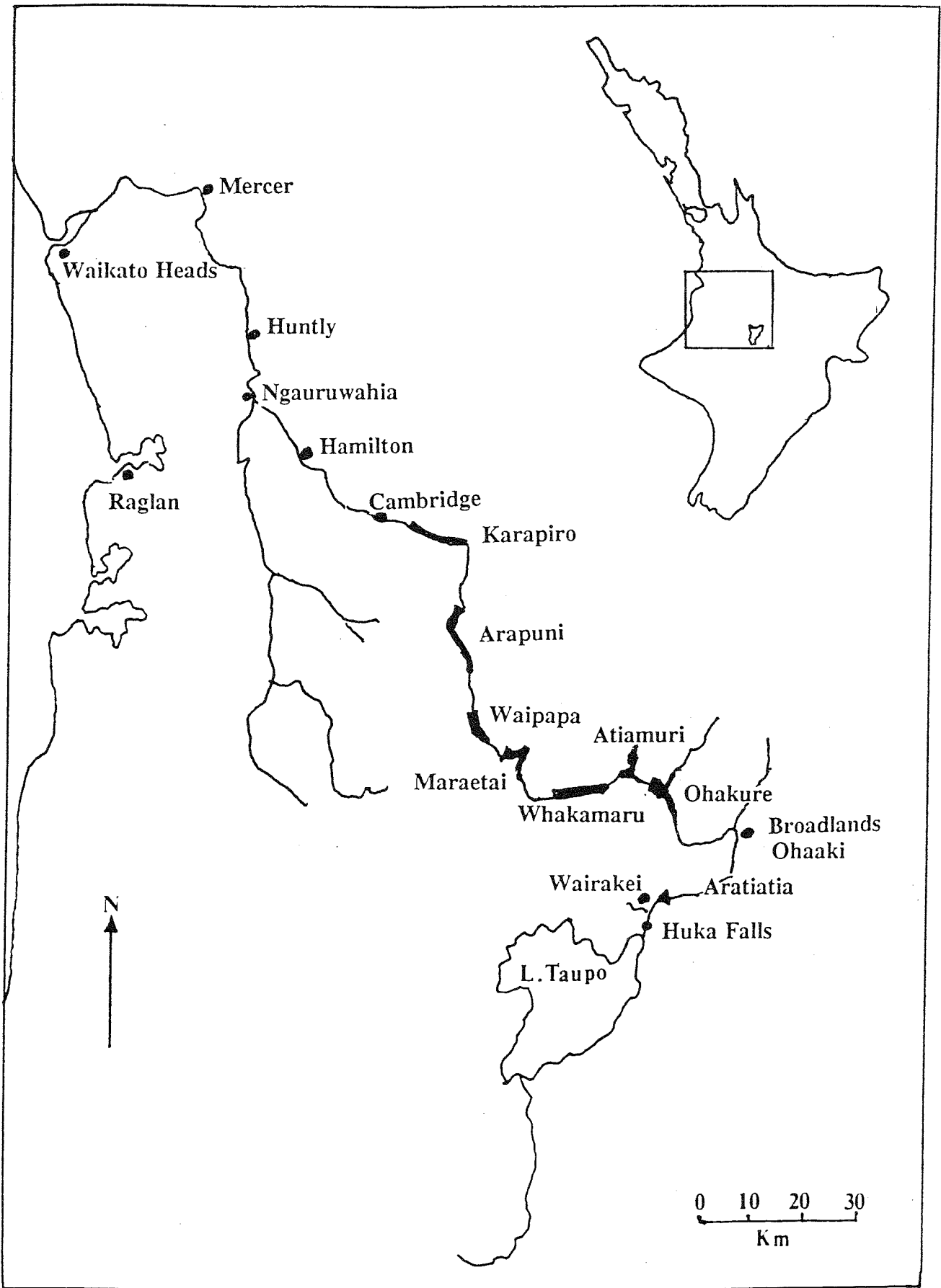


Figure 1 Map of the Waikato River system, North Island, New Zealand.

not used as a drinking water supply and does not include Aratiatia in which the arsenic level exceeds $0.05 \mu\text{g mL}^{-1}$.

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 $400 \mu\text{g g}^{-1}$ As.

Some of the biota of the Waikato River, such as aquatic macrophytes, have been reported to contain high concentrations of arsenic. Reay (1971) found up to $650 \mu\text{g g}^{-1}$ (dry weight [dw]) of this element in *Ceratophyllum demersum* among aquatic macrophytes in this river. He estimated that these aquatic plants 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 the suitability of some of these aquatic plants as stock feed, since this might have provided an incentive for the weed to be removed from the river. It was found that sheep, after three weeks eating the lake weed, had a muscle arsenic concentration of $1.13 \mu\text{g g}^{-1}$. The arsenic in the muscle virtually disappeared four weeks after stopping consumption of the weed. There were no health problems reported in the sheep.

The aims of this study were as follows: (1) to investigate the concentration of arsenic in the waters, sediments, aquatic macrophytes and other organisms in or near the Waikato River system; and (2) to investigate the arsenic concentrations of shellfish and mullet taken from the mouth of the Waikato in order to establish the degree of uptake and to evaluate any potential health hazard associated with human consumption of these seafoods.

MATERIALS AND METHODS

Sampling procedures

Samples were collected 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. Second sets of samples of water, weed and sediments were collected between the 1st and 5th of February 1994. Water cress (*Lepidium sativum*), *Nasturtium sp.*, willow (*Salix sp.*), *Potamogeton sp.*, *Spirodela sp.* and snails were collected in April 1994. The sampling sites stretched from Lake Taupo to Port Waikato (Figure 1).

Water samples were collected in 750 mL polythene bottles *in situ*, and refrigerated. The waters were not filtered as to have done so would have given a false impression of the actual situation in which unfiltered water is drunk by local people or is accumulated by organisms. In any case, the natural water is remarkably free of suspended particulate matter.

Analyses were carried out no later than two weeks after collection. Sediments were collected with a sediment collector which consisted of a steel box ($\sim 150 \times 150 \times 150$ mm) with a rope attached. This was thrown into the water and sediment collected by dredging. Samples were stored in sealed polyethylene bags for transport to the laboratory.

Shellfish (*Paphies australis* [pipi], *Austrovenus stutchburyi* [cockle], *Crassostrea gigas* [Pacific oyster], *Mytilus canaliculus* [mussel] and *Potomopergus sp.*) were collected by hand and kept moist and cool (in a refrigerator) until they were prepared for analysis. The shellfish remained alive.

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 and subaquatic plants (*Salix sp.*, *Kunzia ericoides*, *Leptospermum scoparium*, *Leucopogon fasciculatum*, *Cyathodes sp.*, *Pteridium esculentum*, *Dracophyllum subulatum*, *Lepidium sativum* (watercress), *Nasturtium sp.* and *Cytisus scoparius*) were collected by hand.

Sample preparation

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 nylon sieve. Approximately 0.5 g samples were weighed into 50 mL polypropylene containers. 10 mL of conc. 1:1 HF/HNO₃ was added to each sample and two reagent blanks were prepared. The containers were placed in a bath of boiling water until all the acid had evaporated. 12 mL of 2M HCl were added to each container and the samples allowed to dissolve. When the volume of each sample had reached ~ 10 mL it was measured and recorded before storage of the samples in 25 mL polythene containers.

Shellfish were 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 placed in a boiling tube. 5 mL of 70% HN₃ was added to each sample and heating was carried out in heating blocks set at *ca* 100°C until dissolution was complete. The solutions were transferred to measuring cylinders and made up to exactly 10 mL with distilled water. Samples were stored in 25 mL polythene sample containers.

All plant samples were thoroughly washed first in running tap water and then in distilled water. The excess water was allowed to drain off and the samples were stored in a drying cupboard set at 40°C until a constant weight was reached. Each plant was then ground in a mill and the powder stored in polyethylene bags. Approximately 0.2 g of plant material was weighed into a boiling tube and prepared in the same manner as for the shellfish.

Two reagent blanks were prepared for each batch of shellfish, plants and sediments.

Determination of arsenic using hydride generation atomic absorption spectrometry

Arsenic was determined on a GBC 900 spectrophotometer using a purpose-built hydride generation apparatus. The limit of detection was about $0.01 \mu\text{g g}^{-1}$ for solid samples and $0.001 \mu\text{g mL}^{-1}$ for natural waters.

RESULTS AND DISCUSSION

Arsenic in the water of the Waikato River

The arsenic concentrations in water samples collected in November 1993 increased from $0.003 \mu\text{g mL}^{-1}$ at Ngaurawahia (Lower Waikato) to $0.121 \mu\text{g mL}^{-1}$ at Lake Aratiatia (just below the geothermal station at Wairakei – see Figure 1 for locations). The concentration of arsenic in water taken from Huka falls (just above Wairakei) was $0.006 \mu\text{g mL}^{-1}$. We have measured the arsenic content of the main drain at Wairakei as being $3.8 \mu\text{g mL}^{-1}$. This is the major source of arsenic contributing to the $0.12 \mu\text{g mL}^{-1}$ at Lake Aratiatia.

Water samples collected in February 1994 (Figure 2) had arsenic concentrations with a median of $0.044 \mu\text{g mL}^{-1}$ and range of 0.019 – $0.067 \mu\text{g mL}^{-1}$, nearly 50% higher than samples collected in November 1993 where the median was $0.03 \mu\text{g mL}^{-1}$ and the range was 0.003 – $0.121 \mu\text{g mL}^{-1}$. There

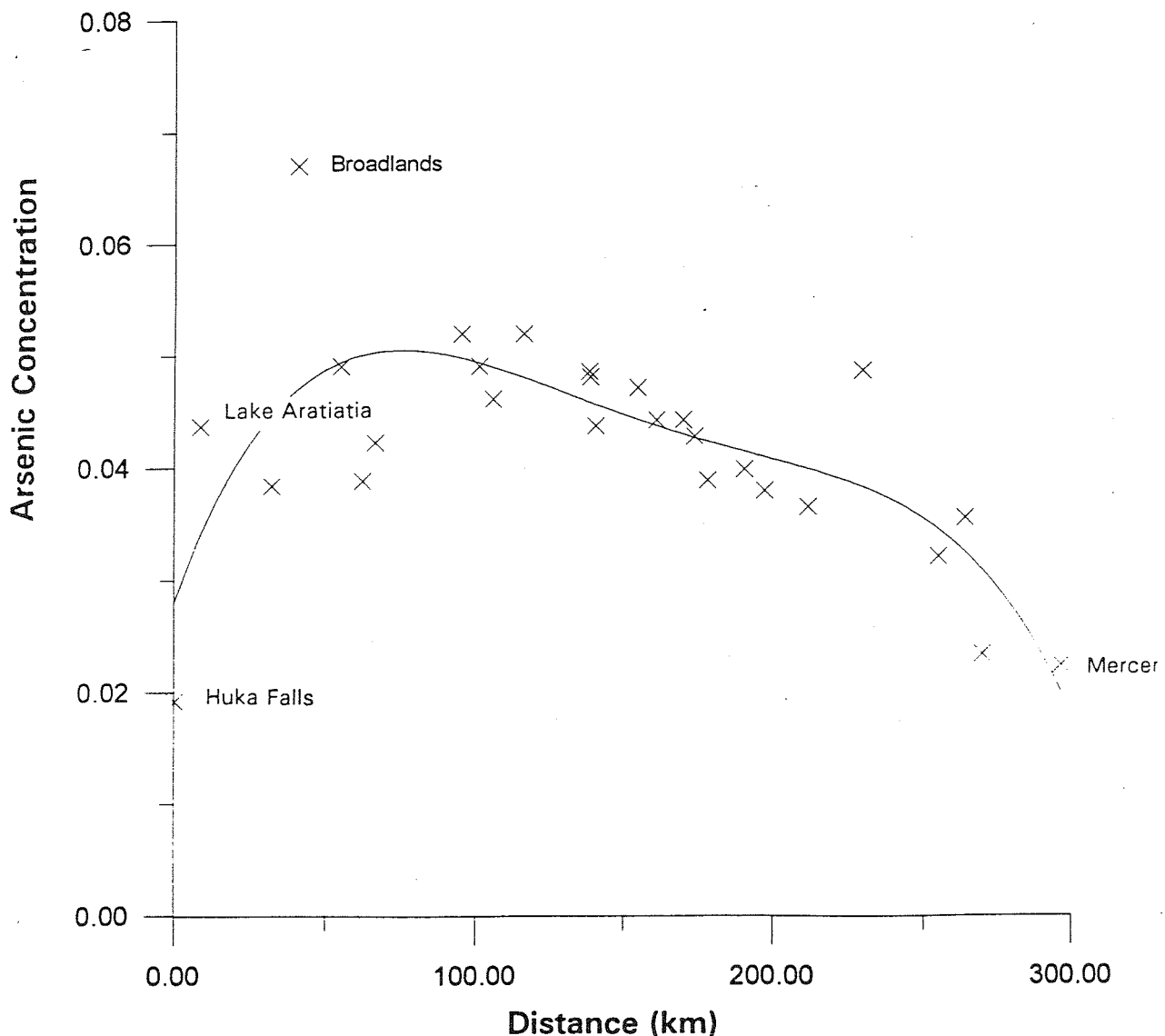


Figure 2 The arsenic content ($\mu\text{g mL}^{-1}$) of water samples taken from the Waikato River system in February 1994.

was a different distribution pattern with the 1994 collections showing a maximum arsenic concentration at Broadlands rather than at Lake Aratiatia. This shows that the arsenic concentration in the water changes over time.

Most of the water samples taken upstream from Lake Atiamuri had arsenic concentrations in excess of the WHO limit for arsenic in drinking water ($0.01 \mu\text{g mL}^{-1}$).

The concentration of arsenic in the water of the Waikato River is well above the world background level of arsenic ($0.0017 \mu\text{g mL}^{-1}$) 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), 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.

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: (1) differences in rainfall or natural geothermal activity between the time of this study and the time of the aforementioned studies; (2) an increase in the amount of arsenic entering the river; and (3) increased desorption from sediments.

The recently commissioned (1989) geothermal power station at Ohaaki may be responsible for some of the increase.

The increase in water arsenic concentrations between the samples taken in late October and those taken in February is probably accounted for by one or more of the temporal factors 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 Lakes Whakamaru and Aratiatia, there were water samples with arsenic concentrations greater than $0.05 \mu\text{g mL}^{-1}$. From Whakamaru to Finley, there were samples with arsenic concentrations between 0.04 and 0.05 mg mL^{-1} . The arsenic concentration in the water of all places north of Lake Aratiatia will probably decrease 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 Lakes Aratiatia to 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 most of the 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; and (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; and (4) removal from the river system. Weeds may be removed from the river system by floating into the sea, being deposited on to the land by floods or humans, or consumed by terrestrial herbivores such as cattle.

Arsenic in the sediments of the Waikato River

The sediments taken from various parts of the Waikato River had arsenic concentrations ranging from $9 \mu\text{g g}^{-1}$ at Huka falls to $156 \mu\text{g g}^{-1}$ at Lake Maraetai (Table 2). 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 $35 \mu\text{g g}^{-1}$. Sediment from the Wairakei main drain had an arsenic concentration of $532 \mu\text{g g}^{-1}$. This drain is a significant source of arsenic input into the Waikato River and the high concentration of this element in sediments reflects its high abundance ($3.8 \mu\text{g mL}^{-1}$) in the ambient water. Although the arsenic content of the water of this drain was high before development of the site for geothermal power, this development has exacerbated arsenic discharge rates.

There was no significant correlation (-0.19 [NS]) between the arsenic concentration of the sediments and distance downstream or the arsenic concentration in the water from which they were taken. 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 $10.3 \mu\text{g g}^{-1}$) and Lake Aratiatia ($4.7 \mu\text{g g}^{-1}$). 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 water depth (Aggett and Kriegman, 1987). As the sediments collected in this study were collected at water 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 are a major sink for arsenic in the Waikato River.

Table 2 Arsenic concentrations ($\mu\text{g mL}^{-1}$) in Waikato River sediments

Location	Arsenic	Location	Arsenic
Raglan	12.1	Lake Maraetai	28.4
Port Waikato	27.3	Whakamaru	31.4
Rangariri	57.1	Atiamuri	37.1
Ngaurawahia	19.6	Ohakuri	27.3
Karapiro	41.7	Aratiatia	30.5
Arapuni	27.6	Wairakei drain	531.9
Waipapa	156.1	Huka Falls	8.7

Arsenic in some aquatic macrophytes from the Waikato River

Three species of aquatic macrophyte (*Egeria densa*, *Ceratophyllum demersum* and *Lagarosiphon major*) from the river were analysed for arsenic. Means and ranges ($\mu\text{g g}^{-1}$ dry weight) were as follows: *Ceratophyllum demersum* 378 and 44–1160; and *Egeria densa* 488 and 94–1120. *Lagarosiphon major* from the Huka Falls contained $11 \mu\text{g g}^{-1}$ arsenic, whereas the same species from Lake Aratiatia had $300 \mu\text{g g}^{-1}$ of this element. *Ceratophyllum demersum* occurred from Lake Aratiatia northwards. *Lagarosiphon major* occurred between Lake Taupo and Broadlands where it was replaced by *E. densa*. All species had arsenic concentrations of up to $1,200 \mu\text{g g}^{-1}$ (0.12%) dry weight. *Egeria densa* and *C. demersum* had arsenic concentrations that had a highly significant inverse correlation (-0.86 [S**] and -0.76 [S**] respectively) with the distance of the plant downstream (Figures 3 and 4). These results show that the above aquatic macrophytes actively extract arsenic from the water in which they grow.

The arsenic concentration of *C. demersum* showed a highly significant (0.65 [S*]) correlation with the arsenic content of the water from which the plant was taken. The arsenic concentration in this plant was $10,000 \pm 2,000$ times the arsenic concentration in the surrounding water. The arsenic concentration in *E. densa* showed no significant correlation (0.41 [NS]) with that of the water from which it was taken. These results indicate that the aquatic macrophytes 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.

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 by possibly competing for the binding sites that would otherwise have been occupied by this phytotoxic element. It is normal farming practice to apply 400 kg ha^{-1} phosphate fertiliser to pumice soils (Hill, 1975) and some of the phosphorus leaches into the waterways of the area. The amount of phosphorus applied to farms around the Waikato River system 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 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, and thus may be used as a bioindicator for the arsenic pollution in an area. The weeds may also have a use as detoxification agents in waterways with high levels of arsenic. Arsenic may be removed from a body of water by growing and periodically removing the macrophytes in a particular

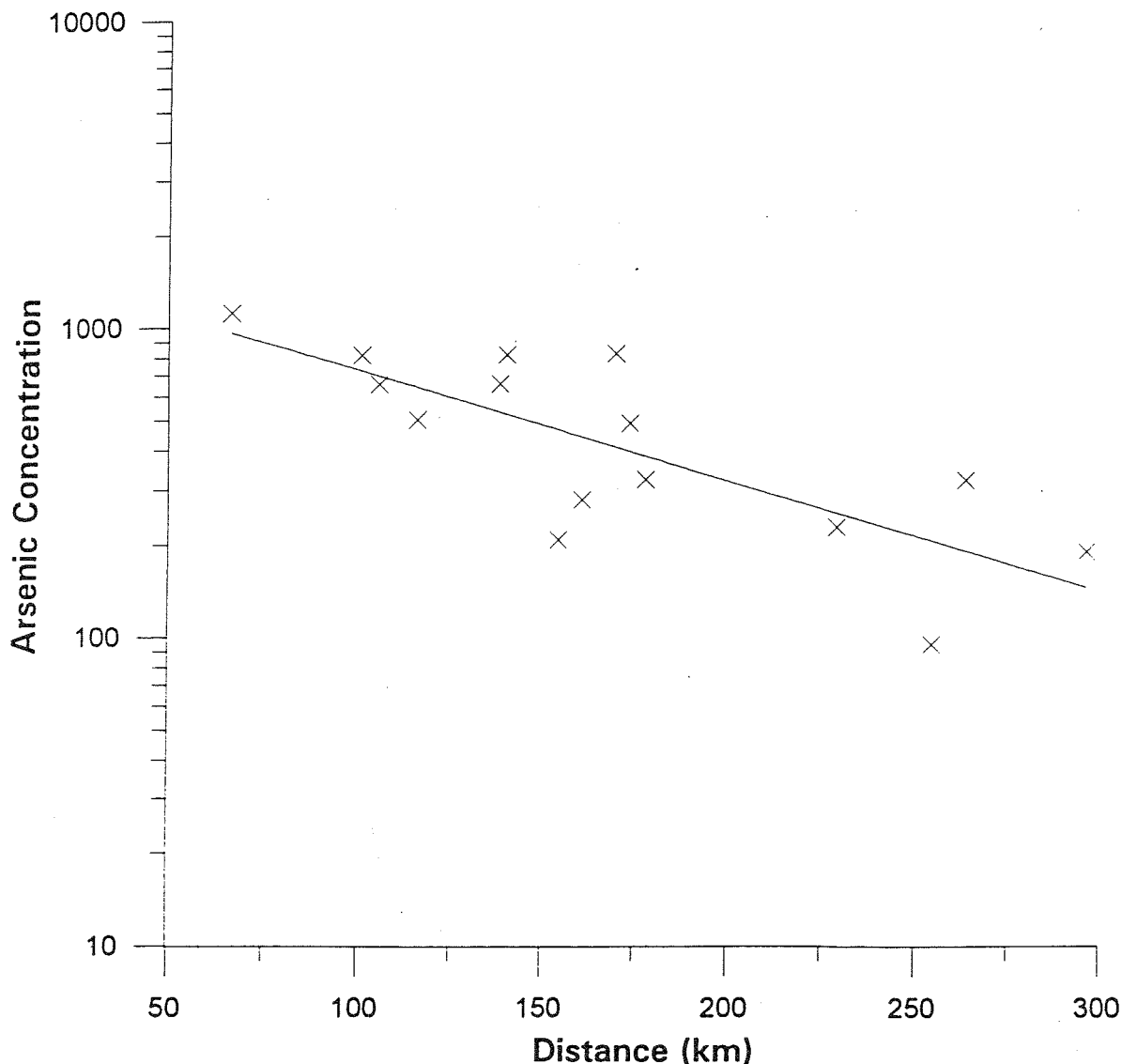


Figure 3 The arsenic content ($\mu\text{g g}^{-1}$ dry weight) in samples of *Egeria densa* expressed as a function of distance (km) of the collection site from the source in Lake Taupo.

area. Lakes such as Lake Rotorua, which still contains large amounts of arsenic from a weed eradication programme 25 years ago, may be detoxified in this manner.

Arsenic in some other organisms from the Waikato River

Water cress collected in late February 1994 from Broadlands was found to contain $306 \mu\text{g g}^{-1}$ dry weight arsenic. Two more samples from the same site collected in April 1994 contained respectively 273 and $659 \mu\text{g g}^{-1}$ d.w. arsenic. A sample collected from Lake Ohakuri contained $30 \mu\text{g g}^{-1}$ d.w. arsenic. 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 ($2 \mu\text{g g}^{-1}$ fresh weight). A sample taken as a control from the Tiritea stream near Massey University had less than $0.001 \mu\text{g g}^{-1}$ d.w. arsenic.

Water cress in the Waikato River is usually harvested about a month after when our samples had been collected, and the arsenic content of the plant may change as the plant matures. 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 levels of this element in the water cress.

Table 3 presents data for arsenic in other organisms from the Waikato River system. Although numbers of samples were too small for meaningful statistical treatment, it is clear that all of the taxa studied had significant levels of arsenic.

Periphyton (Table 3) 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,

Table 3 Mean arsenic concentrations ($\mu\text{g g}^{-1}$ dry weight) in some biota in or near the Waikato River

Organism	N	Arsenic content
Periphyton composite sample)	1	51.0
Potomopergus sp.	3	10.0
Salix sp. – leaves	3	0.3
– twigs	3	2.2
Spirodela sp. duckweed)	1	52.0
Potamogeton sp.	2	316.9
Agrostis sp.	1	2.0
Lepidium sativum water cress)	5	300.0

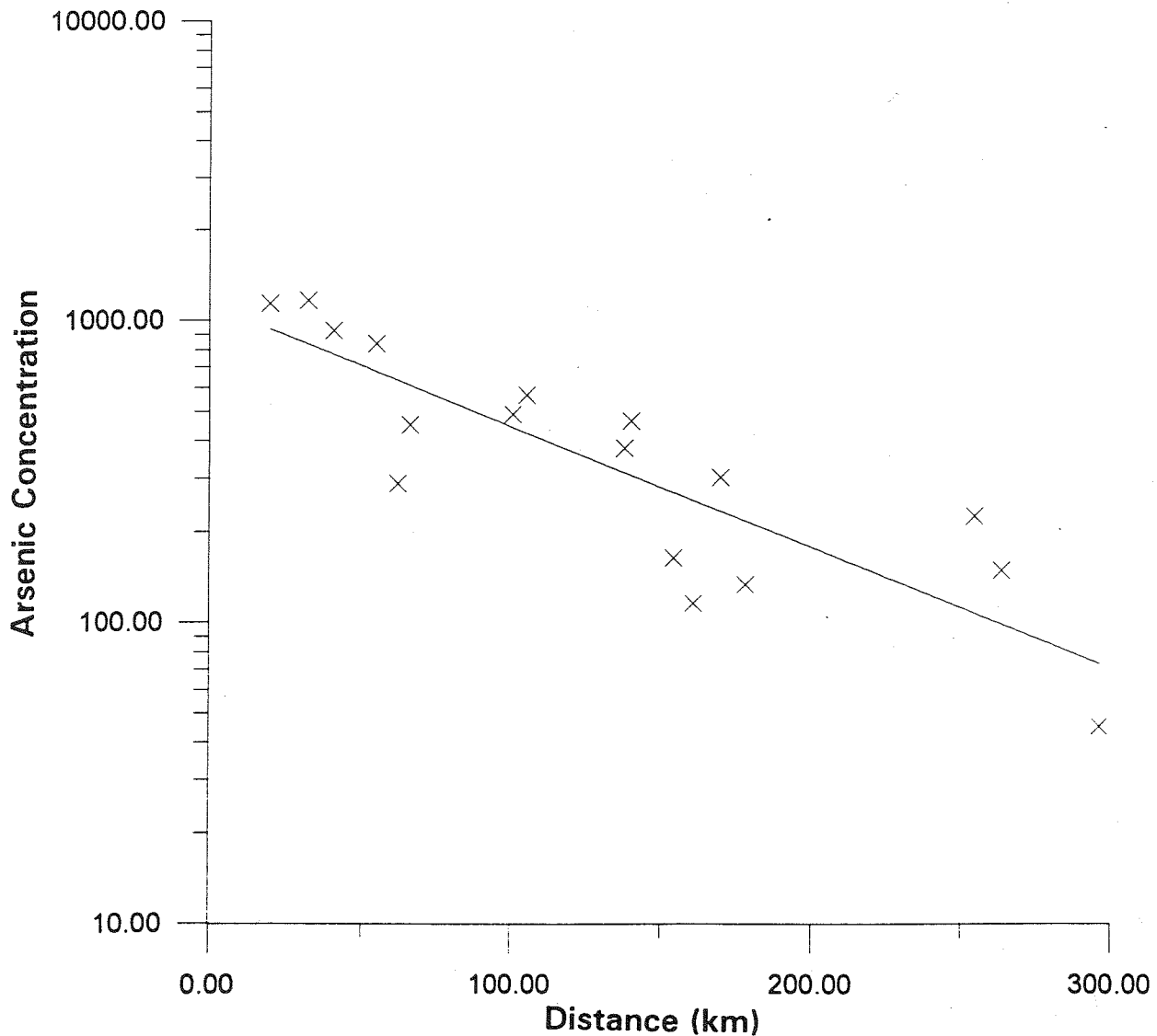


Figure 4 The arsenic content ($\mu\text{g g}^{-1}$ dry weight) in samples of *Ceratophyllum demersum* expressed as a function of distance (km) of the collection site from the source in Lake Taupo.

also has 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, e.g. trout and eels have arsenic concentrations similar to the water in which they live (Robinson *et al.*, 1995). 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.

Arsenic in some shellfish and mullet taken from the mouth of the Waikato River compared with a background area (Raglan)

Shellfish and mullet taken from the estuary at the mouth of the Waikato River were analysed for arsenic. The results were compared with concentrations of this element in shellfish taken from an estuary near Raglan, some 40 km to the south (Table 4). Statistical differences between the two populations were determined by *t*-tests.

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 ($p = 0.00006$) and mussels ($p = 0.0006$) were significantly

higher. 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. None of the animals tested had flesh arsenic concentrations above $2 \mu\text{g g}^{-1}$, the WHO limit for arsenic in foodstuffs.

Table 4 Arsenic concentrations ($\mu\text{g g}^{-1}$ dry weight) in fish and shellfish from the mouth of the Waikato River and from a nearby unconnected estuary near Raglan

Species	N	Mean As	s.d.
Mouth of Waikato River			
Oyster (<i>Saccostrea glomerata</i>)	10	0.69	0.22
Pipi (<i>Paphies australis</i>)	10	1.01	0.21
Cockle (<i>Austrovenus stutchburyi</i>)	10	1.24	0.39
Spiral (<i>Mollusca</i>)	10	0.64	0.29
Mussel (<i>Mytilus edulis aoteanus</i>)	10	1.10	0.75
Mullet (<i>Mugli cephalus</i>)	4	1.11	0.06
Raglan			
Oyster (<i>Saccostrea glomerata</i>)	10	0.32	0.13
Cockle (<i>Austrovenus stutchburyi</i>)	10	1.11	0.77
Mussel (<i>Mytilus edulis aoteanus</i>)	10	0.28	0.05

The molluscs at the mouth of the Waikato river and along its length may be a good indicator of the metals 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 $27 \mu\text{g g}^{-1}$ arsenic compared to the $12 \mu\text{g g}^{-1}$ arsenic in mud from Raglan. Mullet from the mouth of the Waikato River, although herbivorous, contained arsenic levels below $0.04 \mu\text{g g}^{-1}$.

CONCLUSIONS

Arsenic is a ubiquitous pollutant in the aquatic environment of the Waikato River. During the summer months most parts of the upper Waikato River have arsenic concentrations in the water greater than the WHO limit for drinking water. 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 most of the river unusable as drinking water in the summer months. This is very important in view of the proposal to pipe water to Auckland City from the Waikato River in order to relieve periodic droughts. This water would come from the Mercer area where the arsenic level is $0.02 \mu\text{g mL}^{-1}$. We foresee no real problem with this proposal because the WHO limit is extremely conservative and in any case the piped water would only represent about 10% of the city supply and would be diluted with 90% rain catchment with negligible arsenic levels.

Arsenic accumulates in the sediments and aquatic macrophytes of the river. 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. These future studies should include arsenic determinations on samples taken along the whole length of the river and arsenic uptake experiments.

Other organisms in the Waikato River also 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.

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