

Mercury and arsenic in trout from the Taupo Volcanic Zone and Waikato River, North Island, New Zealand

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ABSTRACT

Mercury and arsenic levels were determined in the flesh and livers of rainbow trout (*Oncorhynchus mykiss* Richardson) and brown trout (*Salmo trutta* L.) from lakes of the Taupo Volcanic Zone, and some locations on, or near, the Waikato River, North Island, New Zealand. All the fish sampled had measurable amounts of mercury in their flesh. Some trout from Lakes Rotorua, Rotoiti, and Rotomahana and trout from the Puwheto stream had flesh mercury concentrations above the World Health Organization's limit for mercury in foodstuffs. There were significant positive correlations between the flesh mercury concentration and the body weight and/or length of the trout. Brown trout taken from Puwheto had higher flesh mercury concentrations than rainbow trout taken from the same area. This may have been because the brown trout had a greater average length. Arsenic concentrations in the flesh of all the trout were of the same order of magnitude as the water from which they were taken and therefore pose no threat to human health because of the lack of accumulation of this element.

Keywords: Heavy metals, mercury, arsenic, trout.

INTRODUCTION

Certain heavy metals such as mercury and lead are known to accumulate in biological tissue. Animals near the top of the food chain, tend to have the highest heavy metal concentrations. This is particularly pronounced in marine and aquatic environments, where the food chains tend to be longer and more complex.

Trout (*Oncorhynchus mykiss* Richardson and *Salmo trutta* L.), as well as being an attraction to tourists and a food source, are the top natural predators in the Taupo Volcanic Zone. It has been shown previously (Weissberg and Zobel, 1973; Brooks *et al.* 1976; Kim, 1994) that rainbow trout from some lakes contain considerable amounts of mercury, in some cases greater than the foodstuff limit of $0.5 \mu\text{g g}^{-1}$ set by the World Health Organisation (WHO). Over 90% of the mercury in trout is in the highly toxic methyl form (Weissberg and Zobel, 1973; Kim, 1994). No work has been done on the mercury content of brown trout in New Zealand.

The source of mercury in the aquatic environment of the Taupo Volcanic Zone and Waikato River is hydrothermal emissions (Weissberg, 1975), both natural (hot springs) and anthropogenic (geothermal power stations). It is well documented (Sarbutt, 1964; Ritchie, 1961; Liddle, 1982) that the hydrothermal emissions also contain considerable amounts (up to $6 \mu\text{g mL}^{-1}$ [ppm]) of the toxic metal arsenic.

Aggett and Aspell (1980) determined arsenic in the flesh of five rainbow trout caught from lake Taupo and Broadlands. It was found that the flesh arsenic content of the trout was of the same order of magnitude as the water from which they were caught, and because of this lack of accumulation, no risk to human health was posed. While arsenic does not seem to accumulate in trout in a manner similar to mercury, larger numbers of fish from more locations needed to be analysed

before arsenic could be dismissed as a potential health hazard to humans.

The aims of this study were:

- (1) To provide an up-to-date inventory of the flesh mercury concentrations in trout from the lakes of the Taupo Volcanic Zone and Waikato River. Such an investigation is timely because the recently commissioned Ohaaki (Broadlands) geothermal power station discharges a greater-than-natural volume of geothermal water into the Waikato River.
- (2) To investigate the flesh mercury concentration in brown trout (*Salmo trutta*) from the Taupo Volcanic Zone because of the sparsity of data for this species compared to rainbow trout.
- (3) To investigate the concentration of arsenic in the flesh of the trout because of the virtual absence of data on this subject.

THE TEST AREA

The Taupo Volcanic Zone covers an area of 6000 km² in the central North Island, New Zealand. It extends from White Island south-west to Mt Ruapehu in a long narrow belt (Figure 1). The area features five active volcanoes: White Island, Mt Tarawera, Mt Tongariro, Mt Ngauruhoe and Mt Ruapehu.

Geologically, the Taupo Volcanic Zone forms a trough some 3.5 km deep. On each side of the trough 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 are common in fields of geothermal activity.

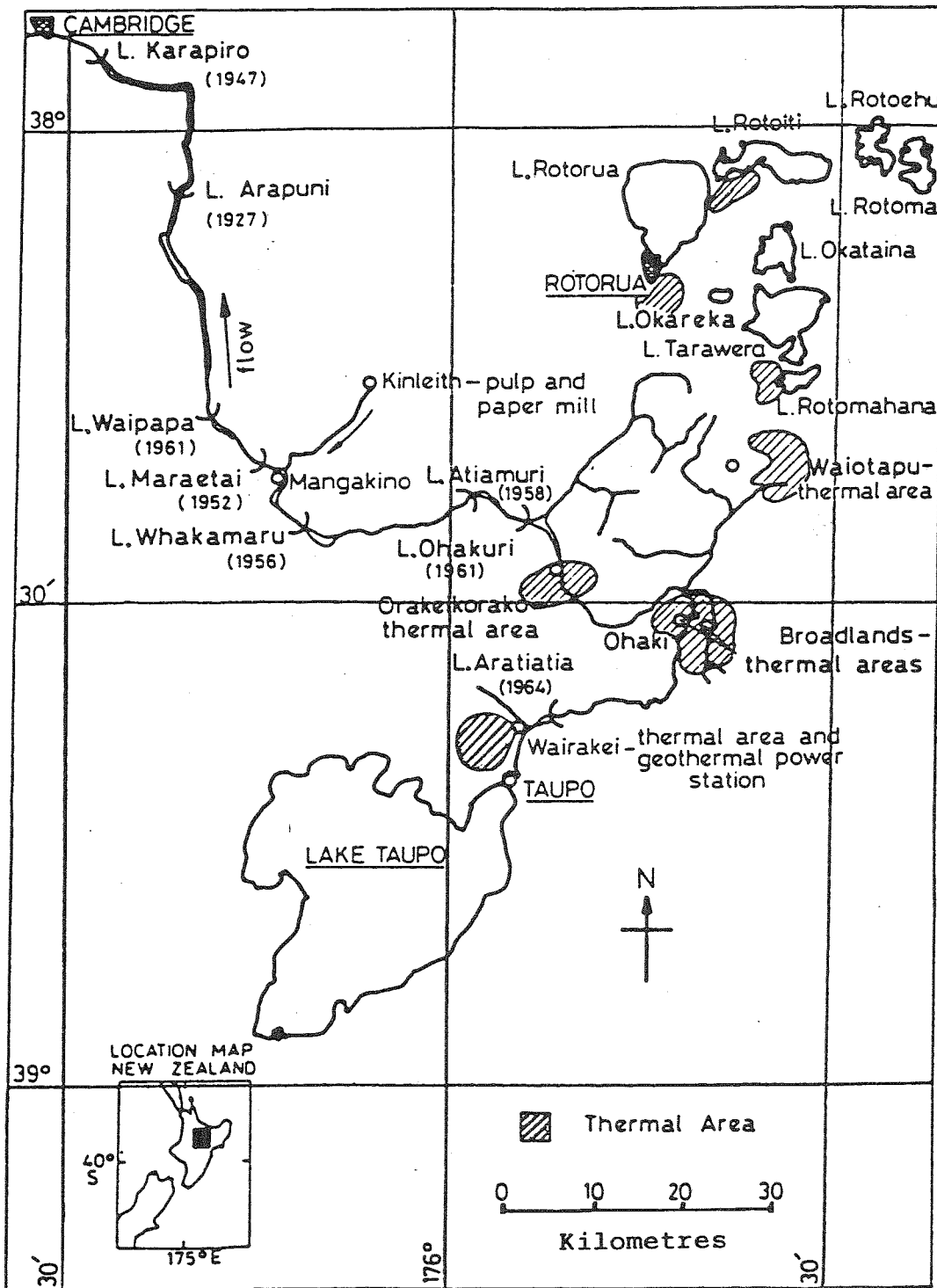


Figure 1. Map of the Taupo Volcanic Zone, New Zealand.

There are two geothermal power stations in the Taupo Volcanic Zone, Wairakei, commissioned in 1968 and Ohaaki, commissioned in 1989. Both of these stations release hydrothermal water and condensed steam of geothermal origin into the Waikato River at a faster rate than would occur naturally.

The Taupo Volcanic Zone contains at least 32 natural lakes as well as eight man-made ones along the length of the Waikato River. Many of the natural lakes are associated with geothermal activity (McCull, 1975), having geothermal waters either flowing into the lake, or upwelling in the lake itself. Some lakes have also had 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 Rotorua near Hamilton 24 years after the application of a sodium arsenate herbicide. This lake has no geothermal inflows.

MATERIALS AND METHODS

Sampling

Rainbow trout (139 fish) were taken from Lakes Taupo, Rotorua, Rotokakahi, Okareka, Rototiti, Rotoma, Tarawera, Okataina, Rotoehu, Rerewhakaaitu, Rotomahana, Rotokawa, and Blue Lake during a fishing competition in Rotorua in

November 1993. The sex, weight, and origin of the trout were recorded. A piece of flesh from behind the head and a section of liver were taken from each specimen.

The samples were stored in polythene bags in a refrigerated container. They were subsequently frozen (-18°C) on the evening of the day they were collected.

Rainbow trout (57) and brown trout (11) from the Waikato River were taken from Lakes Maraetai and Atiamuri and surrounding tributaries of the Waikato River in September 1994. The length and head widths of the fish were recorded, and a flesh sample of each was refrigerated at 4°C before analysis.

Sample preparation

Samples (0.5–2.5 g wet wt) of muscle or liver were weighed into a boiling tube. Five mL of 70% HNO_3 was added to each tube which was then heated to ca. 100°C in an electrically heated metal block until the sample had dissolved. Each solution was transferred to a measuring cylinder and made up to exactly 10 mL with distilled water. Samples were stored in 25 mL polythene containers. Two reagent blanks were prepared for every 40 samples.

Determination of mercury and arsenic using hydride generation atomic absorption spectrometry

Mercury and arsenic were determined using a GBC 900 spectrophotometer combined with a purpose-built hydride generation apparatus. The conditions used for the analysis of each element are given in Table 1.

Table 1. Conditions used for the determination of mercury and arsenic by flameless atomic absorption spectrometry.

	Mercury	Arsenic
Lamp current	3 mA	8 mA
Wavelength	253.7 nm	193.7 nm
Slit width	0.5 nm	1.0 nm
[NaBH_4]	2%	2%
Cell temperature	room temperature	950°C

Table 2. Concentrations of mercury ($\mu\text{g g}^{-1}$ wet weight) in flesh and livers of trout from some lakes in the Taupo Volcanic Zone (means are geometric).

	Rotorua	Tarawera	Okataina	Rotoiti	Rotoma
N	20	20	20	23	-
Av. fish wt. (kg)	1.43	1.98	2.11	1.93	1.31
Mean flesh Hg conc.	0.46	0.09	0.06	1.11	0.08
s.d. range	0.23–0.93	0.054–0.17	0.03–0.11	0.06–0.19	0.03–0.20
Mean liver Hg conc.	0.76	0.12	0.06	0.98	0.06
s.d. range	0.30–1.88	0.04–0.34	0.01–0.22	0.23–4.2	0.01–0.68
	Rotoehu	Rotomahana	Aniwhenua	Galatea	Ohakure
N	17	15	1	6	1
Av. fish wt. (kg)	1.26	1.42	3.03	3.21	0.73
Mean flesh Hg conc.	0.11	1.24	0.06	0.04	0.14
s.d. range	0.06–0.19	0.98–1.56	-	0.01–0.14	-
Mean liver Hg conc.	0.14	2.53	0.04	-	0.42
s.d. range	0.10–0.23	1.54–4.15	-	-	-
	Taupo	Rerewhakaaitu			
N	7	2			
Av. fish wt. (kg)	1.40	1.85			
Mean flesh Hg conc.	0.065	0.15			
s.d. range	0.03–0.11				

RESULTS AND DISCUSSION

Mercury in rainbow trout from the Taupo Volcanic Zone and the Waikato River

Mercury concentrations ($\mu\text{g g}^{-1}$ wet weight) in trout from the Taupo Volcanic Zone and the Waikato River are shown in Tables 2 and 3. Since the data were lognormally distributed, concentration data were logarithmically transformed and therefore, average values are shown as geometric means and, standard deviations as a range.

Most of the trout had flesh mercury concentrations below the WHO limit for mercury in foodstuffs ($0.5 \mu\text{g g}^{-1}$). There were, however, four lakes (Rotoiti, Rotomahana, Rotorua and Rotoehu) where fish had mercury concentrations in excess of this limit. These were Lakes Rotoiti, Rotomahana, Rotorua and Rotoehu. In the first two lakes, the average mercury content of the fish exceeded $0.5 \mu\text{g g}^{-1}$ mercury. This was significantly greater than any of the other lakes as determined from *t*-tests (Table 4). In general, in lakes where the mean mercury content of trout flesh was below $0.5 \mu\text{g g}^{-1}$, there was no significant difference in this value between the lakes.

The livers of the trout had mercury concentrations in some cases up to three times higher than the flesh. The relative standard deviation of mercury in the livers was also higher. Lakes containing fish with an average flesh mercury concentration greater than $0.12 \mu\text{g g}^{-1}$, had fish with significant to highly significant correlations between liver and flesh mercury concentrations. In lakes containing fish with an average flesh mercury concentration less than $0.12 \mu\text{g g}^{-1}$, there was no correlation between liver and flesh mercury concentrations.

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 (Table 5).

Trout from the Waikato River area had highly significant positive correlations between the length of the fish, head width, and flesh mercury concentration (Table 6). These correlations indicate 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

Table 3. Concentrations of arsenic and mercury ($\mu\text{g g}^{-1}$ wet weight) in trout from the Waikato River and nearby streams.

	Kawhiti	Maraetai	Atiamuri	Mangrun	Mangstr	Puwheho
N	9	7	2	7	10	22
Length ¹ (mm)	364	339	398	350	332	348
Flesh [As] ²	0.02	0.03	0.02	0.04	0.05	0.05
S.d. range	0.01–0.05	0.02–0.06	–	0.02–0.07	0.02–0.07	0.03–0.09
Flesh [Hg] ²	0.16	0.14	0.32	0.14	0.16	0.14
S.d. range	0.10–0.27	0.09–0.21	–	0.11–0.19	0.11–0.22	0.05–0.37

¹Average, ²geometric mean. Mangrun = Mangakino runoff, Mangstr = Mangakino stream.

Table 4. *t*-tests (values of *p*) for differences in trout flesh mercury concentrations for trout from different natural lakes in the Taupo Volcanic Zone.

	A	B	C	D	E	F	G	H
B	0.00(S**)							
C	0.00(S**)	0.02(S*)						
D	0.00(S**)	0.00(S**)	0.00(S**)					
E	0.01(S)	0.35(NS)	0.21(NS)	0.00(S**)				
F	0.00(S**)	0.21(NS)	0.01(S*)	0.00(S**)	0.25(NS)			
G	0.00(S**)	0.00(S**)	0.00(S**)	0.02(S)	0.00(S*)	0.00(S**)		
H	0.00(S**)	0.07(PS)	0.27(NS)	0.00(S**)	0.10(NS)	0.06(PS)	0.00(S**)	
I	0.00(S**)	0.06(PS)	0.27(NS)	0.00(S**)	0.25(NS)	0.03(S)	0.00(S**)	0.18(NS)

N.B. Values of $p < 0.01$ are shown as 0.00.

A = Rotorua, B = Tarawera, C = Okataina, D = Rotoiti, E = Rotoma, F = Rotoehu,

G = Rotomahana, H = Galatea, I = Taupo.

S** very highly significant ($p \leq 0.001$)

S* highly significant ($0.001 < p \leq 0.01$)

S significant ($0.01 < p \leq 0.05$)

PS possibly significant ($0.05 < p \leq 0.1$)

NS not significant ($p > 0.1$)

Table 5. Correlation data (*r*) for mercury in trout of lakes of the Taupo Volcanic Zone.

Lake	Wt vs. flesh Hg	Wt vs. liver Hg	Flesh Hg vs. liver Hg
Rotorua	0.66(S*)	0.12(NS)	0.92(S**)
Tarawera	-0.16(NS)	0.29(NS)	0.11(NS)
Okataina	0.19(NS)	0.18(NS)	0.01(NS)
Rotoiti	0.11(NS)	0.21(NS)	0.99(S**)
Rotoma	-0.23(NS)	–	–
Rotoehu	0.25(NS)	0.10(NS)	0.61(S*)
Rotomahana	0.71(S*)	0.51(PS)	0.77(S**)
Galatea	-0.50(NS)	–	–
Taupo	-0.74(PS)	–	–

Table 6. Table of correlations (*r*) between the mercury content, length of fish, and head width for trout from the Waikato River.

	Length	Head width
Head width	0.67(S**)	
Mercury content	0.55(S**)	0.40(S**)

between the size of the fish and mercury concentration in the flesh for trout from Lake Taupo (Table 5). There was no correlation between the mercury concentration in the liver and the weight of the fish in any of the lakes.

The mercury levels found in the fish are somewhat lower than those reported by Brooks *et al.* (1976) and the average

weight of the fish was heavier. The mercury concentrations in fish from lakes Rotorua, Tarawera, and Rotomahana are similar to methylmercury concentrations reported by Kim (1994) for the same lakes. As the concentration of mercury in the waters of these lakes was below detection limits ($< 0.005 \mu\text{g mL}^{-1}$), it would appear that there is a strong accumulation of mercury up the food chain. Strong correlations between the body weight (length) 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 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 Brooks *et al.* (1976), the maximum recommended consumption of trout flesh from various lakes was calculated using the acceptable daily intake (ADI) of mercury set at $30 \mu\text{g}$ for an adult by Grimstone (1972). The calculations (Table 7) make the assumption that all the mercury in the trout is in the methyl form. Weissberg and Zobel (1973) and Kim (1994) showed that this was the case in virtually all the mercury in trout sampled by them.

For all but three of the lakes (Rotorua, Rotoiti and Rotomahana), it is extremely unlikely that many people would consume fish at a rate that would exceed the acceptable daily intake of mercury. 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 higher, and the consequent ADI value may be slightly lower. 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 occur 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 of a fish that has a slow rate of growth.

Mercury in brown trout from Puwheto, Waikato River

Brown trout (11 – with an average length of 47.4 cm) taken from Puwheto had a geometric mean of 0.28 $\mu\text{g g}^{-1}$ mercury in their flesh (s.d. 0.11–0.70 $\mu\text{g g}^{-1}$). As with rainbow trout, there was a highly significant ($r = 0.77 S^*$) correlation between the length of the fish and the mercury concentration in the flesh. Although concentrations were significantly ($p < 0.01$) higher than the flesh mercury concentration of rainbow trout taken from the same area (Table 8), the average length of the fish was greater so there was insufficient information to conclude that brown trout have higher flesh mercury concentrations than rainbow trout.

Table 7. Maximum allowable daily consumption (g wet weight) of trout flesh by adult humans to keep within an acceptable daily intake of 30 μg of mercury.

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	41

A difference in flesh mercury concentration between brown trout and rainbow trout may be explained by one of the following: (1) differences in the fish's ability to excrete arsenic, or (2) differences in diet. The results indicate that brown trout from other areas in the Taupo Volcanic Zone are likely to have elevated flesh mercury concentrations. It is probable that many brown trout from Lakes Rotorua, Rotoiti and Rotomahana have flesh mercury concentrations above the WHO limit.

Arsenic in trout from the Taupo Volcanic Zone and the Waikato River

Some of the trout taken had measurable amounts of arsenic (Tables 3 and 9). Determinations made on trout from the Taupo Volcanic Zone revealed that the concentration of arsenic in the flesh for all trout tested was of the same order of magnitude as the water from which they were taken. The liver of the trout generally had a lower arsenic concentration, often below detection limits. Surprisingly, trout from lakes with the highest arsenic levels in the waters (Rotomahana and Rotoma), had flesh arsenic levels below the detection limits. Trout from lakes with relatively high water arsenic levels (Lakes Tarawera and Okataina, Table 9) had measurable amounts of arsenic in their flesh. All trout of both species taken from the Waikato River area had measurable amounts of arsenic in their flesh (Table 3).

None of the trout tested had arsenic concentrations above the WHO limit for arsenic in foodstuffs (2 $\mu\text{g g}^{-1}$). There were no significant correlations between the flesh arsenic concentration and fish weight, length, head width, or mercury concentration. These findings reinforce the conclusions of Aggett and Aspell (1980) that arsenic in trout from these areas poses no threat to human health. The low arsenic levels in trout is surprising since the arsenic concentration in the water of these lakes is more than an order of magnitude greater than the water mercury concentration. This may be explained if arsenic can be eliminated from biological tissue more readily than mercury and thus does not accumulate as strongly up the food chain.

Table 9. Concentrations of arsenic ($\mu\text{g g}^{-1}$ wet weight) in the flesh of trout from Lakes Tarawera and Okataina.

	Tarawera	Okataina
No. samples with measurable As	11	12
Mean (geometric) arsenic content	0.031	0.014
Standard deviation range	<0.007–0.075	<0.002–0.047

Table 8. *t*-tests (values of *p*) for differences in mercury concentrations in brown and rainbow trout from different locations in the Waikato River.

	A	B	C	D	E	F
B	0.20(NS)					
C	0.03(S)	0.00(S*)				
D	0.20(PS)	0.42(NS)	0.04(S)			
E	0.36(NS)	0.25(NS)	0.01(S*)	0.27(NS)		
F	0.20(NS)	0.43(NS)	0.01(S*)	0.48(NS)	0.20(NS)	
G	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.

A = Kaiwhiti, B = Maraetai, C = Atiamuri, D = Mangakino runoff, E = Mangakino stream, F = Puwheto.

CONCLUSIONS

All brown and rainbow trout from the Lakes of the Taupo Volcanic Zone and the Waikato River had measurable ($> 0.005 \mu\text{g g}^{-1}$) amounts of mercury in their flesh. Some rainbow trout from lakes Rotorua, Rotoiti, Rotomahana, and Rotoehu, and some brown trout from Puwheto stream, near the Waikato River, had flesh mercury concentrations above the WHO limit for mercury in foodstuffs ($0.5 \mu\text{g g}^{-1}$). Trout from these lakes, should therefore, not constitute a large proportion of human diet.

There were strong positive correlations between the mercury concentration in the flesh of the trout and the weight (length) of the fish, implying that mercury accumulates with time in the fish as it grows.

Brown trout from Puwheto stream, had on average, a higher flesh mercury concentration than rainbow trout from the same area. This may be explained however, by the fact that the average length of the fish was longer, suggesting that the fish were older.

The levels of arsenic in the flesh of the trout were of the same order of magnitude as the water from which they were taken. This indicates that arsenic does not accumulate as strongly up the food chain as does mercury. The levels of arsenic in the flesh of the trout pose no threat to human health.

Further work can be done on the mercury levels in brown trout of other lakes, particularly those lakes where there are high mercury levels in rainbow trout.

Periodic surveys need to be done on mercury levels in trout from all lakes which at present and in the past have contained mercury levels near or above the WHO limit for mercury (Lakes Rotorua, Rotoiti, Rotomahana, and Rotoehu). Any future industrial developments which have the potential to release mercury into the aforementioned lakes need to be carefully assessed.

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