MERCURY IN THE WAIKATO RIVER

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ABSTRACT

The Waikato River as it flows (152 m³/s annual mean) from Lake Taupo in North Island, New Zealand, to the Tasman Sea receives approximately 270000 t/a of dissolved salts from geothermal fluids including 190 t/a of As, 1400 t/a of B, 710 t/a of Li, 88t/a of Rb and 50 kg/a of Hg, from both natural fluid emissions and the Wairakei Geothermal Power Station. This discharge of Hg has been considered as partly responsible for high concentrations of Hg, commonly exceeding 0.5 mg/kg (wet flesh), in trout from the river. An estimated 1020 kg of Hg is retained in the fine-grained river sediments but this accounts for only a part of the lifetime discharge of 1500 kg from the Wairakei Geothermal Power Station. Elemental mercury entering the Wairakei Station with geothermal steam is only partly oxidised in the turbine condensers and it is postulated that the elemental fraction remaining in the cooling water discharge is lost to the atmosphere and so does not contribute to the load on the river. Mass flow measurements at Aratiatia, the dam immediately downstream from Wairakei, confirms the loss of Wairakei Hg from the river water, but' some of this loss may be deposition into sediment. Loss to the atmosphere, is a mechanism which might be utilised for removing Hg from condensate wastes and so protecting the aquatic environment from geothermal Hg.

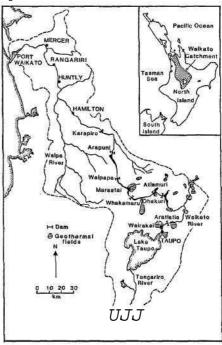
INTRODUCTION

The Waikato River (Fig. 1) is the largest river in North Island, New Zealand, and rises on the south eastern flanks of Mount Ruapehu, a volcano in the centre of the island. After flowing for 95 km, the river (called the Tongariro at this point) becomes the largest inflow to Lake Taupo. This lake of 616 km² surface area and 97 m average depth receives a small amount of geothermal fluid from natural emissions slightly enhanced by man's activities (Timperley and Vigor-Brown, 1985). The outflow from Lake Taupo, again called the Waikato Ri²er, has a present annual average flow of 152 m /s. The surface of the lake is 357 m above sea level and the river falls over most of this altitude within the next 150 km. From this point on the water flows slowly for 180 km to eventually enter the Tasman Sea just to the southwest of Auckland.

Several geothermal fields exist within the catchment of the Waikato River (Fig. 1) although the natural fluid discharges from these fields are relatively small. These fluids are hot dilute saline solutions (Table 1) with high concentrations of silica and significant amounts of some potentially hazardous substances.

In 1929 the first dam for hydroelectric power generation was constructed at Arapuni (Fig. 1) and since then almost the entire energy potential of the river has been tapped with a total of eight dams feeding nine stations. The reservoirs behind these dams have changed the character of the river from a fast, turbulent, flowing system to a lake-like environment with fine-grained organic-rich sediments

Fig 1 The Waikato River catchment



and thermal stratification-overturn cycles. This new environment has a substantial impact on the behaviour of mercury in the river.

An approximate mass budget for the Waikato River (Figure 2) indicates that prior to industrial/agricultural development, natural geothermal fluid emissions mostly into Lake Taupo contributed about 2.1 kg/s of dissolved salts or about 9% of the salts carried by the river immediately downstream of all geothermal inputs. The Wairakei Geothermal Power Station which was fully commissioned in 1958, increased the geothermal contribution of dissolved salts by 6.4 kg/s to give a total geothermal contribution of 8.5 kg/s or 30% of the total salts downstream of all geothermal inputs. Although the major geothermal contributors to the dissolved salts are Na, Cl, and Si, the minor constituents, As, Hg, B, Li and Rb are of most ecological interest.

Over the past 15 years several studies have focussed on the fate and behaviour of As, Hg, Li, Rb, and B in the river. This paper reviews the findings of previous studies on Hg and also presents some new results.

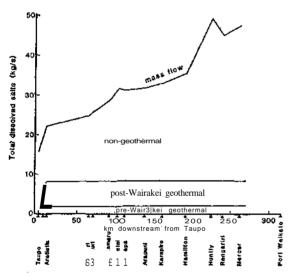
The first published study of Hg in the Waikato River (Weissberg and Zobel, 1973) was undertaken in response to concern about losses of Hg from a chloralkali plant at the N.Z. Forest Products pulp and paper mill discharging into Lake Maraetai. This study discovered high concentrations of Hg in the trout and sediments not only downstream from the mill but also upstream. The downstream concentrations were not surprising in view of the

TABLE 1: Composition of the major geothermal fluid contributions to the Waikato River and Lake Taupo. Concentrations in mg/kg

	Wairakei ¹	Tokaanu ²
Na K Ca Mg Cl SO4 HCO. SiOX Lii ¹ Rb Cs As Hg B	1200 200 25 0.4 2200 55 10 580 12 2.5 2.5 3.5 0.0013	1740 160 37 1.3 3050 49 32 230 23 1.3 3.2 6.4
Г	8	-

^Geothermal Research Centre data. Bore 8, Mahon and Klyen (1968).

Fig 2 Total dissolved salts in the Waikato River



maximum total Hg losses from the mill of 830 kg/a prior to mid-1971. About half of this loss was presumed to enter the Waikato River. The upstream concentrations of Hg in trout and sediments lead the authors to discover the magnitude and extent of Hg discharges from geothermal systems. A later study confirmed the high concentrations of Hg in trout from the River (Brooks et al $_{\rm t}$ 1976) and further data has since been obtained from Lakes Taupo and

A summary of existing data is given in Table 2. Three sets of data are now available for trout from Lake Taupo and these give a reliable mean value of between 0.1 and 0.2 mg/kg. New data for Lake Aratiatia show that concentrations of Hg in trout from this lake are not significantly higher than the concentrations in trout from Lake Taupo. Concentrations in Ohakuri, Atiamuri and Whakamaru represent the total influence of all geothermal Hg inputs to the river. The data available from Lake Maraetai and further downstream were all influenced by the pulp and paper mill discharge.

Subsequent studies focussed on waters, including some geothermal fluids, of the upper catchment and concentrations from less than 0.02~pg/1 to 2.6~pg/1 were found (Weissberg, 1975). Included in this study was the discharge from the Wairakei Geothermal Power Station of waste geothermal water from which steam had already been separated. The concentration

found was 0.15 ug/1 but with a flow of $1.3 \text{ m}^3/\text{S}$; the total annual discharge was only 6 kg. It was recognised at this time that most Hg in geothermal fluids probably entered the steam phase when the fluid boiled and this was confirmed in a later study which established the annual discharge from the Wairakei Station as about 55 Kg (Weissberg and Rhode, 1978). It was widely presumed that this Hg accumulated into the sediments of the reservoirs where it underwent methylation and subsequent bioaccumulation into trout.

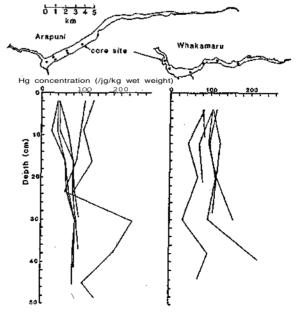
TABLE 2: Mean concentrations of Hg (mg/kg fresh weight in flesh), and mean weights for trout, from the Waikato River and Lake Taupo

		(1)	(2)	(3)
Taupo	mean concentration weight n	0.11 1.56 76	0.19 1.78 21	
Aratiatia	me w n	0.18 1.48 50		
Ohakuri Atiamuri				0.53
Whakamaru	me W n		0.32 1.48 5	
Maraetai	me W n		1.4 1.48 6	0.70 0.89 20
Wai papa Arapuni Karapi ro				1.12

- Timperley, unpublished data
- Brooks et al, 1976 Weissberg and Zobel, 1973.

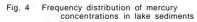
When the trout Hg data for Lake Aratiatia were obtained the apparent inconsistancy between the concentrations found and the presence of the Wairakei discharge into this lake was recognised.

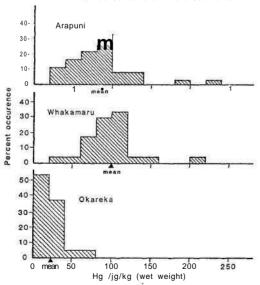
Fig. 3 Mercury in Waikato River lake sediments



Since that time two studies have measured Hg in sediments of Lakes Arapuni and Whakamaru, the 8th and 4th reservoirs downstream from Lake Taupo

(Timperley, 1985; Timperley and Sheppard, 1986). Six cores were taken from each lake and sections of each core were analysed for total Hg (Figure 3) and other physical parameters such as water content, dry weight, and weight loss on ignition at 450°C. these data, typical Hg concentration with depth profiles were established for each morphologically distinct part of the reservoirs. The concentrations were then integrated over the estimated sediment surface areas and depths to give estimates of total Hg retained in the lake bed sediments. The values obtained were 205 kg for Lake Arapuni and 153 kg for Lake Whakamaru. The difference was largely due to the different volumes of sediment in each reservoir; actual sediment Hg concentrations were very similar (Figure 4). This similarity gives some confidence to an extrapolation of these results to all the reservoirs of the river. Assuming that the other reservoirs have similar types of sediment, sediment areas and depths (there is independent evidence that these assumptions are valid for Lake Ohakuri) then the total Hg retained in the reservoir sediments is about 1020 kg. The error on this estimate is unlikely to be greater than $\pm 30\%$. The annual discharge of Hg from the Wairakei Power Station was estimated to be 55 kg in 1977 (Weissberg and Rohde, 1978) and recent measurements gave a value of 44 kg (author's unpublished data). If an average of 50 kg/a is assumed for the operating life of the Station, 30 years, then the total Hg discharged from the station to the river is 1500 kg. Even allowing for the error in the estimate of Hg retained in the river sediments there is a strong indication that a substantial proportion of the Wairakei discharge has been lost from the river system, particularly when allowance is made for the natural input of Hg to the river. The natural input can be estimated only approximately from sediment Hg concentrations in a approximately from sediment Hg concentrations in a non-geothermal lake such as Lake Okareka, about 80 km north of Taupo. The mean sediment Hg concentration in this lake is 23 ng/kg (wet weight) (Figure 3) and assuming this value for the Waikato River sediments gives a non-geothermal pool of Hg of 215 kg in the river sediments. Thus on this very approximate budget about 50% of the Wairakei Power Station discharge has been lost from the river system. system.





Mercury in geothermal fluids preferentially concentrates into the steam phase on boiling as indicated by the steam:water Hg mass ratio of about 13:1 in the Power Station effluents. The Hg entering the station in the steam phase is volatile elemental ${\rm Hg}(0)\,,$ but my investigations have established that this ${\rm Hg}(0)$ is only partially

oxidised in the turbine condensers. These condensers operate by spraying river water, about 13 m/s, into the steam, 0.33 m/s, exiting the turbines. This mixture flows 150 seconds from A Station and 80 seconds from B Station to the outfall where the temperature is 27°C. My measurements at the outfall are shown in Table 3. Although the total Hg leaving the station varied the ratio of elemental to oxidised Hg was consistently about 50%.

TABLE 3: Mercury in the Wairakei Geothermal Power Station cooling water/condensate discharge. Data given as mean (ug/kg) and standard deviation.

Date	Hg(O)	Hg_{Total}	$Hg(0)/Hg_{Total}$
20/6/88	-	0.100 ± 0.015	-
1/7/88	0.056 ± 0.002	0.112 ± 0.034	0.50
22/7/88	0.041 + 0.003	0.079 + 0.005	0.52

It has been experimentally determined that the steam:water distribution ratio for Hg(O) at 27°C is about 15400 and this value implies that Hg(O) floating in a warm layer on the surface of Lake Aratiatia has a good chance of being lost to the atmosphere by volatilisation. Figure 5 presents the water flow into and out of Lake Aratiatia and the Hgtotal concentrations in the outflow from the lake over a 24 hour period. The flow through the Aratiatia hydroelectric station varies from 0 to almost 300 m/s over a 24 hour period whereas the inflow of Hg to the lake from Wairakei remains constant. This leads to the variations observed in outflowing Hg concentrations.

Fig 5 Water flow and Hg concentrations in Lake Aratiatia

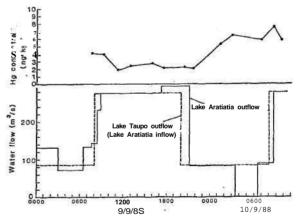


Table 4 summarises the mass balance results for the 24 hour period. Only 38% of the Hg input to the lake appeared in the outflow. It is suggested that overall these results could be explained by a loss to the atmosphere of 50% of the Wairakei input, i.e. 56 g, plus sedimentation in Lake Aratiatia of 16 g leaving 45 g to flow out of the lake.

TABLE 4: Hg mass balance for Lake Aratiatia over a 24 hour period, 0800 on 9 September 1988 to 0800 on 10 September 1988. Units are g.

Inflow/Outflow	In	Out	In/Out
Wairakei	112		
Lake Taupo	5		
Aratiatia Hydroelectric Station Tail race		45	0.38

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If this suggestion is correct then the Wairakei input to the Waikato River downstream from Lake Aratiatia is much smaller, i.e. 16 kg/a than previously thought, i.e. 50 kg/a. The low Hg sedimentation rate into Lake Aratiatia also explains the lower than expected concentrations of Hg in trout from this lake.

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