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Mercury Concentrations in Ambient Air of the Rotorua, New Zealand, Geothermal Area

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The city of Rotorua in the central North Island of New Zealand is built on and around a major geothermal area. The inhabitants of Rotorua are known to be exposed to geothermal emissions. However, these exposures have been poorly characterised and, until recently, whether the emissions had any health effects on those who live there had been little studied (Bates et al. 1997, 1998).

A recent epidemiologic study that compared the Rotorua territorial local authority area with the rest of New Zealand, suggested an elevated rate of disorders of the peripheral nervous system (ICD 350-359) (Relative risk estimate = 1.35, 95% Confidence interval 1.21-1.51) within the area (Bates et al. 1998). Other disorders of the central nervous system (ICD 340-349) were also elevated, as were neurological disorders of the eye and adnexa. Although the relative risk estimates were not so highly elevated that they could not have been accounted for by bias or confounding, the question arose as to whether they might be attributable to geothermal exposures in the area. In that regard, two possibilities were apparent: hydrogen sulphide and mercury. Both of these chemicals are known to be discharged from geothermal vents.

Although a certain amount is known about hydrogen sulphide levels in the Rotorua ambient air (Graham & Narsey, 1994) no information was available about levels of mercury either in Rotorua geothermal discharges or in the ambient air of the city. However, some indirect evidence suggested that mercury could be among the chemicals geothermally discharged in the Rotorua area. In particular, there are some data indicating that hair mercury levels may be elevated in the Rotorua area (Siegel & Siegel, 1985) and trout from lakes in the area appear to have elevated methyl mercury levels (Weissberg & Zobel, 1973; Rim, 1995).

The present investigation was undertaken to obtain preliminary information on levels of mercury in Rotorua ambient air.

MATERIALS AND METHODS

Eleven sites for monitoring were selected: four in areas expected to be exposed to high geothermal emission levels, three in areas where such exposures were expected to be medium and four where geothermal exposures were expected to be low.

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Samples were collected by pumping air through mercury traps. Each trap consisted of a 6 mm diameter glass tube, with a swelling of about 15 mm diameter in the middle. The swelling was packed with gold-coated sand. In the laboratory, traps were prepared for use by heating them to expel any mercury, and, after cooling, sealing the ends with Parafilm®. Prepared tubes were stored in a glass jar that had been partially plated on the inside with Silver to adsorb any mercury vapour entering the bottle.

Battery-powered personal air sampling pumps were used. The flow rates available from the pumps when attached to the mercury traps ranged from 1.3 to 2 L/min.

For sample collection pumps were sited in inconspicuous locations, 1 to 2 m above the ground. The initial flow rate was checked using a rotameter. The flow rate was checked and recorded whenever the pumps were revisited. At the conclusion of sampling, the traps were sealed at both ends with Parafilm®, and returned to the silver-plated bottle.

The total air volume sampled was calculated as the time integral of the measured flow rates. The calculation assumed a linear change of flow rate between the measurements. Usually the flow rate decreased over time as the batteries discharged. In the case of the pumps that stopped between visits to the sites (see Results), the last measured flow rate was taken as the flow rate over the last interval.

A transportable atomic absorption analytical system specifically set up to measure mercury vapour with high sensitivity and specificity, was used to determine the amount of mercury on the traps. The system consisted of an optical bench, with a direct mains-powered mercury lamp at one end, and a photomultiplier at the other. Pinhole optics were used, with a long shroud on the photomultiplier to minimise the effects of ambient light. An absorption cell, 0.75 m long, was set between the lamp and the photomultiplier.

The mercury traps were analysed in the evening of the day of sampling. Mercury on the traps was released by heating with a wire heating coil slipped over the traps. Air was pumped through the trap at about 100 mL/min by an aquarium pump, with flow rate controlled by a micrometer valve. The air carried the released mercury into the centre of the absorption cell, from where it flowed outwards to both ends. Peaks were displayed on a chart recorder. The height of the absorption peak was used to calculate total mercury released.

Calibration standards were made by taking measured volumes of mercury-saturated air in a syringe, injecting this through a septum into the air line, and absorbing onto a cold mercury trap. This mercury was then released by heating with the coil, and obtaining a calibration peak. The temperature of the mercury-saturated air container was measured and used to determine the mass of the mercury injected.

The analytical calibration curve was prepared using four different aliquots of mercury-saturated air, and was repeated at the end of the analytical run. Two separate containers of mercury-saturated air were used, with identical results.

The system was found to be sensitive to 0.2 ng of mercury. Average mercury concentration in the sampled air was calculated by dividing the total mercury measured by the volume of air that had passed through the sampler,

RESULTS AND DISCUSSION

Sample collection occurred over two consecutive days. Generally, sampling started in the morning, between 9.00 am and noon, and continued for the chosen sampling period, usually four or eight hours. The first samples were collected on 25 March 1996. There was a south-east wind of 5-10 knots and an initial temperature of 10°C rising to 19°C. Pumps and mercury traps were placed at all the sites listed in Table 1. The sites were visited again approximately 4 hours later to collect the traps.

When they were revisited, some of the pumps were found to have stopped functioning. This was probably due to the additional load placed on the pumps by the higher flow resistance of the mercury traps, compared to the usual filters, and by operating the pumps at the highest available flow rate. For pumps that had stopped, the total time of pumping is not known. In calculating ambient air mercury levels a total volume of sampled air equivalent to the full sampling time has been used. This would lead to underestimates of mercury concentrations. However, based on operating experience with these pumps, it is unlikely that the pumps that stopped functioning were running for less than half of the intended period. Therefore, the degree of underestimation is unlikely to exceed a factor of two.

The second set of samples was collected on 26 March 1996. There was a south-east to south-west wind of O-5 knots, with a temperature of 10°C rising to 21°C. The results from the first day indicated that the ambient mercury concentrations were low at the suburban sites. Therefore, the second day's sampling concentrated on sites where concentrations were expected to be higher. Two pumps were used at each of the Kuirau, PAPRO, Whakarewarewa, and NIWA sites. At each site one pump was scheduled to run for 4 hours, and the other for 8 hours. Flow rates were reduced in an effort to ensure that the batteries would last the whole period. Each site was visited approximately every 1-2 hours.

All four pumps designated for 4-hour sampling were still running at the end of the period. Two of the other pumps stopped between the 7 hour and 8 hour visits to their sites. One of these had a minute counter, which recorded its total running time. The other pump had no minute counter, but, because of frequent visits to the site, its total running time was known within reasonable limits.

Table 1. Results of Rotorua ambient air sample measurements for mercury

	Geothermal exposure level	Site name†	Mercury concentration measured (ng/m^3)		
Sampling day			25 March	26 March 1996	
Sampling time			4 hours	4 hours	8 hours
	High	Whakarewarewa	> 0.9 §	3.2	3.5-4.0
		PAPRO	- ‡	1.5	2.3
		Kuirau	> 1.1	17	20
		Geneva	1.1		
	Medium	NIWA	- ‡	2.6	1.4
		Ngapuna	> 0.9		
		Otonga	< 0.6		
	Low	Sunset	< 0.6		
		Porikapa	1.5		
		Iles	0.7		
		Grant	0.9		

† Name of site for ease of reference. Precise details of sites available from authors.
‡ No result due to pump failure.
§ Additional sampling for 1.5 hours produced a result of < 1.2 ng/m^3 of mercury.

Results from the analysis of the mercury traps are given in Table 1. For those instances where the pumps were found to have stopped, the estimated mercury concentrations are preceded by ">". Ambient mercury concentrations less than the limit of detection are preceded by "<".

The absence of any poisoning effect of other components of the Rotorua air was confirmed by demonstrating that, after sampling, the traps still absorbed and released mercury, as expected, from mercury-saturated air.

To the best of our knowledge, the data presented here are the first ambient air measurements of mercury in the Rotorua geothermal region. Although the sites were selected arbitrarily, on the basis of likely exposures to geothermal emissions, and the sampling took place over a narrow period of time, there is no reason to believe that measurements are not indicative of the extent of mercury exposure in Rotorua.

All the samples from the suburban sites, where exposure was expected to be low, produced low concentrations of mercury (<0..6 to 1.5 ng/m^3).

Of the samples from the sites expected to have medium exposure, the Otonga Road site showed no detectable mercury (<0.6 ng/m^3). The Ngapuna site was in the same range

as the suburban sites (although the measurement was an underestimate because of pump failure). The NIWA site had no detectable mercury on the first day (possibly because of pump failure), although it produced detectable, but low, mercury concentrations on the second day (1.4 to 2.6 ng/m^3).

On the first day of sampling the sites expected to have been subject to high geothermal exposures produced concentrations no higher than the suburban sites, but higher concentrations were evident on the second day. On the second day the mercury concentration at the PAPRO site was 1.5 to 2.3 ng/m^3, at the Whakarewarewa site 3.2 to 4.0 ng/m^3, and at the Kuirau Park site 17 to 20 ng/m^3.

The observed differences between the two days may be attributable to differing wind conditions. On the first day the wind was fairly steady, while on the second day it was lighter and sometimes calm.

The Kuirau Park site showed the greatest difference between the two days. At this site the pump was concealed in vegetation close to Lake Kuirau, a large hot pool, and also within 20 metres of a busy road (Lake Road). On the first day of sampling the plume of steam from the hot pool was mostly carried steadily to the Northeast, not directly towards the sampling site. On the second day the sampling site was mostly enveloped in the cloud of geothermal steam.

Mercury concentrations in ambient air have been measured at other New Zealand sites. Bibby & Patterson (1988) measured mercury concentrations over several months at two sites in the Wellington area. At Baring Head, on the south coast, air sampled during southerly winds had mercury concentrations ranging from 0.5 to 1.3 ng/m^3. This is essentially Antarctic air. In a light industrial area, the mercury concentrations ranged from 0.6 to 3.1 ng/m^3, with one outlying value of 6.2 ng/m^3.

The present measurements in Rotorua air are, in general, not substantially higher than these previously measured concentrations in the Wellington area.

The levels of mercury vapour in air found in this investigation are very low compared to levels which have been associated with human health effects or standards to protect against such effects. The current health-based occupational exposure limits recommended by the World Health Organisation for metallic mercury vapour are 25 µg/m^3 (as a time-weighted average for long-term exposure) and 500 µg/m^3 (Peaks, short term exposure) (IPCS, 1991).

Recommended exposure limits for general population exposure to mercury are somewhat lower, but still considerably higher than the levels detected in this investigation. In its Air Quality Guidelines for Europe the World Health Organization (1987) recommends a guideline value for mercury of approximately 1 µg/m^3 as an annual average, irrespective of the form of mercury in the air. The U.S. Environmental

Protection Agency has developed a reference concentration for mercury vapour of 0.3 $\mu g/m^3$, which is considered to be safe over a lifetime of exposure (EPA 1990).

In conclusion, the mercury levels we detected are, without exception, very low, even in those areas where geothermal emission exposure is likely to be high. It is probable that if we had carried out more extensive monitoring in the Rotorua area then we would have found situations where mercury levels were higher than those found in the present study. However, such mercury levels would need to be, say, two or more orders of magnitude greater than the highest levels we detected to even begin to be of concern.

It is possible that much higher concentrations of mercury might occur in confined spaces. However, in such situations, the acute toxicity of hydrogen sulphide would be of much more concern than the possibility of chronic mercury toxicity from prolonged exposures. A number of deaths have occurred in Rotorua because of hydrogen sulphide build-up in confined spaces.

Despite the low mercury levels we measured, it would be desirable if at some future tie, a similar survey was carried out to confirm our results and to ensure that there has been no increase in the levels of geothermal mercury emissions.

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