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MERCURY WET DEPOSITION: AN AUSTRALIAN STUDY TO ASSESS IMPACT OF COAL FIRED POWER STATIONS

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Abstract

Near-power station (coal-fired) sites are believed to be prone to elevated Hg deposition fluxes. Total Hg (THg) in daily rainfall samples at a near-field and a far-field station have been monitored, employing ultra-clean sampling techniques and cold vapour atomic fluorescence spectrometry (CVAFS) analysis. For samples collected between June to December 2006, THg concentrations varied between 0.9 - 12.5 ng/L and 5.8 - 21.3 ng/L with average daily wet deposition fluxes of 4.7 and 24.0 ng THg/m^2-day for the far and near-field sites respectively. While a two-sample t-test reveals the near-field site to have higher rainfall mercury (significant at the 95% level), at this stage because of differences in sampling periods we cannot infer the near-field site to be relatively "impacted".

Strong correlation of THg fluxes with precipitation volume was found which suggests scavenging of reactive gaseous mercury species and particulate mercury by precipitation as a mechanism for mercury deposition. Thus, where wet deposition is concerned, the magnitude of the THg fluxes is likely to be dependent on the rainfall patterns, in addition to emission source strength.

Keywords: Australia, coal-fired power stations, mercury, wet deposition flux

1. Introduction

Atmospheric deposition is a multimedia process and the major delivery mechanism for emitted heavy metals like mercury, cadmium, lead, and others to the environment. It is widely recognized as an important link in the cycling of Hg in the environment and can be a primary source of Hg to remote lakes and soils, especially in the absence of direct discharges.

Mercury accumulated in topsoil, is lost to surface waters and the toxic methyl mercury (the organic form of mercury that accumulates in the food chain) content in large fish often exceeds the recommended limit in many countries. Toxicological studies indicate trace amounts of methyl mercury lead to neurological problems, thereby raising interest in characterizing Hg emission sources in the environment.

The National Pollution Inventory (NPI) reports an annual emission of 28 tonnes of anthropogenic Hg in Australia with coal-fired power stations ranking on the list of major anthropogenic mercury emitters (NPI, 2007). On the NPI environmental hazard spectrum of 0-3, Hg and its compounds register at 2.0 (CSIRO 2007). Looking beyond Australia, the USEPA, in 2005, issued the *Clean Air Mercury Rule* with the intent to cap and reduce mercury emissions from coal-fired power stations.

Mercury mainly exists in coal associated with iron pyrites and is relatively enriched in coal samples with higher density. Although the mercury content of coal is very low, significant release of mercury occurs due to the high volatility of mercury at coal combustion temperatures.

The environmental fate of emitted Hg is closely related to its speciation. Out of the three emitted forms of Hg, the elemental form (Hg^0) is highly volatile and water-insoluble and so does not undergo significant deposition close to source. Divalent Hg (Hg^{II}) is water-soluble and Hg^p is a particulate form. The latter two species comprise oxidized mercury and are more readily deposited to near-source regions.

Where power station emissions are concerned, significant fractions of Hg emissions (~50%) can be of the oxidized forms (Carpi 1997). Regions in the vicinity of coal combustion based facilities (near-field sites) are considered potential hotspots as consequent high deposition fluxes to such regions render them highly vulnerable to mercury related environmental consequences.

In this study we are assessing mercury deposition fluxes in the Hunter Valley region of New South Wales, Australia. The upper region of the Hunter Valley harbours Australia's largest coal-fired power station (Bayswater Power Station). Combined with Liddell Power Station located nearby, Bayswater provides 40% of the State's electricity supply.

Wet deposition monitoring involves capturing rainfall, snow and fog, etc., to quantify deposition of emitted pollutants. In the initial stage of the study, monitoring of *wet* deposition fluxes of mercury via rainfall has been conducted at a near-field site in the upper Hunter Valley. A far-field site has also been monitored on the outskirts of Sydney, the largest city in New South Wales. This paper discusses the mercury *wet* deposition data obtained to date.

2. Methods

2.1. Sampling Periods and Stations

Far-field and near-field sampling sites were selected for sampling. The far-field site was chosen 150km from the power station based region of New South Wales to characterize a "background" site removed from the source.

2.1.1 Far-field Station

This is at the Macquarie University campus in North Ryde, Sydney (33°46'S, 151°07'E, 55m asl).

This site is nearby Sydney's M2 motorway and 150km south-south east of the power stations in the Hunter Valley (see Figure 1). It has an automatic weather station and gives the advantage of online access to real-time and archived data. Sampling was started in June 2006, and is to be continued for a year from then.

2.1.2 Near-field Station

The year-long sampling campaign was commenced in November 2006 at Glennies Creek, (32°27'S, 151°06'E, 78m asl).

The sampling station is 10km located south east of the power stations. The Bayswater and Liddell power stations are located on either side of the road along the Singleton-Muswellbrook stretch of the New England Highway (Figure 1). The sampler was stationed inside a fenced hilltop area on a private property off the New England Highway.

2.2. *Wet-only* Rainwater Sampler

Wet-only rainwater samplers are designed to open only during a precipitation event so as to minimize contamination from dry deposition and blowing dust.

We used the Ecotech Model 200 *wet-only* rainwater sampler which has a tipping bucket rain gauge to activate sampler lid opening during a rainfall event. The rain gauge requires 0.25 mm of rainfall in order to activate the sampler. An inbuilt microprocessor enables programming of the sampler lid to open after two tips within a 1 minute period and close after 1 minute of no tips.

The microprocessor acts as a data logger with a real-time clock and is capable of storing the rainfall start and stop date/time, and totalized rainfall during that period. Data is downloaded onto a laptop.

The internal surfaces of the sampler that come into contact with the rainwater (Figure 2) are composed of inert materials to avoid contamination of rainwater due to chemically labile species. All tubing is lined internally with hytrel® (DUPONT) and the carousel is all-Teflon.
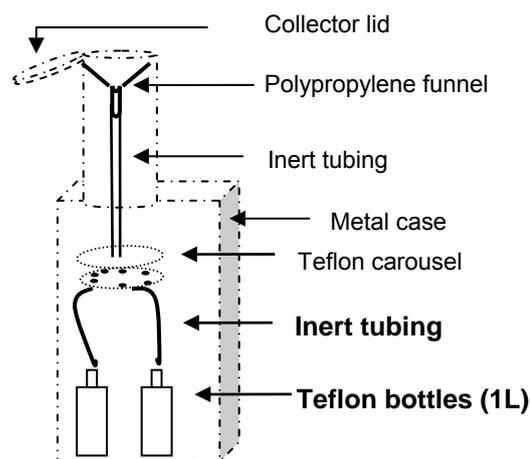

Figure 2. Points of contact of rainwater with the sampler (full lines). The sampling train is labelled in bold fonts.

2.3. Sampling Protocols

2.3.1 Cleaning Procedures

Ultra-clean sampling protocols are used as far as practical. A clean room and reverse osmosis deionized water (Milli-Q) is used for solution preparation and cleaning procedures. The Milli-Q water was analysed for total mercury (THg) as described in Section 2.4. Data is shown in Table 1.

Teflon (FEP, a fluorinated ethene propene copolymer) bottles are highly recommended for storage of low-mercury environmental aqueous

samples (Parker and Bloom 2005, Sekaly et al. 1999), and 1L bottles are used for sampling.
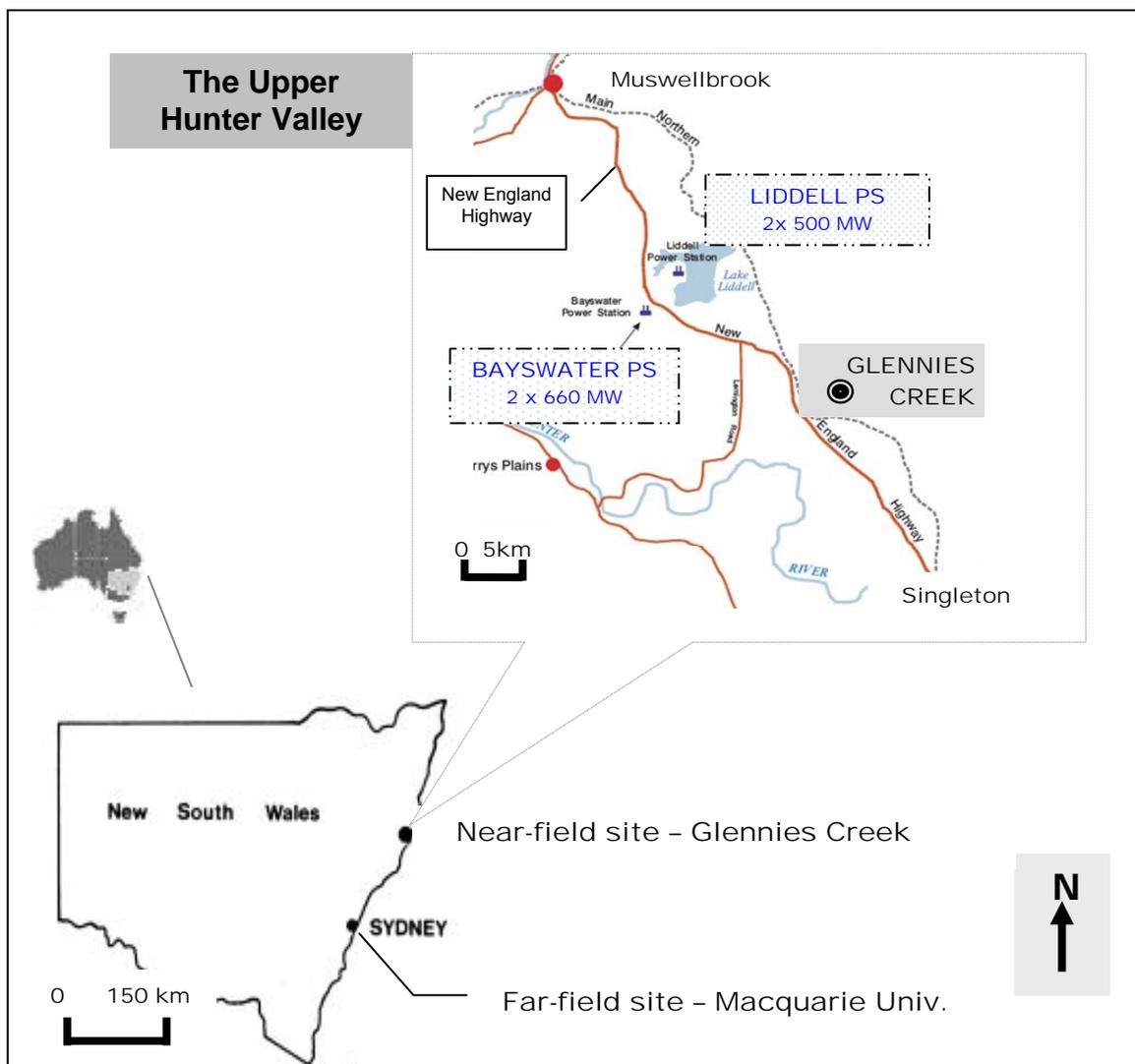
Figure 1. Sampling site locations. The near-field site is at Glennies Creek.

All detachable sampler internals (inert tubing-Teflon bottle, Figure 2) have been subjected to a 13-day cleaning procedure before attaching to the sampler. These were first soaked in extran detergent for a day, rinsed with Milli-Q water and then acid washed by soaking for 3 days each in 10% AR HCl and 50% AR HNO_3. They were then soaked in Milli-Q water for 72 hours, dried and double bagged until use.

2.3.2 Field Procedures

Before starting fieldwork, the non-detachable components of the sampler were washed thoroughly in the field with 2M HCl solution followed by Milli-Q water.

Prior to commencement of sampling, field blanks are generated by pouring Milli-Q water through the funnel, and collected into a clean sampling bottle, analyzed for total mercury (Table 1) and data correction is applied to the samples.

Table 1. Blank and method recovery data.

Sample	THg (ng/L)
Milli-Q	≤ 0.1
Field Blank	0.2 (n = 4)
1% Fluka Ultra Trace HCl	0.5 (n = 2)
BCR 579	Measured: 2.0 (n = 3) *Certified: 1.85 ± 0.2*

Precipitation of dissolved ions present in the sample may alter total Hg data and this is counteracted by sample acidification (Landis & Keeler 1997). The sampling bottles are pre-charged with 10mL of 1% Fluka Ultra Trace HCl. The acid is analyzed for total mercury (Table 1) and data correction applied.

The sampler facilitates multi-bottle collection and daily rotation of the bottles allows collection of daily rainwater samples. Powder-free nitriles gloves are worn while removing, handling, and replacing the sampling train. Once removed from the sampler, samples and field blanks are double bagged and kept refrigerated until analysed.

2.3.3 Sample volumes

The instrument was calibrated against the automatic weather station (AWS) based at the far-field site. A good correlation between the AWS precipitation depths and sampled volumes confirmed representative sampling of rainfall.

Sample volumes are determined using the collected sample mass and the density of water at STP conditions.

Additionally, the sampler microprocessor counts for each bottle, the number of bucket tips during the period when the collector lid was open (ie, when collecting rainfall). One bucket tip collects approximately 1.36mL and this allows calculation of volume of rainwater collected per bottle (Ecotech, 2006). Initial checks were made to assess the validity of this approach and it was found to be accurate within $\pm$ 5% of the measured volumes.

2.4. Chemical Analysis

Total mercury (THg) includes inorganic mercury and minor concentrations of organic methylmercury. THg measurements are reported in nanograms per litre of rainwater.

The analysis was done at the CSIRO Analytical Laboratory as per USEPA Method 1631: *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry* (CVAFS).

The method limit of detection calculated as $3\sigma_{reagent\ blank}$ is 0.1 ng/L. Reproducibility of duplicate sample analyses generally are within $\pm$5%. Method recovery, determined using the certified reference material BCR 579 (Hg(II) in seawater), is 108% (Table 1).

For analysis, the samples are brought to room temperature and 80mL of the sample used for analysis. For low volume samples, the entire sample had to be used.

To assess if loss of mercury from the sample matrix to the bottle walls was occurring, remaining portions of four larger volume samples were acidified to 0.4% v/v with trace pure HCl and allowed to react for 45-90 minutes. Re-analysis revealed no difference in the total mercury content of the samples before and after acidification, indicating that mercury species in the sample are not being retained by the Teflon bottle. This also confirms that the Fluka Ultra Trace HCl preservative effectively retains dissolved mercury in

solution. Namiesnik (2002) has suggested that lowering of storage temperature of samples also tends to counter 'wall memory effect".

3. Results and Discussion

3.1. Total Mercury (THg)

Table 2 summarises the data to date. These are based on daily rainfall samples. It is noted that these levels fall below the WHO recommended value for drinking water quality (1000 ng/L).

Table 2. Summary of rainfall total mercury data.

	Far-field	**Near-field**
Sampling Period	Jun–Dec 06	Nov-Dec 06
THg (ng/L)		
Mean	4.2	11.4
VWM	2.8	9.5
Range	0.9 – 12.5	5.8 – 21.3
Stdev	3.0	8.6
n	21	3

Figure 3 depicts that higher THg levels tend to occur for the low volume samples. This demonstrates the phenomenon known as "first flush effect" whereby all the atmospheric Hg is deposited with the first few milliliters of rainfall. This also means that higher volume samples generally tend to be diluted.
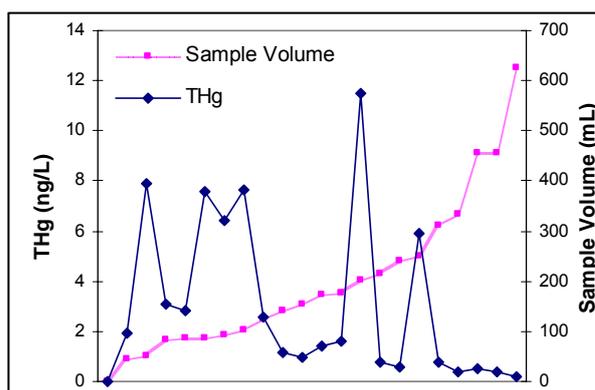

Figure 3. Inverse relation between sample volumes and THg.

Volume-weighted mean (VWM) concentrations were computed for the two sites as per Equation 1. A VWM is not biased by high THg in small volume samples and thus is a better indicator of the average for a group of precipitation samples.

$$\frac{\sum_n \text{concentration} \times \text{sample volume}}{\sum_n \text{sample volume}} \qquad \textit{... Equation 1}$$

Noting the higher THg mean and VWM values at the near-field site, the THg data was subjected to a two-sample t-test to investigate the statistical significance of this relationship. The raw data did not satisfy the assumptions (normality of errors with common standard deviations at the two sites) required for the test to be valid. However, when applied to the log-transformed THg levels to compare the means, we found t = 3.94 with 32 degrees of freedom giving a p-value (0.0004) indicating that the levels were different (significant at the 95% level).

We are of the view that the limited number of samples and the fact that the samples were mainly summer based for the near-field site would have influenced this outcome. Further sampling is being carried out to assess this view.

3.1.1 Comparison with similar studies

Feng et al. (2002) measured THg in precipitation at a Chinese coal mine based site. Higher THg was reported than is the case in this study (Figure 4). While the Hg content in Chinese coals varies a lot, the Hg content reported in the Feng et al. study was higher Hg (0.53 mg/kg) relative to the lower reported average Hg content of Australian coals (0.04 mg/kg) (CSIRO 2007). This may explain the observed difference.
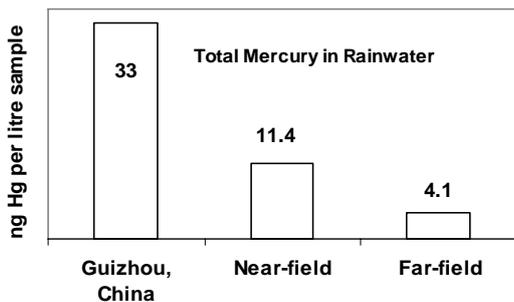

Figure 4. Comparison of THg in rainwater.

Additionally, studies conducted in the United States through the Mercury Deposition Network (MDN) observed THg concentrations in precipitation generally below 100 ng/L in areas not directly influenced by an emissions source (including suburban and urban locations). Levels much higher (exceeding 1000 ng/L) however, were found downwind of anthropogenic mercury sources (USEPA 1997). These sources, however, were not limited to coal-fired power plants only, but included other anthropogenic emitters like municipal waste combustors, chlor-alkali plants and other coal-fired utilities.

3.2 Wet Deposition Fluxes

Wet deposition flux is the product of the precipitation-phase concentration, the rate of precipitation, and the surface area of the body of interest. Fluxes provide a convenient way of comparing deposition at different sites as they account for the individual rainfall rates of different study sites.

3.2.1 Daily fluxes

In a similar approach to that used by Fulkerson et al. (2006), daily THg wet deposition fluxes have been calculated using THg concentrations, cumulative daily precipitation volumes and the surface area of the Ecotech Model 200 wet deposition collector.

The tipping bucket rain gauge linked to the deposition sampler is capable of providing cumulative rainfall data for each day, week or month as desired. In our case the samples were collected on a daily base, and so the data logger recorded values for the total number of bucket tips per day have been used to calculate daily cumulative precipitation volumes (L).

Daily fluxes ($ng/m^2/day$) were then calculated as per Equation 2.

$$\frac{THg_{(ng/L)} \times \text{volume}_{(L/day)}}{0.1075_{(m^2)}} \qquad \textit{... Equation 2}$$

For the far-field site, daily fluxes span the range (0.3 - 22.1) ng/m^2-day with an average of 4.7 ng/m^2-day. Higher fluxes are observed for the near-field site (average of 24.0), plotted here against daily cumulative daily precipitation in Figure 5.
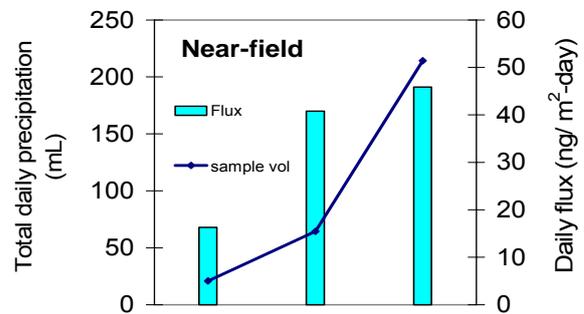

Figure 5. Daily THg fluxes in relation to total daily rainfall.

3.2.2 Variations in wet deposition fluxes

As evident from Figure 5, the near-field site shows a trend of increasing flux with increasing amounts

of precipitation. A good correlation between the two parameters is also apparent for the far-field site (Figure 6) which suggests that about 60% of the variance in mercury wet deposition is explained by the precipitation amount.

Precipitation Volume-Flux Correlation
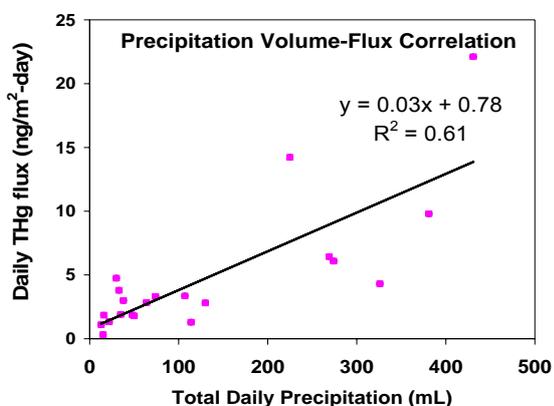
$y = 0.03x + 0.78$
$R^2 = 0.61$

Figure 6. Far-field site daily THg flux with respect to daily cumulative precipitation

These observations agree with studies that have reported a strong positive linear relationship between rainfall depth and mercury deposition (Fulkerson and Nnadi 2006, Sakata and Marumoto 2005). It has been suggested that this is because mercury wet deposition is dominated by mercury bound to airborne particles (Hg_P) and the water-soluble gaseous form (reactive gaseous mercury, RGM) which are readily scavenged by precipitation.

4.   Conclusion

The higher THg volume weighted mean at the near-field (Hunter Valley) site suggests higher atmospheric Hg loading at this site relative to the far-field site. Additionally, the daily THg fluxes at the near-field site are higher. Supported by the test for statistical significance (95% level) it appears that near-field site is relatively "impacted" in comparison with the far-field "background" site.

However, in the "near" site only three measurements were taken which occurred during summer and for the "far" site, 21 samples were spread over 6 months covering summer and winter periods. Hence we conclude that further sampling is essential to successfully assess the impact of coal-fired power stations to the Hunter Valley site.

Acknowledgments

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