Modelling atmospheric mercury from power stations in the Latrobe Valley, Victoria

K.M. Emmerson, M.E. Cope, S. Lee, M.F. Hibberd and P. Torre

ABSTRACT

This paper reports on results from a study of mercury sources and sinks in the Latrobe Valley, Victoria. The objective of the study is to investigate the contribution of the atmospheric mercury emissions from Latrobe Valley power stations compared to the other mercury sources in the region. Anthropogenic mercury is under the spotlight due to the recent (2013) Australian commitment to reduce these emissions under the Minamata Convention. The current work builds on previous CSIRO modelling that treated mercury species as transported inert tracers subject to deposition. Here, a chemistry scheme is implemented to transfer the mercury between its elemental, reactive gas and particulate phases. A demonstration model is set up for March 2005, but it could be used for any period, and also for longer decadal studies. The results show that the power stations contribute less than 1% to the total mercury concentrations modelled in the Latrobe Valley. Mercury concentrations are dominated by the atmospheric background and natural emissions from vegetation, soil and water. The maximum dry and wet deposition fluxes from the power stations emissions are predicted to be 0.24 μg/m^2/month and 0.26 μg/m^2/month respectively, with these maximum depositions occurring very close to the power station stacks. To elicit seasonal and annual changes in atmospheric mercury in the Latrobe Valley, it is recommended that future modelling with representative verification measurements be undertaken over a number of years. This modelling will enable better understanding of the impacts of mercury on the local populations and environment.

Keywords: Mercury, Victoria

INTRODUCTION

Mercury is a naturally occurring metal found in cinnabar deposits throughout the world and also in other valuable deposits such as coal. In most industrial processes mercury is released as a by-product, because it is a component in many fuels and raw materials. Some anthropogenic emission sources are decreasing over time, for example individual power plants now have better technology which reduces mercurial emissions. On the other hand, emissions of mercury from waste light bulbs are increasing as people convert to the energy efficient compact fluorescent globes.

The total global emission of mercury from all sources amounts to approximately 6000-9000 tonnes per year (UNEP, 2013). This large range highlights the uncertainty inherent in global inventories. The total global emission can be roughly broken down into current anthropogenic sources (30%), natural sources (10%) and re-emission of mercury from terrestrial ecosystems (60%).

The portion of mercury that is re-emitted is as a result of many years of mercury deposition since industrial activity began. If anthropogenic sources are curbed now, the concentration of mercury re-emitted to the atmosphere in future will be reduced.

Uptake of mercury in the soil by vegetation allows plants to act as mercury reservoirs. The plant may emit gaseous elemental mercury (Hg(0)) from leaves, along with transpired water, or if the plant is burned. Within the soil, mercury is de-absorbed from soil particles and subsequently diffused as Hg(0) into the atmosphere. This process is temperature dependent (Shetty *et al.* 2008).

Nelson *et al* (2012) constructed the first detailed Australian emissions inventory for mercury, totalling 205.3 tonnes per year. Most sources are natural; 140 tonnes per year from soils, 42 tonnes per year from bushfires, and 8 tonnes per year from vegetation. Anthropogenic mercury emissions are 15.3 tonnes per year. The greatest anthropogenic sources in Australia are from gold smelting 50%, coal fired power stations (15%), production of alumina (12%) and copper, zinc, lead and silver smelting (4%).

Mercury is exchanged between the atmosphere and terrestrial systems. Atmospheric mercury primarily exists as elemental mercury vapour Hg(0). Being relatively insoluble, Hg(0) has a global residence time of about 0.5–2 years in the atmosphere and thus is available to be transported over long distances (Lin *et al.* 2006). Atmospheric mercury also exists in a gaseous divalent form; reactive gaseous mercury (RGM), and in particulate form (Hg(P)). RGM is highly soluble in water and thus is readily deposited close to its source by wet and dry deposition. Hg(P), which exists mainly in the fine particle size fraction (<$PM_{2.5}$), is predominantly lost through cloud water scavenging and wet deposition. RGM and Hg(P) generally have much shorter atmospheric lifetimes than Hg(0).

Atmospheric mercury can be transformed into methyl mercury through bacterial action upon deposition to water surfaces. It is at this point mercury is able to enter the food chain. In this form, it is extremely toxic to animal and aquatic life. The World Health Organisation's guideline for inorganic mercury vapour (Hg(0)) in air is 1 μg/m^3 as an annual average (WHO 2000), whilst Worksafe Australia (1995) has an occupational exposure standard of 50 μg/m^3 as an 8 hour time weighted average. These toxic health effects are the reason that the United Nations Environment Program (UNEP) developed the Minamata Convention (UNEP 2013). The Convention was signed on 10th October 2013 by 94 countries in a bid to reduce anthropogenic emissions of mercury to the environment.

MODELLING STUDY

CSIRO has undertaken a modelling study of the release, transport and dispersion of emissions from mercury (Hg) sources, including coal fired power stations, in the Latrobe Valley in Victoria, Australia. In the United States a cap on mercury emissions has been set for coal burning power stations. It is important to understand the relative importance of mercury emissions in the Australian context.

There are four power stations located close together in the Latrobe Valley; Yallourn, Hazelwood and Loy Yang A and B. Their locations are shown in Figure 1.

The Valley is bounded to the north by the Baw Baw section of the Great Dividing Range, which rises to ~1500m; and to the south by the Strzelecki Ranges, peaking at ~740m. The topography can inhibit dispersion under stable conditions and tends to constrain the stack-height winds to be predominantly westerlies or easterlies, transporting emissions along the valley.

Transport modelling was conducted for Hg(0), RGM and Hg(P). The Nelson *et al.* (2012) atmospheric mercury emission inventory was used, with assumptions being made for the atmospheric background as well as for natural emissions from vegetation, soil and water, as no local measurements have been taken. Account was taken of the different solubility of each mercury species and the subsequent differing rates of deposition. The chemical transport modelling system was used to generate ambient concentrations and deposition patterns of mercury for the whole of Australia, nested down to the Latrobe Valley at a grid spacing of 0.03° (~3 km) in the horizontal for March 2005. This month was set up as a demonstration run which could be taken forwards in future for any run length (e.g. for decadal trend studies).

Prognostic meteorological modelling was used for the prediction of meteorological fields including wind velocity, temperature,

and water vapour mixing ratio (including clouds), radiation and turbulence. The meteorological fields force key components of the emissions and the chemical transport model. The model used there is the Conformal Cubic Atmospheric Model, CCAM, which is a global stretched grid atmospheric simulation model (McGregor and Dix 2008). CCAM has demonstrated capabilities in meteorological predictions in previous studies across Sydney (Cope *et al.* 2013) and performed better than TAPM or WRF in a comparison project across NSW (Emmerson 2014).

The chemical transport and particle dynamics modelling was undertaken using the CSIRO Chemistry Transport Model (CTM; (Cope *et al.* 2004)). This work builds on a previous CSIRO modelling study by Cope *et al* (2009). The CTM is a three-dimensional Eulerian chemical transport model with the capability of modelling the emission, transport, chemical transformation, wet and dry deposition of a coupled gas and aerosol phase atmospheric system. The chemical transformation of gas-phase species was modelled using an extended version of the Carbon Bond 5 mechanism (Sarwar *et al.* 2008) with updated toluene chemistry (Sarwar *et al.* 2011). The mechanism was also extended to include gas and aqueous phase mercury chemistry from Lei *et al.* (2013), excluding the halogen species. That is, the model did not consider methyl mercury, which was mentioned in the introduction. However the deposition flux of atmospheric mercury to water surfaces was calculated. The model uses emission inventories to account for species such as SO_2, NO_X and particulate matter from sources such as motor vehicles and industries.

The aim of this study was to investigate the contribution of the Latrobe Valley power stations to the total mercury concentrations. Because of the use of coupled gas and aqueous phase chemistry in the model, the contribution from the power station emissions was determined by comparing results from an 'all sources' model run (including the emissions of atmospheric mercury from the four power stations situated within the Valley, as detailed in Table 1, together with all other Australian sources) with a 'without mercury from the LV power stations' model run (just all other Australian sources). The difference between the two model runs shows the effects of mercury from the power stations in isolation.

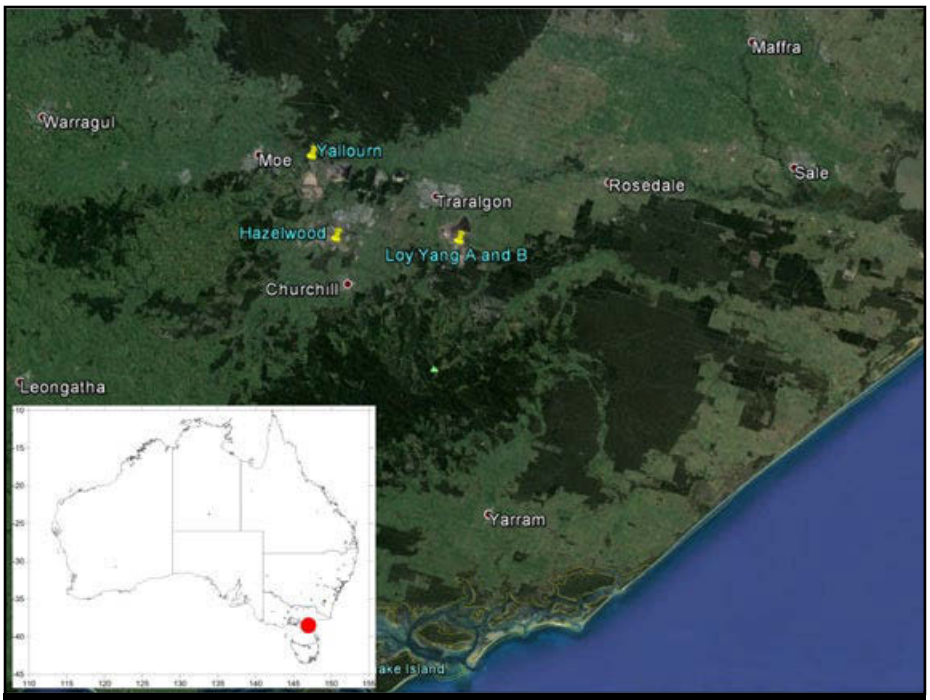

Figure 1. Map of the Latrobe Valley, Victoria showing the position of the power stations in blue text.

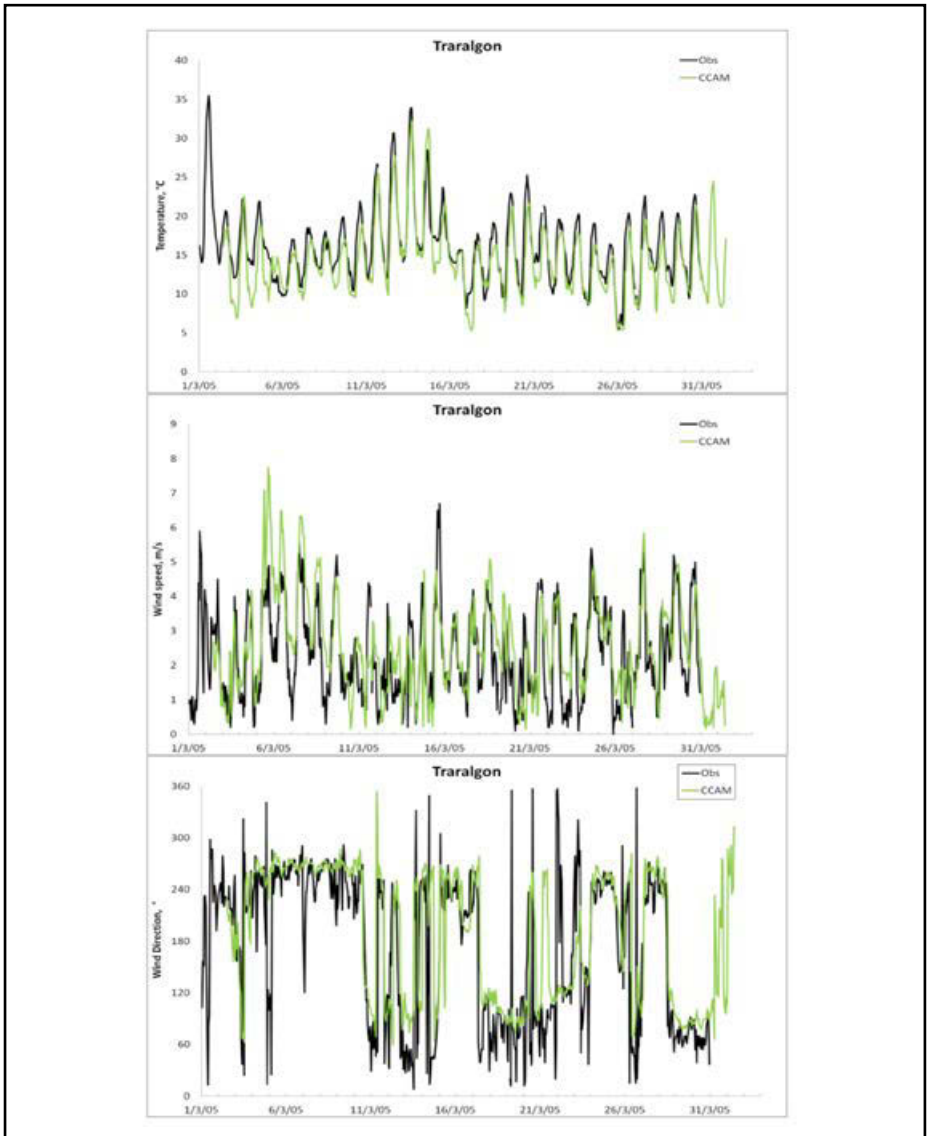

Figure 2. Examples of CCAM meteorological output compared with observations for Traralgon during March 2005. Temperature, wind speed and direction are shown.

RESULTS

Meteorology

To have confidence in the model predictions, there must be confidence in the host meteorological model, CCAM. Figure 2 shows a comparison of temperature, wind speed and wind direction data between the model and Environmental Protection Authority measurements at Traralgon.

CCAM predicts the data very well. For temperature, CCAM describes the diurnal patterns in the observed data (with an R^2 value of 0.77), but does not achieve the peak daily temperature. CCAM also tended to predict a lower minimum temperature than the measurements. The model predicted wind speed and direction very well, with indices of

agreement above 0.8. Capturing wind speed and direction is important in terms of the dilution and transport of emissions away from sources. There is a high level of confidence that CCAM will predict the correct direction and transport times for pollutants in the Latrobe Valley.

Mercury modelling

Modelled concentrations and deposition fluxes from the Latrobe Valley power stations are shown from the surface layer of the model in Figure 3 to Figure 5. The results are not shown for the all sources model run to save space, but their maximum and average concentrations/fluxes were computed. The results are given as follows: the concentration due to the power station emissions is given before brackets containing (the percentage the power station concentrations represent of the total concentration from all sources, followed by the all source mercury concentration). For example, 15 ng/m^3 (10%, 150 ng/m^3). Each plot shows the outline of the Latrobe region with grey contour lines denoting the topography in metres (marked at 150m, 350m, 650m and 950m), black dots show locations of five local towns and the Latrobe Valley power stations (Y= Yallourn, HW = Hazelwood, LY = Loy Yang A and B). The coloured contours show the concentration/flux of interest. Topography plays an important role in the distribution and deposition of each species, and is a helpful indicator for why a species may adopt a particular spatial pattern.

Figure 3 shows the total mercury concentrations from the Latrobe Valley power stations. The majority of effects are seen within the Valley itself, in an east-west direction. The topography acts to 'trap' surface concentrations especially at night when the height of the boundary layer collapses due to colder overnight temperatures. The Hazelwood power station stack is shorter (137m) than the other stacks in the Valley and means that this source is highlighted the most in the concentration plots. The emissions from the taller stacks are more dispersed by the winds, thus concentrations do not build up nearby. The contribution of the four power station stacks is less than 1% of the 'all sources' run, with concentrations predicted to be 0.0012 ng/m^3 (0.09%, 1.37 ng/m^3) on average, with a maximum concentration of 0.015 ng/m^3 (0.95%, 1.58 ng/m^3).

In terms of average monthly concentrations (not shown), the modelled Hg(0) made up around 67% of the 'all source' mercury, with RGM forming 19% and Hg(P) 14%. Nelson *et al* (2009) report measurements at Macquarie University of total gas phase mercury (TGM), which is considered to be Hg(0) + RGM. The current study shows TGM concentrations predicted to be 1.36 ng/m^3 on average, with a maximum concentration of 1.55 ng/m^3, which are within the 1-2 ng/m^3 range reported at Macquarie University in 2007.

Figure 4 shows the total dry deposition flux of mercury species resulting from the Latrobe Valley power station emissions. The calculation of dry deposition uses a

Table 1. The four power station stacks in the Latrobe Valley, shown with their mercury emissions

Power Station	Location °E,°N	Stack height, m	Hg(0) g/s	RGM g/s	Hg(P) g/s
Hazelwood	146.39 -38.27	137	4.23 x 10^{-4}	3.39 x 10^{-4}	8.47 x 10^{-5}
Loy Yang A	146.58 -38.26	260	2.52 x 10^{-4}	2.02 x 10^{-4}	5.04 x 10^{-5}
Loy Yang B	146.59 -38.25	260	4.98 x 10^{-4}	3.98 x 10^{-4}	9.96 x 10^{-5}
Yallourn	146.34 -38.18	168	4.28 x 10^{-4}	3.42 x 10^{-4}	8.56 x 10^{-5}

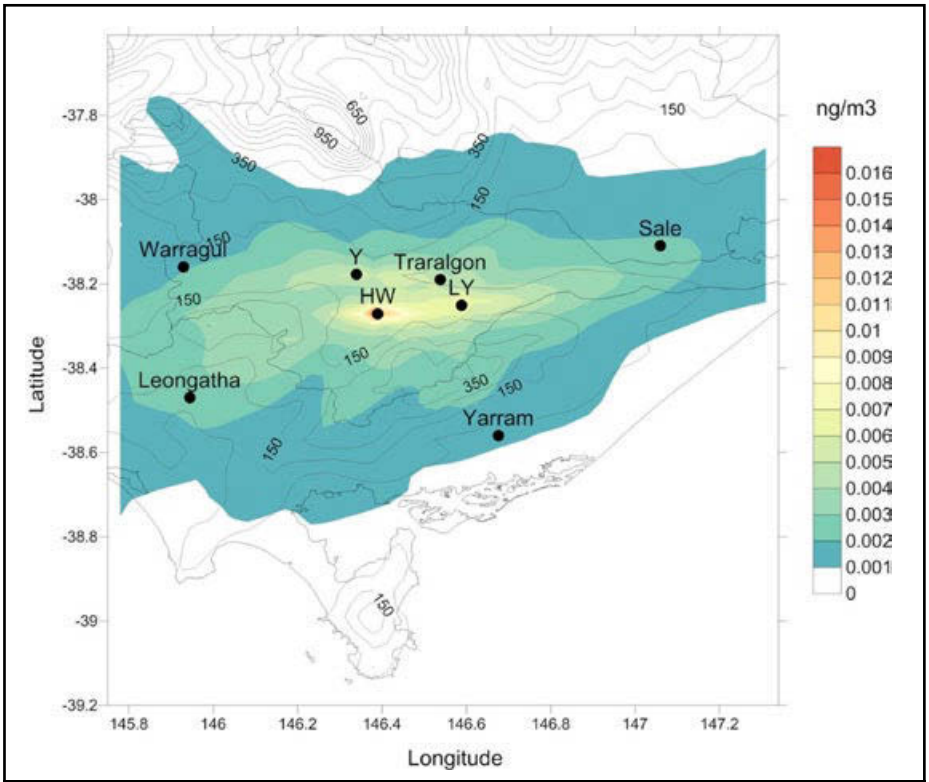

Figure 3. Average monthly concentration of total mercury (ng/m^3) due to the Latrobe Valley power stations Y= Yallourn, HW = Hazelwood, LY = Loy Yang A and B.

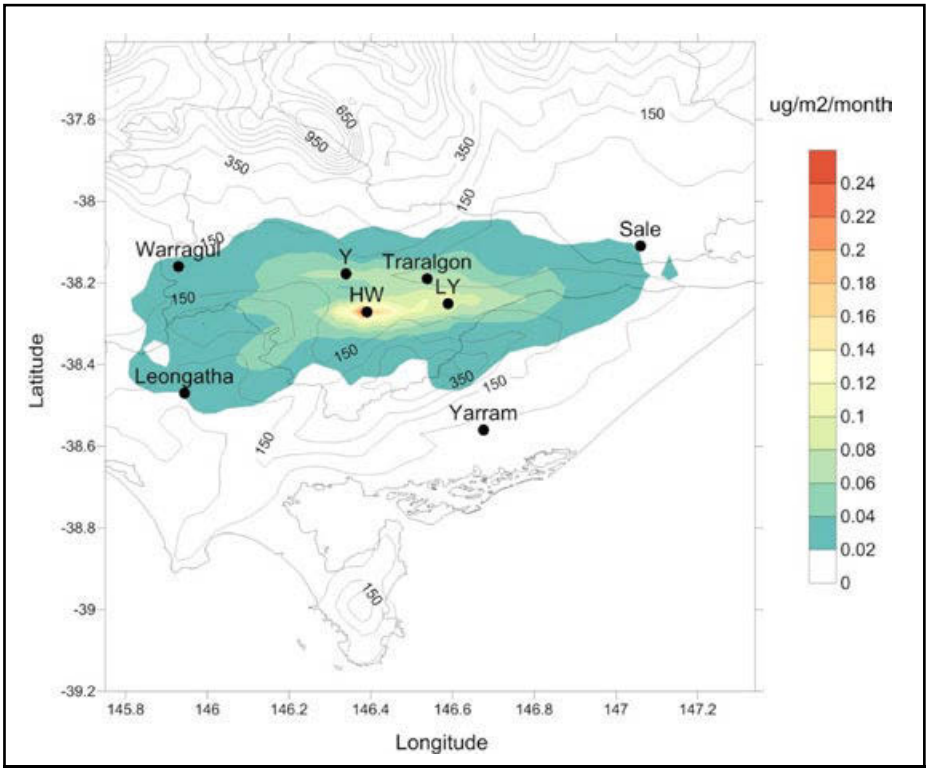

Figure 4. Dry deposition flux of total mercury (µg/m2/month) due to the Latrobe Valley power stations Y= Yallourn, HW = Hazelwood, LY = Loy Yang A and B.

'resistance' analogy whereby each land surface is given a value dependent on whether it attracts or resists mercury. The soil resistance for Hg(0) is six orders of magnitude higher than for RGM (3.6 x 10^7 s m^{-1} compared to 28 s m^{-1}), thus there is no appreciable deposition of Hg(0) over land compared to RGM. The dry deposition of mercury due to the Latrobe Valley power stations is 0.01 μg/m^2/month (2.6%, 0.38 μg/m^2/month) on average, with a peak flux of 0.24 μg/m^2/month (10%, 2.39 μg/m^2/month).

In terms of wet deposition, the peak fluxes are located very close to the point of emission and are mainly composed of RGM. This is due to its high solubility. RGM has a Henry's law coefficient seven orders of magnitude greater (1.4 x 10^6 M atm^{-1}) than Hg(0) (0.11 M atm^{-1}), which is relatively insoluble. The particulate phase Hg(P) species is scavenged into cloud droplets and rained out. Average wet deposition fluxes for the power station in isolation are 0.002 μg/m^2/month (1.1%, 0.21 μg/m^2/month) and the peak fluxes are 0.26 μg/m^2/month (37%, 0.69 μg/m^2/month). Whilst there is a greater percentage contribution to the peak concentrations, they tend to very localised to the power station regions themselves.

In terms of maximum deposition from all sources there is far more dry deposition occurring (78%) than there is wet deposition. In the case of power stations in isolation there is a fairly even split between wet and dry deposition.

Dutt *et al.* (2009) measured wet deposition fluxes in the Sydney and Hunter Valley regions of NSW, finding 3.2 – 3.8 μg/m^2/yr. The current study modelling shows average wet deposition fluxes of 0.21 μg/m^2/month from all sources. Assuming this represents a monthly average, it is equivalent to an annual wet deposition flux of 2.5 μg/m^2/yr. This is within the ballpark of the above measurements, showing that this model produced credible results.

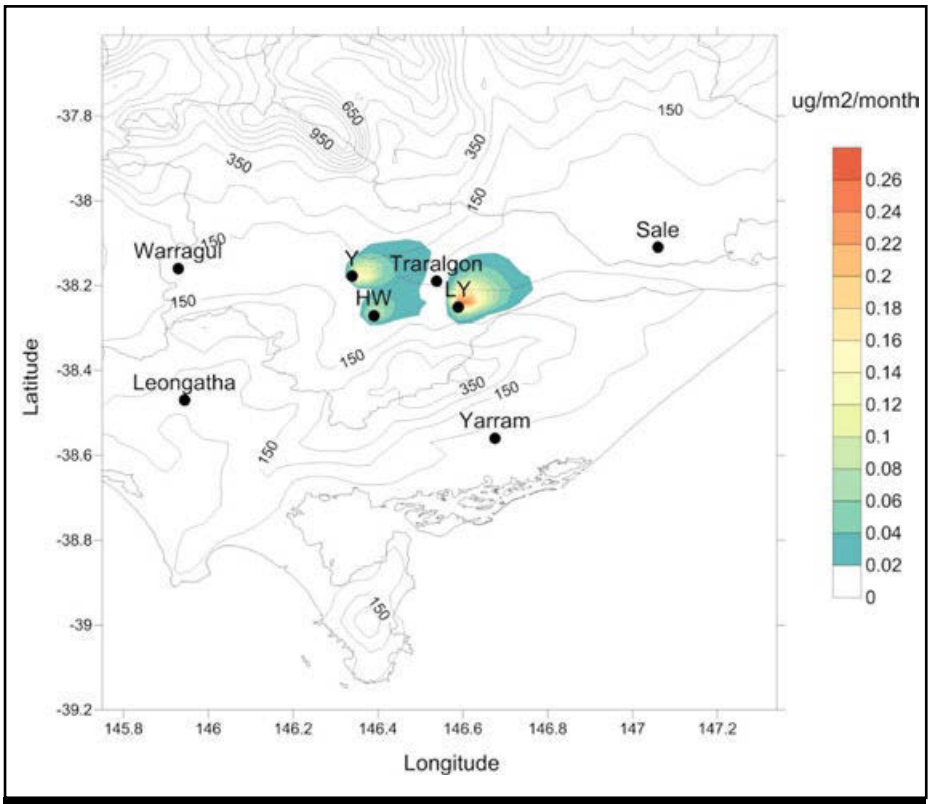

Figure 5. Wet deposition flux of total mercury (μg/m2/month) due to the Latrobe Valley power stations Y= Yallourn, HW = Hazelwood, LY = Loy Yang A and B.

CONCLUSIONS

This work investigated the sources and sinks of mercury in the Latrobe Valley, Victoria, paying particular attention to the four power stations located there. The project used the Australian emission inventory of mercury built by Nelson *et al* (2012), and built on the previous CSIRO modelling study by Cope *et al* (2009). Two major improvements to the original model were made. The first involved use of a different host meteorological model, CCAM, which has shown consistent improvements in meteorological predictions over TAPM in a number of previous modelling studies. The second improvement was to implement a gas and aqueous phase mercury chemistry scheme. This enabled chemical processing of the mercury between the gas, aqueous and particulate phases. The new model was used in a nested grid system down to 3km over the Latrobe Valley for March 2005. The modelling system is suitable for longer term (decadal) trend studies of mercury in Australia.

The power stations contributed less than 1% of the total mercury concentrations modelled in the Latrobe Valley, with their contribution to concentrations predicted to be 0.0012 ng/m^3 on average, with a maximum of 0.015 ng/m^3. Mercury concentrations from all sources were predicted to be 1.37 ng/m^3 on average, with a maximum of 1.58 ng/m^3, which are within the range of measurements reported recently Nelson *et al* (2009). Hg(0) is the biggest reservoir of mercury concentrations in the model (67%) with RGM (13%) and Hg(P) (14%) holding less of the total mercury.

The dry deposition flux from all sources was predicted to be 0.38 μg /m^2/month on average, with a maximum of 2.39 μg/m^2/month. The Latrobe Valley power stations contributed between 2.6% and 10% of this total flux, the higher fluxes occurring very close to the power station stacks. In general the distribution of dry deposition fluxes occurred in an east-west direction along the Valley. For wet deposition the model predicted fluxes of 0.21 μg/m^2/month on average, with a peak of 0.69 μg/m^2/month with the power stations contributing between 1.1% and 37% of this total, again with the highest deposition located very close to the power station stacks. RGM is very soluble and is readily deposited very close to the emission source.

FURTHER WORK

On a research level, it would be worthwhile investigating the inclusion of halogen chemistry in the modelling to determine its impact on mercury concentrations. Halogens are predominantly found in marine environments and whilst important globally, they were not included in this study. However to include them, we would need an emissions inventory of them for the Australian region.

The outcome of this project is a modelling system suitable for longer term (up to decadal) trend studies of mercury in Australia. The current one month study would need to be expanded to model at least a full 12 months in order to understand seasonal effects, and longer term to understand annual trends in mercury concentrations in the Latrobe Valley, and also their impact on the population and environment.

REFERENCES

Cope, M. E., G. D. Hess, S. Lee, K. Tory, M. Azzi, J. Carras, W. Lilley, P. C. Manins, P. Nelson, L. Ng, K. Puri, N. Wong, S. Walsh, and M. Young. 2004. The Australian Air Quality Forecasting System. Part I: Project description and early outcomes. Journal of Applied Meteorology **43**:649-662.

Cope, M.E., M.F. Hibberd, S. Lee, H. Malfroy, J. L. McGregor, C.P. Meyer, A.L. Morrison, and P.F. Nelson. 2009. The transportation and fate of mercury in Australia. Final report. Centre for Australian Weather and Climate Research, Australia.

Cope, M. E., M. D. Keywood, K. M. Emmerson, I. Galbally, S. Crumeyrolle, B. Miljevic, K. Boast, S. Chambers, M. Cheng, E. Dunne, R. Fedele, R. Gillett, A. Griffiths, J. Harnwell, S. Lawson, S. B. Molloy, J. Powell, F. Reisen, Z. Ristovski, P. Selleck, J. Ward, C. Zhang, and J. Zen. 2013. The Sydney Particle Study. CSIRO, Australia.

Dutt, U., P. F. Nelson, A. L. Morrison, and V. Strezov. 2009. Mercury wet deposition and coal-fired power station contributions: An

Australian study. Fuel Processing Technology **90**:1354-1359.

Emmerson, K. M. 2014. The Air Quality Model Ensemble Project, The Centre for Australian Weather and Climate Research, Australia.

Lei, H., X. Z. Liang, D. J. Wuebbles, and Z. Tao. 2013. Model analyses of atmospheric mercury: present air quality and effects of transpacific transport on the United States. Atmospheric Chemistry and Physics **13**:10807-10825.

Lin, C. J., P. Pongprueksa, S. E. Lindberg, S. O. Pehkonen, D. Byun, and C. Jang. 2006. Scientific uncertainties in atmospheric mercury models I: Model science evaluation. Atmospheric Environment **40**:2911-2928.

McGregor, J. L. and M. R. Dix. 2008. An updated description of the Conformal-Cubic atmospheric model. In "High Resolution Numerical Modelling of the Atmosphere and Ocean". Springer New York.

Nelson, P. F., A. L. Morrison, H. J. Malfroy, M. Cope, S. Lee, M. F. Hibberd, C. P. Meyer, and J. McGregor. 2012. Atmospheric mercury emissions in Australia from anthropogenic, natural and recycled sources. Atmospheric Environment **62**:291-302.

Nelson, P. F., H. Nguyen, A. L. Morrison, H. Malfroy, M. Cope, M. F. Hibberd, S. Lee, J. L. McGregor, and C. P. Meyer. 2009. Mercury Sources, Transportation and Fate in Australia. Final Report to the Department of Environment, Water, Heritage & the Arts RFT 100/0607.

Sarwar, G., K. W. Appel, A. G. Carlton, R. Mathur, K. Schere, R. Zhang, and M. A. Majeed. 2011. Impact of a new condensed toluene mechanism on air quality model predictions in the US. Geoscientific Model Development **4**:183-193.

Sarwar, G., D. Luecken, G. Yarwood, G. Z. Whitten, and W. P. L. Carter. 2008. Impact of an updated carbon bond mechanism on predictions from the CMAQ modeling system: Preliminary assessment. Journal of Applied Meteorology and Climatology **47**:3-14.

Shetty, S. K., C. J. Lin, D. G. Streets, and C. Jang. 2008. Model estimate of mercury emission from natural sources in East Asia. Atmospheric Environment **42**:8674-8685.

UNEP. 2013. Global mercury assessment: sources, emissions, releases and environmental transport. United Nations Environment Program, chemicals branch, Geneva, Switzerland.

WHO. 2000. Air quality guidelines for Europe, Copenhagen, World Health Organization Regional Office for Europe.

Worksafe Australia. 1995. Adopted national exposure standards for atmospheric contaminants in the occupational environment [NOHSC:1003(1995)].

AUTHORS

Kathryn Emmerson, Senior Research Scientist[1]

Martin Cope, Principal Research Scientist[1]

Sunhee Lee, Principal Project Scientist[1]

Mark Hibberd, Principal Research Scientist[1]

Paul Torre, Principal Expert in Air Quality[2]

[1]CSIRO Oceans and Atmosphere Flagship, Aspendale, VIC 3195.

[2]EPA Victoria, GPO Box 4395, Melbourne, VIC 3001.

Contact: kathryn.emmerson@csiro.au