

## **Part 3 – Atmospheric**



## Natural emissions of atmospheric mercury from the Norris-Mammoth geothermal area, Yellowstone National Park, USA

MICHAEL ABBOTT, JEFFREY EINERSON, & RANDY LEE

Idaho National Engineering and Environmental Laboratory, PO Box 1625, Idaho Falls, Idaho, USA; E-mail: bot@inel.gov

**Abstract:** In the fall of 2003, we measured mercury surface-to-air flux at eight locations along the Norris-Mammoth corridor in the northwestern part of Yellowstone National Park, USA. Fluxes were scaled-up over time using multiple regression models of meteorological and soil concentration data.

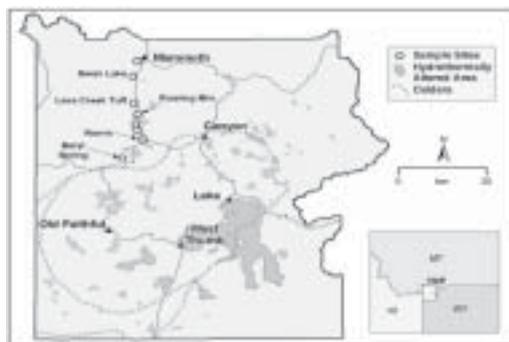
**Key words:** mercury flux, geothermal, natural emissions

### INTRODUCTION

Significant efforts have been made in the last five years to better quantify natural atmospheric sources of mercury (Hg) to better understand its biogeochemical cycling and to help develop emission control strategies. In general, geothermal areas have been found to produce the highest area-averaged fluxes, although point measurement from mine waste sites can be higher ( $> 10,000$  ng/m<sup>2</sup> hr) (GUSTIN ET AL., 2003).

Yellowstone National Park in northwestern Wyoming (Figure 1) is one of the world's largest active geothermal systems, and Hg flux had not been previously measured there. In this study, we measured Hg flux in mid-September and October 2003 at the following eight locations along the Norris-Mammoth corridor (N-M) in northwestern Yellowstone: (1) hot springs travertine at Mammoth, (2) alluvial deposits at Swan Lake Flat, (3) the Lava Creek Tuff welded ash flow (Mt. Holmes

site), (4) the acidic, vapor-dominated system at Roaring Mountain, (5) east of Nymph Lake, (6-7) acidic hydrothermally altered surfaces at Frying Pan Springs and Norris Geyser Basin, and (8) Beryl Spring, a neutral-chloride feature south of the N-M. Continuous (4 to 24-hr) gaseous Hg(0) flux was measured using a dynamic flux chamber (DFC) and Tekran® analyzer, except at the six Norris sites where a smaller DFC and portable gold trap system was used (1-hr samples). Flux was calculated by  $(C_{out} - C_{in})Q/A$ , where  $C =$  DFC



**Figure 1.** Study area in the Norris-Mammoth corridor, Yellowstone National Park.

outlet and inlet concentrations ( $\text{ng}/\text{m}^3$ ),  $Q$  = DFC flushing rate ( $\text{m}^3/\text{hr}$ ), and  $A$  = DFC surface area ( $\text{m}^2$ ).

## RESULTS AND DISCUSSION

The Swan Lake Flat site exhibited a typical background site diel response ( $3.5 \text{ ng}/\text{m}^2\text{-hr}$  max), but the Mt Holmes site (Lava Creek Tuff) was significantly higher, averaging  $10\text{-}15 \text{ ng}/\text{m}^2\text{-hr}$  (Figure 2). The Nymph and Beryl sites had higher fluxes, averaging  $44$  and  $61 \text{ ng}/\text{m}^2\text{-hr}$ . Negligible flux was observed at Mammoth. Very high fluxes were measured at Frying Pan Springs (average of  $460 \text{ ng}/\text{m}^2\text{-hr}$ ) and Roaring Mountain (average of  $1600 \text{ ng}/\text{m}^2\text{-hr}$ ). The Norris gold trap samples showed highly variable fluxes ranging from  $-22$  at Echinus Geyser to  $2900 \text{ ng}/\text{m}^2\text{-hr}$  at Emerald Springs. The remaining Norris sites averaged  $112 \text{ ng}/\text{m}^2\text{-hr}$ . A 24-hour diel measurement was made on the fan at Roaring Mountain in mid-October (24-hour average of  $942 \text{ ng}/\text{m}^2\text{-hr}$ ; max of  $2100 \text{ ng}/\text{m}^2\text{-hr}$ ) which confirmed the high rates

observed there in September and found little difference in flux across 5 sampling sites on the fan.

During the September sampling at Roaring Mountain, the observed flux increased markedly when DFC flushing rate was increased from  $10 \text{ L}/\text{min}$  to  $26 \text{ L}/\text{min}$ . HONG ET AL. (2002) found that flux can be significantly ( $\sim 50\%$ ) underestimated because of suppression of emission potential resulting from internal accumulation of emitted Hg. Observed fluxes were therefore corrected to an optimum flushing rate ( $Q_{\text{opt}}$ ) of  $55 \text{ L}/\text{min}$  using equations (30) and (31) from HONG ET AL. (2002). This increased the observed fluxes by factors of  $\sim 2\text{-}3$ , which is consistent with findings in a Nevada flux comparison study (GUSTIN, 1999), where similar DFCs were found to have fluxes that were  $\sim 3\text{-}5$  times lower than those measured by adjacent micrometeorological methods.

At the Roaring, Swan, and Mt. Holmes sites, fluxes were well predicted by multiple regressions of solar radiation and wind speed

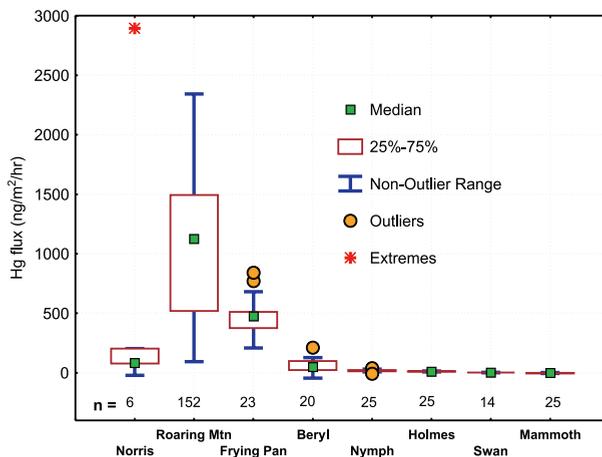


Figure 2. Boxplot of measured fluxes.

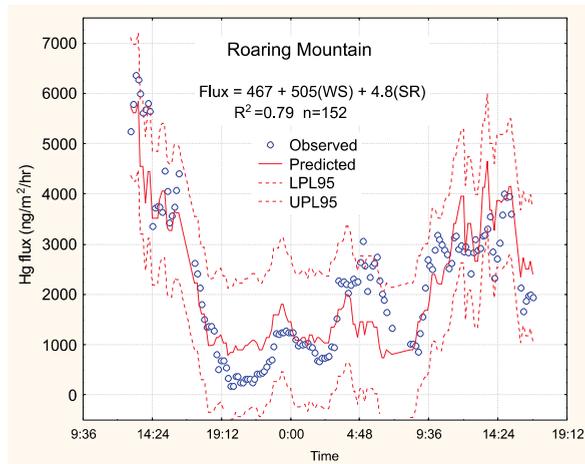


Figure 3. Modeled flux at Roaring Mountain.

(Figure 3). Also, a good correlation ( $R^2 = 0.69$ ) was found between the natural log of the flux calculated at  $Q_{opt}$  ( $F_{opt}$ ) and the natural log of soil concentration at all sites. For Roaring, Swan, and Mt. Holmes, 1-hour fluxes over an entire year were calculated using the regression equations and 1-year (2001) of hourly Yellowstone meteorological data (YEL408 CASTNET at Lake). Annual-average fluxes were then calculated by averaging the 1-hour modeled fluxes over the

time the sites are typically not covered in snow (Figure 4). Annual-average fluxes at the other sites were estimated by multiplying the average daytime flux ( $F_{opt}$ ) at each site by the ratio of the modeled annual-average flux to modeled daytime flux at Roaring Mountain during the other sites' sampling times. The average flux at Norris was calculated from the soil regression equation and the geometric mean of Norris soil concentrations (800 ppb,  $n=400$ ) determined by PHELPS AND BUSECK (1980).

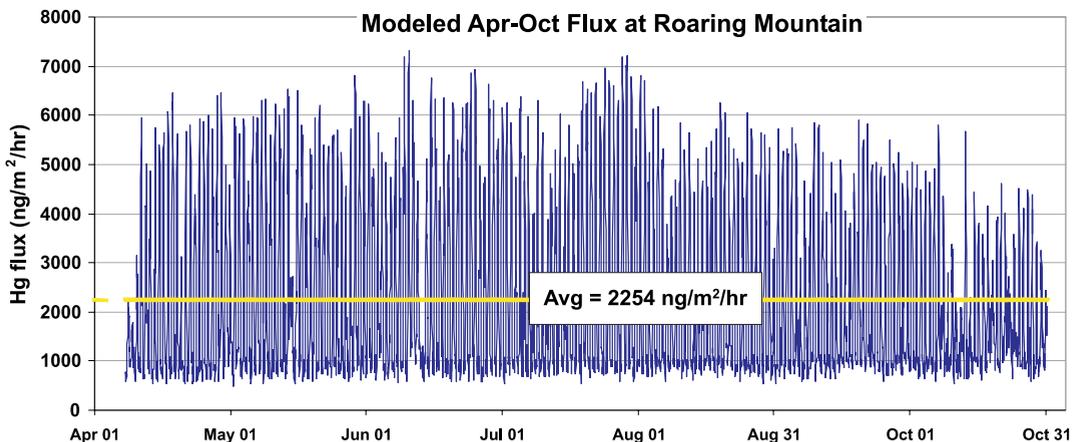


Figure 4. Annual flux modeling at Roaring Mountain.

**Table 1.** Fluxes and predicted emissions from sampled areas in the N-M corridor.

Site	Flux (ng/m <sup>2</sup> -hr)					Area (km <sup>2</sup> )	Emission (kg/y)
	Average Observed (+/-)		Average F <sub>opt</sub>	Model Annual (+/-)			
Roaring Mountain <sup>a</sup>	1036	139	2179	2254	67	2.75	31
Norris Geyser Basin	560	1151	585 <sup>b</sup>	244	115	3.2	4
Frying Pan Springs	463	126	879	583	47	0.007	0.02
Beryl Hot Springs	60	73	114	119	28	0.015	0.01
Nymph Lake	19	7	58	38	3	0.0085	0.002
Lava Creek Tuff	11	2	33	28	2	1220	58 - 171 <sup>c</sup>
Swan Lake Flat	2.5	0.9	6	9	1	24.8	0.4 - 1 <sup>c</sup>
						<b>Total =</b>	<b>93 - 207</b>

a. 27-hour average.

b. From soil regression equation; average, excluding high/low = 468 ng/m<sup>2</sup>-hr.

c. Lower value calculated using observed fluxes; higher value calculated using Qopt (55 L/min).

Annual emissions were estimated by multiplying the annual-average fluxes by the surface area of each feature and by an estimate of the number of snow cover-free days in a year (207) (Table 1).

## CONCLUSIONS

Acidic hydrothermally altered surfaces at Roaring Mountain and Norris Geyser Basin were found to have very high surface flux rates (>2000 ng/m<sup>2</sup> hr) compared to other active geothermal (non Hg mining areas) areas in the U.S. At Roaring Mountain, fluxes correlated well with solar radiation and wind speed, which provided long-term model predictions using hourly meteorological data from the area. The largest contributor to total Hg annual emissions, however, was the Lava Creek Tuff formation due to the higher

than background fluxes observed there and the area's large size. Total annual Hg emissions from the N-M area are estimated to be 93-207 kg/y, which is 11-24 % of the 851 kg/y emitted from all of Wyoming's coal-fired power plant industry. These results suggest that additional measurements are needed to assess large areas in Norris Geyser Basin, tuff formations, and the many other acidic hydrothermally altered surface in the Park (total of 36.4 km<sup>2</sup>) that were not sampled.

## Acknowledgements

This work was funded through the INEEL Laboratory Directed Research and Development program under DOE Idaho Operations Office Contract DE-AC07-99ID13727. Special thanks to Mark Engle at the University of Nevada-Reno for his valuable assistance in both the measurements and the analysis.

## REFERENCES

- GUSTIN, M. S., LINDBERG, S., MARSIK, F., CASIMIR, A., EBINGHAUS, R., EDWARDS, G., FITZGERALD, C., KEMP, R., KOCK, H., LEONARD, T., LONDON, J., MAJEWSKI, M., MONTECINOS, C., OWENS, J., PILOTE, M., POISSANT, L., RASMUSSEN, P., SCHAEDELICH, F., SCHNEEBERGER, D., SCHROEDER, W., SOMMAR, J., TURNER, R., VETTE, A., WALLSCHLAEGER, D., XIAO, Z., & ZHANG, H. (1999): Nevada STORMS project: Measurement of mercury emissions from naturally enriched surfaces; *J. Geophys. Res.*, Vol. 104 (D17), pp. 21,831-21,844.
- GUSTIN, M. S., COOLBAUGH, M., ENGLE, M., FITZGERALD, B., KEISLAR, R., LINDBERG, S., NACHT, D., QUASHNICK, J., RYTUBA, J., SLADEK, C., ZHANG, H., ZEHNER, R. (2003): Atmospheric mercury emissions from mine wastes and surrounding geologically enriched terrains; *Env. Geol.*, Vol. 43, pp. 339-351.
- HONG, Z., LINDBERG, S., BARNETT, M., VETTE, A., & GUSTIN, M. (2002): Dynamic flux chamber measurement of gaseous mercury emission fluxes over soils. Part 1: simulation of gaseous mercury emissions from soils using a two-resistance exchange interface model ; *Atmos. Environ.* 36, pp. 835-846.
- PHELPS, D. & BUSECK, P. (1980): Distribution of soil mercury and the development of soil mercury anomalies in the Yellowstone Geothermal Area, Wyoming ; *Economic Geology* 75, pp. 730-741.

# Investigation of the Henry's Law coefficient for elemental mercury

MARIA ANDERSSON<sup>1</sup>, INGVAR WÄNGBERG<sup>2</sup>, KATARINA GÄRDFELDT<sup>1</sup> AND JOHN MUNTHE<sup>2</sup>

<sup>1</sup>Department of Chemistry, Gothenburg University, SE-412 96 Göteborg, Sweden;  
E-mail: maria80@chem.gu.se

<sup>2</sup>IVL Swedish Environmental Research Institute, SE-402 48 Gothenburg, Sweden

**Abstract:** In this work the Henry's law coefficient for elemental mercury was determined using a novel technique based on direct measurements at temperatures between 5 and 35 °C for MQ- water and for artificial seawater. The results from the MQ-water experiments are in agreement with an earlier study (SANEMASA, 1975). However, in contrast to this study our results indicate no salting out effect at the temperature interval investigated here. According to our study the Henry's law coefficient in both MQ and artificial sea-water is obtained by using the following equation:

$$H = \exp(-2708.4 / T + 15.151)$$

Where H is the Henry's law coefficient and T is the temperature in Kelvin.

**Key words:** Henry's law, partitioning coefficient, artificial seawater, MQ-water

## INTRODUCTION

The biogeochemical cycle of mercury is complex involving transport and transformation of the metal in the atmosphere as well as in terrestrial and aquatic compartments where it also is a subject for bioaccumulation. Unlike other heavy metals oxidised atmospheric mercury species may after deposition undergo reduction forming elemental mercury which may be reemitted to the atmosphere. In order to assess the environmental cycling of mercury the volatilisation of mercury species in aquatic compartments needs to be estimated. Various models have been applied and commonly the Henry's law coefficient (H) describing the distribution of mercury between the aqueous and gaseous phase is used in these models. In literature several studies are presented where H is calculated by determination of the solubility of

mercury in water combined with the vapour pressure of mercury. However, these studies are not in agreement.

In this work the Henry's law coefficient for elemental mercury was determined between 5 and 35 °C in MQ- and in artificial seawater (35 PSU), using a novel technique.

The technique is based on direct measurements of the partitioning of mercury between the aqueous and gaseous phase. The experimental setup, figure 1, consists of an extractor composed by a jacketed glass tube covered by insulation in order to perform experiments under dark conditions at desirable temperatures. Mercury-free nitrogen gas was introduced through a glass frit positioned at the bottom of the extractor. Into the nitrogen gas flow mercury vapour was injected. The amount of mercury extracted from the water

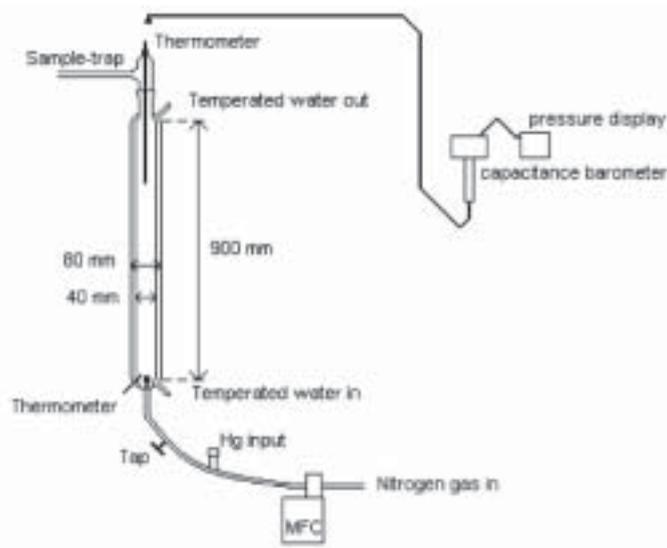


Figure 1. Experimental setup.

column was measured as a function of time by adsorbing mercury onto a series of gold traps situated at the outlet of the extractor. The traps were exchanged every 10 min.

The gold trap was analysed in an analytical line and the mercury were detected with a cold vapour atomic fluorescence spectrophotometer, CVAFS.

In order to prevent possible oxidation of mercury either  $\text{SnCl}_2$  and  $\text{HCl}$  or  $\text{NaBH}_4$  and  $\text{NaOH}$  was added to the experimental solutions.

## RESULT AND DISCUSSION

Assuming mass balance in the system the following equation (1) can be applied, which describes the decrease of  $\text{Hg}^0$  dissolved in the water during the extraction.

$$\frac{dC_{(aq)}}{dt} = \frac{Q * H' * C_{(aq)}}{V_{(aq)}} \quad (1)$$

where  $C_{(aq)}$  is the aqueous mercury concentration in the water during extraction,  $Q$  is the flue rate of purging gas,  $V_{(aq)}$  is the water volume in the extractor and  $H'$  is the dimensionless Henry's law coefficient, described as:

$$H' = \frac{[\text{Hg}_{(g)}]}{[\text{Hg}_{(aq)}]} \quad (2)$$

Where  $[\text{Hg}_{(aq)}^0]$  and  $[\text{Hg}_{(g)}^0]$  are the concentration in gaseous and liquid phase respectively.

Integration between  $C_0$  and  $C_{(aq)}$  corresponding to  $t$  at time 0 and  $t$ , gives

$$\frac{C_{(aq)}}{C_0} = e^{-\frac{Q * t * H'}{V_{(aq)}}} \quad (3)$$

this may also be expressed as:

$$C_{(aq)} = C_0 e^{-\alpha} \quad (4)$$

where  $\alpha$  is corresponds to:

$$\alpha = \frac{Q * t * H'}{V_{(aq)}} = \frac{V_{(g)} * H'}{V_{(aq)}} \quad (5)$$

Repeated extractions from the water column with subsequent gas volumes,  $V_{(g)}$ , are expressed as:

$$C_{(aq)}(n) = C_0 e^{-n\alpha} \quad (n = 1, 2, \dots) \quad (6)$$

The amount of mercury collected on the sample trap during each extraction corresponds to:

$$V_{(aq)} C_{(aq)}(n-1) - V_{(aq)} C_{(aq)}(n) \quad (7)$$

This can also be expressed as:

$$m_{Hg}(n) = V_{(aq)} C_0 (e^\alpha - 1) e^{-n\alpha} \quad (8)$$

The natural logarithm of equation (8) is

$$\ln(m_{Hg(n)}) = -n\alpha + V_{(aq)} C_0 (e^\alpha - 1) \quad (9)$$

If  $\ln(m_{Hg(n)})$  is plotted versus  $n$ , a straight line should be obtained, with a slope equal to  $\alpha$  and an intercept equal to  $V_{(aq)} C_0 (e^\alpha - 1)$ .  $H'$  is calculated from the slope using equation (5), where  $V_{(g)}$  and  $V_{(aq)}$  are known (Figure 2).

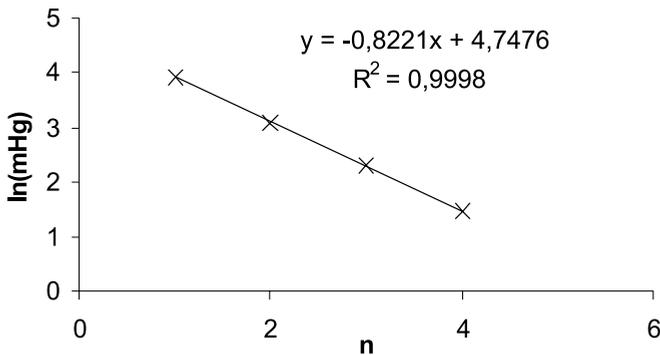


Figure 2. Example of an experimental plot.

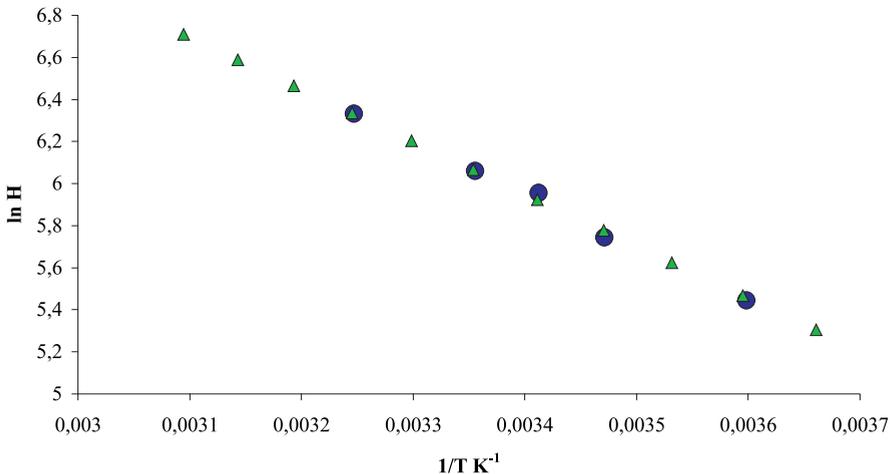


Figure 3. Comparison MQ-water: SANEMASA ( $\blacktriangle$ ) and ANDERSSON ET AL. ( $\bullet$ ).

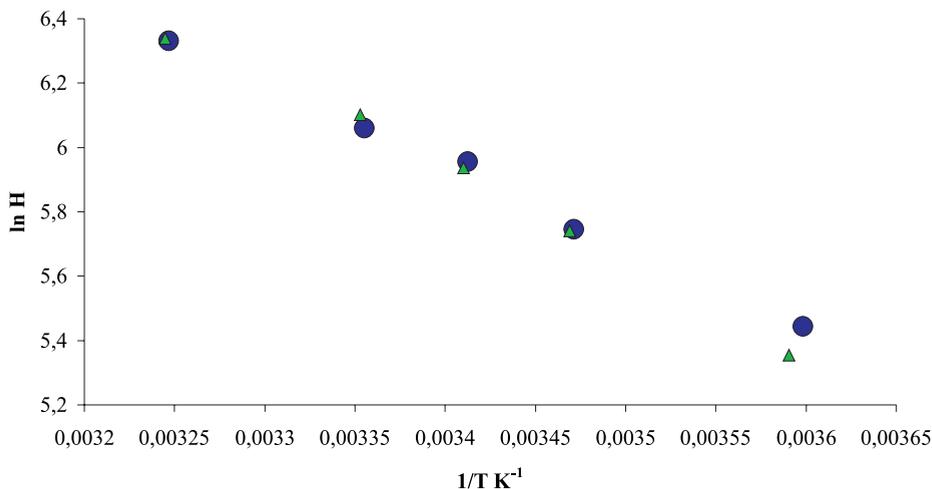


Figure 4. Artificial sea-water (▲) and MQ-water (●).

Our results from the experiments with MQ-water are in agreement with those of SANEMASA (1975), as shown in Figure 3.

However, our data shows that the difference in  $H$  between MQ and sea-water, at corresponding temperatures, is maximally 9 % which is significantly less than previous data presented in literature (23 %) (SANEMASA, 1975).

The equation for the linear regression for the temperature interval 5 to 35 °C obtained in this work is presented as:

$$H = \exp(-2708,4 / T + 15,151) \quad (10)$$

Where  $H$  is the Henry's law coefficient and  $T$  is the temperature in Kelvin.

## CONCLUSIONS

Our investigation of the Henry's law coefficient for elemental mercury in MQ-water at various temperatures between 5 and 35 °C is in agreement with a previous study presented in literature (SANEMASA, 1975). However, our results from the experiments performed in MQ and artificial seawater show no difference of the Henry's law coefficient investigated. This result is in contrast to the result presented by SANEMASA (1975). Hence, according to our results the relevant Henry's law coefficient may be calculated using the same equation (10) for both MQ and artificial sea water at 35 PSU.

## REFERENCES

- SANEMASA, I. (1975): The solubility of elemental mercury vapor in water; *Bulletin of the Chemical Society of Japan*, Vol. 48, pp.1795–1798.

## Daily Trends of Mercury in off Shore Surface Water in the Mediterranean Sea

MARIA ANDERSSON<sup>1</sup>, INGVAR WÄNGBERG<sup>2</sup> AND KATARINA GÄRDFELDT<sup>1</sup>

<sup>1</sup>Department of Chemistry, Gothenburg University, SE-412 96 Göteborg, Sweden,  
e-mail: maria80@chem.gu.se

<sup>2</sup>IVL Swedish Environmental Research Institute, SE-402 48 Gothenburg, Sweden

**Abstract:** Continuously *in situ* measurements as well as manual sampling of dissolved gaseous mercury (DGM) in surface off shore and coastal waters was performed at various locations in the Mediterranean sea during August 4<sup>th</sup> till August 28<sup>th</sup> 2003 and March 17<sup>th</sup> till April 4<sup>th</sup> 2004 on board RV Urania.

The result demonstrates that solar radiation influences the formation of DGM in off shore as well as coastal surface waters showing maximum values of DGM at maximum solar radiation. The influence of solar radiation on DGM formation was also studied by means of surface profile measurements with a spatial resolution of 1, 3, 5, 10, 15 and 20 meters.

**Key words:** Daily variation, off shore sites, surface profile, DGM formation, solar radiation

### INTRODUCTION

Mercury evasion from sea surfaces are important to investigate in order to assess the biogeochemical cycling of mercury. In the Mediterranean area there are several deposits e.g. Almadén (Spain), Idrjia (Slovenia) and Monte Amiata (Italy) from where mercury has been released since ancient time. However, mercury emissions to the environment have increased significantly during the industrial revolution and today mercury is a chronic pollutant problem in lake and sea water in many areas, among them the Mediterranean.

Many scientists has shown the influence of solar radiation on the formation of dissolved gaseous mercury (DGM) and a daily trend in DGM concentration has been recorded at

various coastal sites (AMYOT ET AL, 1994 and 1997; LANZILOTTA AND FERRARA, 2001; GÄRDFELDT ET AL, 2001). On the other hand the occurrence of a daily trend in DGM concentration in off shore waters has been an open question.

Onboard the RV Urania during August 4<sup>th</sup> till August 28<sup>th</sup> 2003 and March 17<sup>th</sup> till April 4<sup>th</sup> 2004, both manual and a continuously *in situ* technique, which was further developed from GÄRDFELDT ET AL, (2002), were used to determine the DGM concentration in off shore surface water and at coastal sites.

The *in situ* equipment consisted of a teflon coated titan funnel or a stainless steel funnel, attached to an adjustable floating ring. Air was introduced through a glass frit under the wider part of the funnel which was

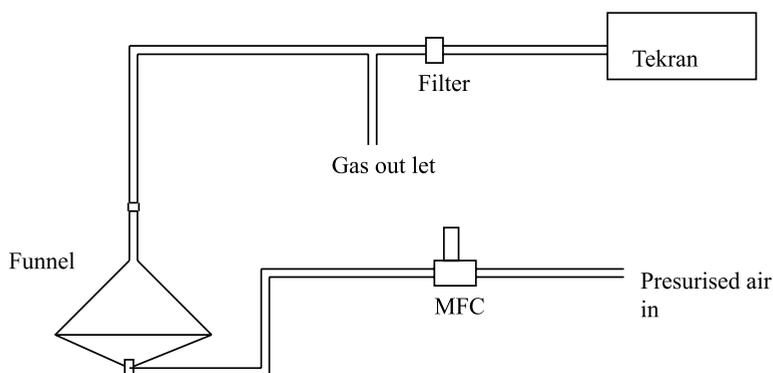


Figure 1. Schematic figure of the *in situ* system.

positioned in the sea water. The air was equilibrated with the water and proceeded through the funnel and lead by Teflon tubings to a Tekran 2357A by which air concentrations of mercury was measured every fifth minute. The actual concentrations in the surface water were determined according to the following equation

$$DGM = \frac{Hg_{air}}{H}$$

where  $Hg_{air}$  was the equilibrated air concentration and  $H$  was the Henry's law coefficient (ANDERSSON ET AL., 2004).

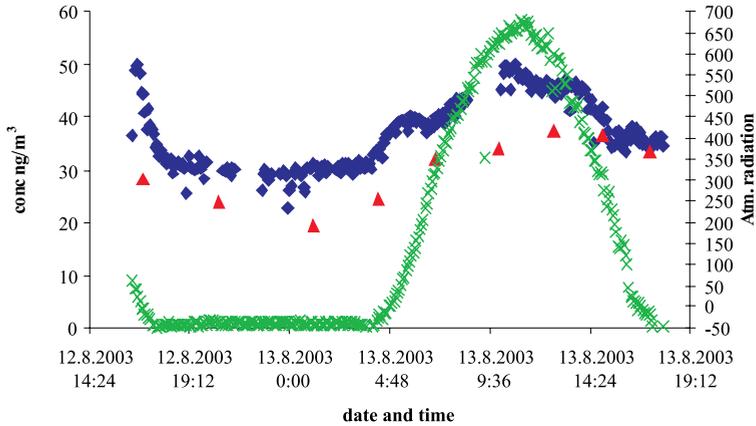
The manual equipment consisted of a Teflon impinger, composed by Saville parts. The impinger could be filled from either Go-Flow bottles or directly, by immersing into the sea. The mercury was extracted from the water by purging with mercury free argon gas and adsorbed on a solid gold sample trap. The mercury was desorbed from the sample trap in an analytical line and detected with a cold vapour atomic fluorescence spectrophotometer (GÄRDFELDT ET AL. 2002).

## RESULT AND DISCUSSION

The measurements performed during summer and early spring season at off shore as well as coastal sites consistently demonstrated that maximum solar radiation at mid-day coincided with maximum DGM concentration. During nights DGM concentrations were generally lower compared to the concentrations measured during daylight. Hence, a diurnal variation has been demonstrated in the off shore waters as well as the coastal sites investigated here.

Comparison between manual and *in situ* technique showed good agreement in DGM data, figure 2

The surface profile measurements showed that DGM, in contrast to some other aqueous parameters e.g. oxygen, temperature and salinity, was not evenly distributed through the surface water column.



**Figure 2.** Daily variation of mercury at lat  $40^{\circ} 00.00\text{N}$  and long  $18^{\circ} 59.96\text{E}$ , August 2003. Comparison between *in situ* and manual sampling.®

◆ *in situ*, ▲ manual, X atm. radiation,

## CONCLUSIONS

A close relation between solar radiation and DGM concentrations in surface water at off shore as well as coastal sites has been demonstrated by using a continuously *in situ* measurements technique.

It was further shown that DGM, in contrast to some other aqueous parameters e.g. oxygen, temperature and salinity, was not evenly distributed through the surface water column.

## Acknowledgement

This work was financed by the European Commission as a part of the MERCYMS project EVK3-2001-00141.

## REFERENCES

- AMYOT, B., GILL, G.A., MOREL, F.M.M. (1997): Production and loss of dissolved gaseous mercury in coastal seawater. *Environmental Science and Technology*; vol. 31, pp.3606-3611
- AMYOT, B., MIELRE, G., LEAN, D.L., MCQUEEN, D.J. (1994): Sunlight-induced formation of dissolved gaseous mercury in lake waters. *Environmental Science and Technology*: vol. 28, pp. 2366-2371
- ANDERSSON, M., WÄNGBERG, I., GÄRDFELDT, K., MUNTHE, J. (2004): Investigation of the Henry's Law coefficient for elemental mercury. *Conference abstract to The 7th International Conference on Mercury as a Global Pollutant, Ljubljana 2004*
- GÄRDFELDT, K., HORVAT, M., SOMMAR, J., KOTNIK, J., FAJON, V., WÄNGBERG, I. AND LINDQVIST, O. (2002): Comparison of procedures for measurements of dissolved gaseous mercury in seawater performed on a Mediterranean cruise. *Analytical and bioanalytical Chemistry*: vol. 374, pp. 1002-1008
- GÄRDFELDT, K., FENG, X., SOMMAR, J., LINDQVIST, O. (2001): Total gaseous exchange between air and water at river and sea surfaces in Swedish coastal regions. *Atmospheric Environment*: vol. 35, pp. 3027-3038
- LANZILLOTTA, E., FERRARA, R. (2001): Daily trend of dissolved gaseous mercury concentration in coastal seawater of the Mediterranean basin. *Chemosphere*: vol. 45, pp. 935-940

## Comparison of Manual and Automated Measurements of Reactive Gaseous Mercury (RGM)

KATRINE ASPMO<sup>1\*</sup>, ENNO BAHLMANN<sup>2</sup>, CATHY BANIC<sup>3</sup>, TORUNN BERG<sup>1</sup>,  
ALEXANDRA STEFFEN<sup>3</sup> & CHRISTIAN TEMME<sup>2</sup>

<sup>1</sup>Norwegian Institute for Air Research, P.O.BOX 100, 2027 Kjeller, NORWAY,  
E-mail: [katrine.aspmo@nilu.no](mailto:katrine.aspmo@nilu.no)

<sup>2</sup>GKSS Research Centre, Geesthacht, GERMANY

<sup>3</sup>Environment Canada (MSC), Toronto, CANADA

**Abstract:** A measurement campaign was undertaken in Ny-Ålesund, Spitsbergen (78°55'N, 11°90'E) during April and May 2003. Four mercury depletion events (MDE) were observed during the study. Three research groups measured reactive gaseous mercury (RGM) at three different measurement spots. All groups observed increased concentrations of RGM as concentrations of GEM decreased. Recorded concentrations of RGM ranged from less than 7 to 450 pg/m<sup>3</sup>. Differences between both measured parallels and the measurements sites were observed, even though no significant differences in the mean GEM concentrations were revealed between the measurement spots.

**Key words:** Mercury depletion events, MDE, Reactive gaseous mercury, RGM, comparison,

### INTRODUCTION

Speciation of atmospheric mercury is important in order to understand the fate of mercury in the environment and mercury's implications on the environment. For the past 5-10 years a lot of work have been undertaken to develop methods to measure inorganic atmospheric forms of mercury, referred to as reactive gaseous mercury (RGM). Different groups has studied RGM at various locations through polar regions, and to ensure comparable data sets an international field campaign was undertaken in Ny-Ålesund, Spitsbergen (78°55'N, 11°90'E), during April and May, 2003.

This work presents measured concentrations of reactive gaseous mercury (RGM) obtained

by three different research groups at three different measurement sites. One group, NILU, measured at the Zeppelin station, which is located at the Zeppelin mountain, 474 m.a.s.l. The station is typically positioned well above frequent ground inversion of the fjord valley. The second group, MSC, measured at the Italian station, which is located in the Ny-Ålesund village, 12 m.a.s.l. The third group, GKSS, measured at "Ny-FID Sund", which is located 500 m east of Ny-Ålesund at about 10 m.a.s.l. The groups used the same principle for collection and quantification of RGM as described by Landis et al, 2002. RGM was collected on KCl coated annular denuder tubes followed by thermal decomposition of RGM quantified as Hg<sup>0</sup>. Further details are shown in table 1.

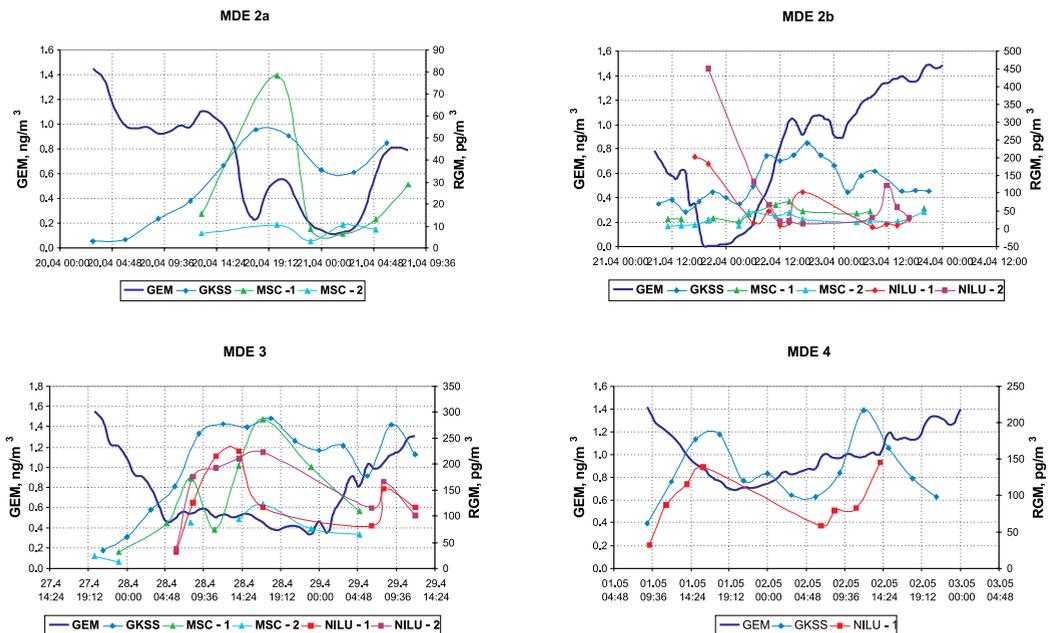
**Table 1.** Summary of methods used by 3 research groups for measurements of RGM.

	NILU	MCS	GKSS
Sampling system	Manuel	Manuel	Tekran 1130
Number of parallels	2	2	1
Sampling site (m.a.s.l.)	474	12	~10
Denuder length : length of active surface (cm)	37,0 : 20,0	50,8 : 25,4	51,4 : 25,4
Sampling flow (lpm)	5	10	8,5
Sampling temperature (°C)	30 – 40	50 - 60	50
Desorbition system	Lindberg furnace	Lindberg furnace	Tekran 1130
Desorbition temperature (°C)	500	500	500
Quantification system	Tekran 2537A	Tekran 2537A	Tekran 2537A

## RESULTS AND DISCUSSION

Four MDE's were detected during the field study, and they are labeled according to Steffen et al, 2004. During non-MDE situations all groups measured RGM-concentrations at the methods detection limit (MDL = 7 pg/m<sup>3</sup>). In general during all events all groups measured increased concentrations of RGM while concentration of GEM decreased, as shown in figure 1 (MDE 1 is not shown in the figure).

During MDE 1 small concentrations of RGM were observed (RGM < 16 pg/m<sup>3</sup>) and the agreement between the sampling sites were good. During MDE 2a higher RGM was observed (max RGM = 80 pg/m<sup>3</sup>). The precision between sets of parallels were in general good (except for one sample), but not the agreement between the sites. Both sites where at sea level, but one site shows 3 times higher values than the other. Concentrations of RGM increased further during MDE 2b. The RGM patterns observed at sea level are

**Figure 1.** Development of RGM-concentrations during 3 MDE's

similar, but off-set by a factor of 3, with the highest RGM-concentration observed when GEM started to increase. RGM observed at Zeppelin were highest earlier in the event when GEM concentrations were the lowest. The precision between the parallels seemed to decrease as the concentration of RGM increased. During MDE 3 all groups measured comparable concentrations of RGM (overall precision within 30 % except for MSC – 2). The precision between parallels measured at Zeppelin was good, except for one sample (overall precision within 15 %). The variability between parallels measured at sea level was high. The RGM-pattern observed during MDE 4 shows two peaks and the measured RGM-concentrations the highest correlation ( $r^2 = 0.93$ ). The agreement between the sites were relatively good, with a discrepancy of 30 %.

Even though the mean GEM concentrations reveals no significant difference between sea level and the Zeppelin station (BERG ET AL, 2003, TEMME ET AL, 2004) we can not, with our current understanding, deduce that RGM measured at the same sites would show similar behavior. The authors concern is the huge differences between parallel samples. Preliminary results from Barrow, Alaska spring 2004 show similar behavior.

Of the two groups measuring manual RGM, MSC followed the guidelines set by LANDIS ET AL, 2002 whereas NILU made a few adjustments, such as reduced sampling flow and shorter denuder length. Both groups used

impactors (cut off  $2.5 \mu\text{m}$ ) as sample inlet. The large differences between the parallel samples might be due to coarse particles entering the system and thus adsorbed to the denuder walls. This is a plausible explanation for the group using reduced sample flow. None of the above mentioned groups were able to attain comparable results. The Arctic is a harsh environment, which might be a possible explanation why comparable parallel samples were not obtained.

## CONCLUSIONS

A comparative study of RGM was conducted in Ny-Åesund, Spitsbergen during spring 2003. All groups observed increased concentrations of RGM as concentration of GEM decreased. The recorded concentrations of RGM differed between the sampling sites and also within sampled parallels. At this point we need more experience to understand whether the differences between the sites are due to real differences or not. The groups' inability to produce comparable parallels reveals the fact that at this point the method is not robust enough to be credible.

## Acknowledgements

This work is funded by the Research Council of Norway. Thanks to the Norwegian Polar Institute for technical, logistical and financial support during the field campaign, and also a special thanks to the Ny-Ålesund community for hospitality, friendliness and warmth.

## REFERENCES

- BERG T., SOMMAR J., WANGBERG I. GÄRDFELDT K., MUNTHE J. AND SCHROEDER W.H. (2003) Arctic mercury depletion events at two elevations as observed at the Zeppelin station and Dirigible Italia, Ny-Ålesund, spring 2002, *J. Physics*
- LANDIS, M., STEVENS, R.K., SCHAEDELICH, F. & PRESTBO, E.M. (2002): Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air. *Environmental Science and Technology*; Vol. 36, pp. 3000-3009.
- STEFFEN, A., ASPMO, K., BANIC, C., BERG, T., EBINGHAUS, R., FERRARI, C., GAUCHARD, P.-A., AND TEMME, C. (2004): Characterizing Mercury Depletion Events in Ny-Ålesund, 2003. *Presented at the ICMGP in Ljubljana, Slovenia, June 27 – July 2, 2004.*
- TEMME, C., ASPMO, K., BAHLMANN, E., BANIC, C., BERG, T., DOMMERGUE, A., EBINGHAUS, R., FERRARI, C., GAUCHARD, P.-A., MAGAND, O., PIRRONE, N., PLANCHON, F., SPROVIERI, F. AND STEFFEN, A., (2004): Repeatability and reproducibility of data from different groups and locations in Ny-Ålesund during the Hg-campaign 2003. *Presented at the ICMGP in Ljubljana, Slovenia, June 27 – July 2, 2004.*

## Systematic studies on the apparent activation energy for mercury emission fluxes (MEFs) from Soils

ENNO BAHLMANN<sup>1\*</sup>, RALF EBINGHAUS<sup>2</sup>, WOLFGANG RUCK<sup>3</sup>

<sup>1</sup>Davidstrasse 3 20359 Hamburg, GERMANY; E-mail: enno.bahlmann@yahoo.de.

<sup>2</sup>GKSS Research Centre Geesthacht, Institute for Coastal Research / Physical and Chemical Analysis, Max-Planck-Str. 1, D-21502 Geesthacht, GERMANY ;

<sup>3</sup>University of Lueneburg, Institute for Ecology and Environmental Chemistry, Scharnhorst-Str. 1, D-21335 Lueneburg, GERMANY

**Abstract:** The apparent activation energy ( $E_a$ ) is an important parameter in improving our understanding of the processes controlling the emission of mercury from soils. We have investigated the effect of major environmental variables on mercury emission fluxes (MEFs) and on the determination of the apparent activation energy for the emission of mercury from soils ( $E_a-F_{Hg}$ ). Our results show that  $E_a-F_{Hg}$  can be expressed as a function of soil texture and total mercury concentration in the soils and will generally increase with increasing clay fraction and decreasing total Hg-concentration in soils. The observed behaviour is in agreement with the Freundlich Adsorption Hypothesis and thus strongly indicate that MEFs over soils are driven by the interfacial equilibrium of  $Hg^o$  between soil matrix and soil air.

**Key words:** air/surface exchange, soil-temperature apparent activation energy

### INTRODUCTION

The correlation between soil temperature and MEF has often been used to calculate  $E_a-F_{Hg}$  (SIEGEL & SIEGEL, 1988; GUSTIN, 1997; CARPI, 1998; POISSANT, 1998). Consequently,  $E_a-F_{Hg}$  has been used to assess the processes controlling the evasion of mercury from soils. For sites with elevated mercury concentrations various groups have reported values between 50 kJ/mol and 60 kJ/mol for  $E_a-F_{Hg}$ , which is quite close to the volatilisation enthalpy of elemental mercury (62 kJ/mol at 25 °C) while for background sites the activation energy seems to be almost twice as high. (SCHLÜTER, 1995) Thus, it has been suggested that the evasion of mercury at sites with elevated mercury concentrations is con-

trolled by direct evasion of elemental mercury from the soil surface, while the emission flux over background soils is effected by further processes such as for example the formation of volatile elemental mercury (SCHLÜTER, 2000) However, the influence of the soil temperature on mercury emission flux may be superimposed by other environmental factors affecting the emission flux and which can bias the determination of  $E_a-F_{Hg}$ .

In order to investigate the effect of soil temperature on mercury emissions fluxes (MEF) and to determine  $E_a-F_{Hg}$  we have carried out flux studies under controlled environmental conditions with a laboratory flux chamber system (BAHLMANN, 2004a) over different soils. The total mercury concentrations in the

soils under investigation ranged from 0.72 to 15.2 mg/Kg. We have determined the fraction of elemental mercury in the investigated soils to 13 + 8 % of total mercury content and found a strong correlation between the total mercury concentration and the Hg<sup>0</sup> fraction.

Over each individual soil we have investigated the effect of soil surface temperature on the mercury emission fluxes under various environmental conditions. For all soils and under all environmental conditions we found a strong exponential correlation between the soil surface temperature (SST) and the mercury emission flux (MEF) with correlation coefficients between 0.81 and 0.999 for MEFs measured under dark conditions and correlation coefficients between 0.718 and 0,981 for MEFs obtained under light conditions. As our experiments have shown that under constant environmental conditions the MEF remains constant for at least 96 h within 7 %, to a first approximation  $Ea \cdot F_{Hg}$  can directly be calculated from the temperature dependency of the MEF.

$$\ln(\text{MEF}) = \ln(k^*) = A + aEa/RT \quad (1)$$

and

$$\text{MEF} = k \times ci = k^* \quad (2)$$

where  $F_{Hg}$  is the mercury flux and  $k$  is the reaction rate constant of the mercury flux,  $Ea$  is the apparent activation energy,  $A$  is the frequency factor,  $T$  is the absolute Temperature and  $R$  is the gas constant.

## RESULTS AND DISCUSSION

Light radiation with a constant intensity (320W7m<sup>2</sup>) leads to a constant offset in the observed flux which is independent of the

soil surface temperature and thus to an under estimation of  $Ea$ . Under the experimental conditions we generally observed a decrease of 50 % to 70 % for the  $Ea$  obtained under light conditions compared to those compared under dark conditions. As the observed offset is supposed to be due to an additional photolytical formation of Hg<sup>0</sup> at the soil surface, the concept of the apparent  $Ea$  may not be applicable for this case as it refers to a thermal controlled reaction. Consequently all experiments carried out under light conditions were excluded from the determination of  $Ea \cdot F_{Hg}$ . However the observed offset is independent of the soil temperature the obtained flux can be corrected for the light induced fraction before calculating the apparent  $Ea$ .

As described in an accompanied contribution to the conference (BAHLMANN, 2004b) the observed flux can vary by about two orders of magnitude with the soil moisture level. Except for dry soils, where we observed an increase of the apparent activation energy up to 200 kJ/mol we did not find any effect on  $Ea \cdot F_{Hg}$ . The observed increase in dry soils is proportional to the increase of the  $Ea$  for the evaporation of water from soils. The increase is supposed to be related to the increasing surface tension and will only have a significant effect, when the soil moisture tension increases above levels of  $3 \cdot 10^5$  hPa.

The operational conditions of the flux chamber e.g. the flushing flow rate and the fan voltage had a strong effect on the overall MEF. An increase of the flushing flow rate from 0.5 L/min to 10 L/min led to an increase of the observed flux of  $950 \pm 90$  % and an increase of the fan voltage from 0 V to 12 V resulted in a mean increase of the flux by a

factor of  $1.75 \pm 0.2$  but variations of this parameters had no significant effect on the determination of the apparent  $E_a$ . Variations of these parameters revealed a relative repeatability standard deviation of  $3.1 \pm 1.8\%$  for the determination of  $E_a$  for each sample compared to a relative repeatability standard deviation of  $3.5\%$  under constant conditions. Thus, if the MEF is given in the Arrhenius form these parameters will only influence the frequency factor.

## CONCLUSIONS

Consistent with previous published results we found that the apparent activation energy for the emission of mercury from soils decreases with increasing total Hg-concentrations in the soils. The obtained  $E_a$ s for soils

with elevated mercury concentrations are 57 kJ/mol and 49 kJ/mol respectively, which is in a good agreement with the values published by SIEGEL & SIEGEL (1988) and GUSTIN (1997), while for background soils our values are somewhat lower. (70-80 kJ/mol compared to about 100 kJ/mol (POISSANT, 1998; CARPI, 1998).

We found that under defined conditions in the absence of light radiation the overall flux, the frequency factor (A) and the apparent activation energy can be expressed as a function of total mercury concentration  $c(\text{Hg})$ , for different soil types (e.g., sandy and clayey soils). At a flushing flow rate of 10.0 L/min, a fan voltage of 6 V and a soil moisture level where the flux became maximal as a function of soil moisture we found the following expression for MEFs over sandy soils.

$$\ln(\text{MEF}) = (-1.508 \cdot \ln(c(\text{Hg})) + 31.984) - (-5.3746 \cdot \ln(c(\text{Hg})) + 63.88) \quad (3)$$

and

$$\ln(\text{MEF}) = (-1.566 \cdot \ln(c(\text{Hg})) + 34.291) - (-5.3558 \cdot \ln(c(\text{Hg})) + 71.791) \quad (4)$$

for MEFs over clayey soils respectively.

The calculated fluxes from equation 3 and 4 respectively are in excellent agreement with the measured fluxes. For the sandy samples we got

$$\text{MEF}_{\text{-calculated}} = 1,0454 \cdot \text{MEF}_{\text{-measured}}, n=4, R^2= 0,9977 \quad (5)$$

And for the clayey samples we got:

$$\text{MEF}_{\text{-calculated}} = 0,9343 \cdot \text{MEF}_{\text{-measured}} \text{ und } R^2 = 0,9990 \quad (6)$$

When comparing the apparent activation energy for Hg-emissions from soils with the vaporization enthalpy of Hg<sup>0</sup> (62 (kJ/mol) the contribution from the temperature dependency of the diffusion which is about 3.5 kJ/mol has to be taken into account, when assuming simple molecular diffusion. Thus an E<sub>a</sub> of 65.5 kJ/mol would correspond to a vaporization enthalpy of 62 kJ/mol.

When assuming, that the mercury emission flux is controlled by the desorption of Hg<sup>0</sup> from the soil surface the E<sub>a</sub> should roughly equal the desorption enthalpy which itself should be in the range of the vaporization enthalpy and further depend on the properties of the surface and the amount of mercury sorbed to the surface. The underlying assumption of the Freundlich adsorption isotherm is, that the adsorption enthalpy decreases logarithmically (becomes less negative) with the coverage rate of the adsorbing surface due to differences of the sorption

side. For the same reason the enthalpy of desorption should also decrease (become less positive) with increasing surface coverage.

The observed relation between the variables describing the flux and c(Hgt) is in agreement with the assumptions of the Freundlich Isotherm and thus reinforce the hypothesis that MEFs over soils are driven by the surface equilibrium of Hg<sup>0</sup>. Therefore we suppose that the observed differences in the E<sub>a</sub>s are related to different energetic properties of the sorption sides in the soils which is at least also the reason for different findings for sandy and clayey soils as the latter have a much higher inner surface.

The possibility to express the MEF in the Arrhenius form as a function of soil texture and soil mercury concentration may provide a cornerstone in up scaling fluxes derived from field measurements and thus in improving estimations of emissions from naturally surfaces.

## REFERENCES

- SIEGEL, S. M., SIEGEL, B. Z. (1988): Temperature Determinants of plant- soil- air mercury relationships; *Water Air Soil Pollution*, Vol. 40, pp. 443 – 448.
- GUSTIN, M., TAYLOR, G. E., MAXEA, R. A. (1997): Effect of temperature and air movement on the flux of elemental mercury from substrate to atmosphere; *Journal of Geophysical Research*, Vol. 102, No. D3, pp. 3891-3898.
- CARPI, A., LINDBERG, S. E. (1998): Application of a Teflon dynamic flux chamber for soil mercury flux: Tests and results over background soils; *Atmospheric Environment*, Vol. 32, pp. 873-882.
- POISSANT, L., CASIMIR, A. (1998): Water-air and soil-air exchange rate of total gaseous mercury at background sites; *Atmospheric Environment*, 32, pp. 883-893.
- SCHLÜTER, K. (2000): Review: evaporation of mercury from soils An integration and synthesis of current knowledge; *Environmental Geology*, Vol. 39, pp. 249-271.
- BAHLMANN, E., EBINGHAUS, R., RUCK, W. (2004a): Development and first tests of a laboratory flux chamber system (LFMS); *Presented at the ICMGP in Ljubljana*, Slovenia, June 27-July 2, 2004.
- BAHLMANN, E., EBINGHAUS, R., RUCK, W. (2004a): Development and first tests of a laboratory flux chamber system (LFMS); *Presented at the ICMGP in Ljubljana*, Slovenia, June 27-July 2, 2004.
- BAHLMANN, E., EBINGHAUS, R., RUCK, W. (2004b): The effect of soil moisture on the emission of mercury from soils; *Presented at the ICMGP in Ljubljana*, Slovenia, June 27-July 2, 2004.

## Development and test of a mercury emission model to describe the air

ENNO BAHLMANN, RALF EBINGHAUS<sup>1</sup> & WOLFGANG RUCK<sup>2</sup>

<sup>1</sup>GKSS Research Centre Institute for Coastal Research /, Max-Planck-Str. 1, 21502, Geesthacht, Germany, e-mail: ralf.ebinghaus@gkss.de

<sup>2</sup>University of Lüneburg, Scharnhorststr. 1, 21335, Lueneburg, Germany, e-mail: ruck@uni-luenebuerg.de

**Abstract:** Based on intensive laboratory studies we have developed a kinetic model which describes the air/surface exchange of mercury over soils. Comparisons of modeled fluxes with measured fluxes under controlled conditions in the lab have shown a fairly good agreement between both and shown the capability of the model to describe the mechanisms controlling the emission of mercury from soils as well as the influence of the most important environmental variables, such as soil temperature, soil moisture, solar radiation and further meteorological parameters such as windspeed.

The model is driven by a temperature controlled flux and by a light controlled flux. The mercury emission potential for the light induced flux is a function of total mercury concentration ( $c(\text{Hg})$ ) in the soil, soil texture and soil moisture. which control the phase equilibrium of  $\text{Hg}^{\circ}$  in the soil. The light induced mercury emission potential is given by  $c(\text{Hg})$ , soil moisture the spectral distribution and the intensity of the solar radiation, which control the photochemical reaction of divalent mercury species at the soil surface. The soil air transfer of  $\text{Hg}^{\circ}$  is modeled by means of a simple two layer resistance model.

**Key words:** modelling, air/surface exchange

## Air surface exchange of atmospheric mercury in Southern Canada during colder seasons

RIPON BANIK<sup>1\*</sup>, XIAOHONG XU<sup>1</sup>, PAUL HENSHAW<sup>1</sup>, ABIR BASU<sup>1</sup>, LAURIER POISSANT<sup>2</sup>

<sup>1</sup>Department of Civil and Environmental Engineering, University of Windsor, 401 Sunset Ave., Windsor, Ontario, Canada N9B 3P4; \*E-mail: banik1@uwindsor.ca.

<sup>2</sup>Meteorological Service of Canada, Environment Canada, 105 McGill (7<sup>th</sup> floor), Montréal, Québec, Canada H2Y 2E7.

**Abstract:** Total gaseous mercury (TGM) concentration and mercury flux measurements are conducted using a Tekran mercury analyzer and a flux chamber in Windsor (42°18'N, 83°01'W, average winter temperature -5 °C), Ontario, Canada from Dec 2003 to March 2004. The measured ambient total gaseous mercury concentration had a mean value of 5.3 ng/m<sup>3</sup>, higher than values observed in rural Canadian sites: this is likely due to the impact of local industries in Windsor area and transboundary pollutants from Detroit, MI, USA. The air-surface exchange flux had an average value of 2.6 ng/m<sup>2</sup>/hr, and solar radiation had more profound effect on the mercury flux than air temperature. Diurnal variation of both TGM concentration and mercury flux were observed.

**Key words:** Atmospheric mercury, Total Gaseous Mercury (TGM), Diurnal variability, Air-surface exchange

### INTRODUCTION

Mercury (Hg) has been known as a neurotoxin for a long time. Its (Hg) capability of being transformed to organic form (e.g., methyl mercury) and ultimate bioaccumulation has led to the severity of its contamination problems. Emission of Hg to the environment, from both anthropogenic and natural sources, has been identified as a frequently observed occurrence during the last couple of decades. Recent findings of high level of ambient mercury despite of a decrease in its anthropogenic emission (SEIGNEUR ET AL., 2002) inspire the scientific community to extend their research to better understand the natural sources of Hg. Although several studies have already been conducted on earth surfaces to quantify air-

surface exchange of Hg, most of them were in warmer seasons (POISSANT AND CASIMIR, 1998) whereas we see fairly low temperature during the colder seasons in countries like Canada. Moreover, estimation of annual mercury (Hg) emissions from surfaces over a large area or region requires the integration of measured local or discrete fluxes over space and time.

This study was conducted in Windsor (42°18'N, 83°01'W), Ontario, Canada from Dec 2003 to March 2004. A Tekran mercury vapor analyzer (2537 A) and a polycarbonate flux chamber were used to measure the TGM concentration and the air-surface exchange flux of mercury. Details about the flux calculation can be found in POISSANT AND CASIMIR (1998). All flux data was corrected

with the field blanks. Air temperature and solar radiation were measured as well.

## RESULTS AND DISCUSSION

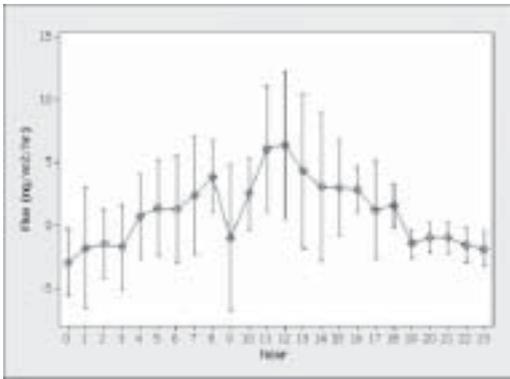
The results from February 10 to 20, 2004 are reported in this paper. The TGM concentration had a mean value of  $5.3 \text{ ng/m}^3$  (Table 1), which is almost two times higher than the mean TGM concentration of  $1.8 \text{ ng/m}^3$  found

in Point Petre and Egbert, Ontario, Canada on February 2003. This was likely due to the impact of local industries and transboundary pollutants from Detroit, MI, USA.

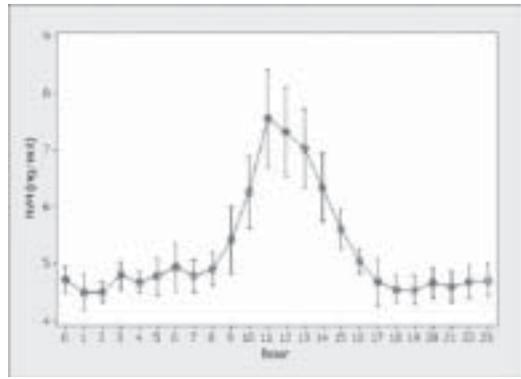
The mercury flux had a mean value of  $2.6 \text{ ng/m}^2/\text{hr}$  during our study period (Table 1). Both evasion ( $\text{flux} > 0$ ) and deposition ( $\text{flux} < 0$ ) of mercury was observed. Hg flux and TGM concentration were following a diurnal variation as shown in Figures 1 and 2.

**Table 1.** Statistical summary of TGM and mercury flux

	Max	Min	Mean	S.d.
TGM ( $\text{ng/m}^3$ )	18.4	3.1	5.3	1.9
Flux ( $\text{ng/m}^2/\text{hr}$ )	75.3	-34.6	2.6	11.4



**Figure 1.** Diurnal variability of Hg flux from February 10 to 20, 2004. The dots and the bars represent the mean and 95 % confidence interval respectively.



**Figure 2.** Diurnal variability of TGM from February 10 to 20, 2004. The dots and the bars represent the mean and 95 % confidence interval respectively.

Figure 1 depicts the variation of mercury flux and shows that the maximum flux was observed at noon followed by a decrease during the late hours. Evasion ( $\text{flux} > 0$ ) was observed mostly during the daytime and depo-

sition ( $\text{flux} < 0$ ) at night. The re-emission of mercury during daytime due to stronger radiation followed by the deposition during nighttime may be responsible for the diurnal variation of TGM, shown in Figure 2.

In Figure 3, the TGM concentration and mercury flux on February 19, 2004 are shown as an example. A diurnal variation is observed with higher TGM concentration and flux during the midday followed by a decrease during the late hours. However, a sudden increase in mercury deposition flux is observed around 5:00 hours. A non-steady state condition caused by local plumes might be responsible for this observation.

Measurements of air temperature and solar radiation along with the mercury flux are shown in Figure 4. The results show that all three followed diurnal cycles. It is observable from Figure 4 that from 9:00 to 14:00

hours air temperature warms up from 2.5 °C to 8.2 °C, solar radiation changes from 87 W/m<sup>2</sup> to 323 W/m<sup>2</sup> and mercury flux increases from 2.2 ng/m<sup>2</sup>/hr to 54.5 ng/m<sup>2</sup>/hr. This indicates to the increase of Hg flux with an increase in solar radiation and air temperature. However, from 14:00 to 19:00 hours, a more than 96 % drop in mercury flux is observed. During the same time period, there is a 97 % decrease in solar radiation, while the air temperature decreases only 45 %. This signifies to the prominent effect of solar radiation on Hg flux over air temperature. This predominant effect of solar radiation on Hg flux is also supported by a stronger correlation (9:00 to 19:00 hours

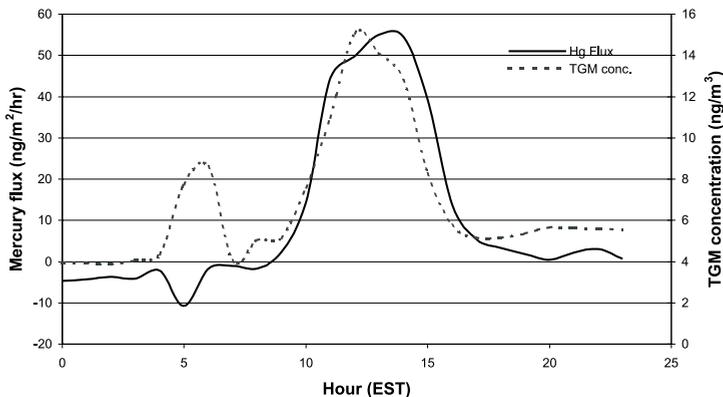


Figure 3. TGM concentration and mercury flux on February 19, 2004.

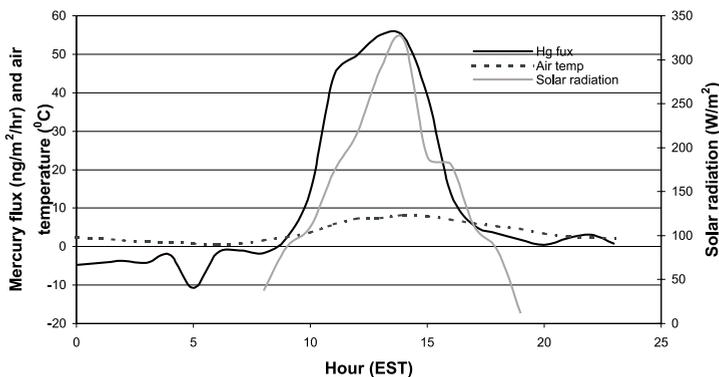


Figure 4. Measured Hg flux, air temperature and solar radiation on February 19, 2004.

data) between Hg flux and solar radiation ( $r = 0.74$ ) than between Hg flux and air temperature ( $r = 0.90$ ).

## CONCLUSIONS

An air-surface mercury flux measurement study was undertaken in Windsor, Ontario, Canada from February 10 to 20, 2004. The measured TGM concentration had an average value of  $5.3 \text{ ng/m}^3$ , which is more than double the average value of  $1.8 \text{ ng/m}^3$  found in Point Petre and Egbert, Ontario, Canada on February 2003. The local or regional an-

thropogenic sources are considered to be responsible for this higher TGM concentration in Windsor. A diurnal variation of TGM concentration and mercury flux was observed during our study period. Re-emission of mercury due to stronger solar radiation during daytime and deposition at night might cause that variation. Solar radiation was found to have more influence on mercury flux than air temperature.

## Acknowledgements

The project is funded by the Natural Sciences and Engineering Research Council of Canada.

## REFERENCES

- POISSANT, L. AND CASIMIR, A. (1998): Water-air and soil-air exchange rate of total gaseous mercury measured at background sites; *Atmospheric Environment* 32, pp. 883-893.
- SEIGNEUR, C., KARAMCHANDANI, P., LOHMAN, K., VIJAYARAGHAVAN, K. AND SHIA, R.-L. (2001): Multiscale modeling of the atmospheric fate and transport of mercury; *Journal of Geophysical Research*. 106, pp. 27795-27809.

## An eddy accumulation system for mercury flux measurements

JESSE O. BASH<sup>1</sup>, DAVID R. MILLER<sup>1</sup>, HUGO THOMAS<sup>1</sup>

<sup>1</sup>Department of Natural Resource Management and Engineering, University of Connecticut, Storrs CT, USA, e-mail: jesse.bash@uconn.edu

**Abstract:** An eddy accumulation system was designed, constructed, and tested to measure the mercury flux from natural surfaces. Fluxes of mercury and water vapor are measured by accumulating air from the updrafts and downdrafts of vertical wind. Simultaneous eddy covariance measurements of water vapor fluxes are used as a continuous *in situ* calibration of the system. Measured mercury fluxes over a winter leafless hardwood forest canopy do not exhibit the expected diurnal pattern. The preliminary results of this study suggest that the mercury exchange process with a leafless hardwood forest is wind driven.

**Key words:** Relaxed eddy accumulation, Conditional sampling, Foliar emissions, Surface flux

### INTRODUCTION

The contribution of biogenic and physiochemical mercury emissions from land and water surfaces have recently been estimated to be roughly equivalent to anthropogenic emissions (PIRRONE ET AL., 2001; LINDBERG ET AL., 1998). However, little is known about the magnitude on the dynamic of these natural mercury emissions from forests, which is the primary land cover in the Northeast (NE) United States.

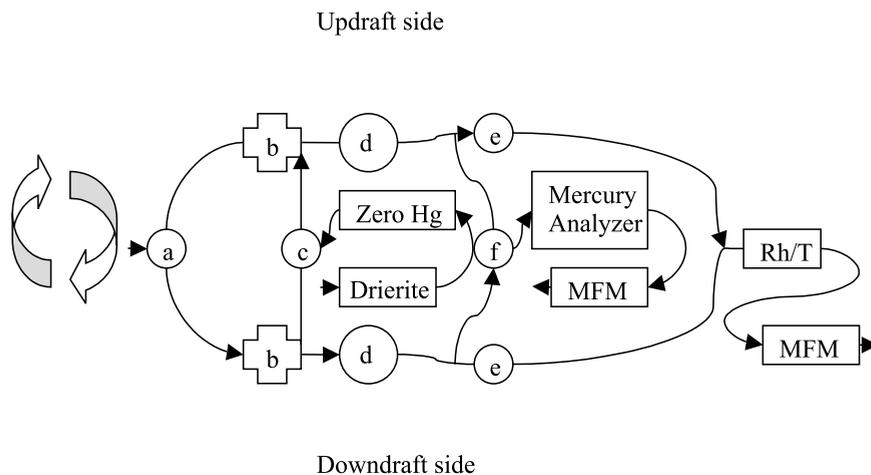
The eddy covariance (EC) technique is the method of choice for measuring the turbulent flux of gaseous scalars above forest canopies. However the EC technique requires fast response measurements, at least 10 Hz, of gas concentration and vertical wind speed perturbations and currently no instrument has been devised that can measure

ambient mercury concentrations at this frequency. Dynamic flux chambers (DFC) and modified Bowen ratio (MBR) techniques have been used to measure natural mercury fluxes but both have theoretical and logistic drawbacks for use above forest canopies (COBOS ET AL., 2002; GILLIS AND MILLER, 2000).

The relaxed eddy accumulation technique is another option, which eliminates many of the problems listed above. The REA technique separates the air at a point above the forest into the updrafts and downdrafts, which entrain air across a vertical concentration gradient. Fluxes can then be calculated by measuring the average concentration of mercury in the air in the updrafts, the average concentration of mercury in the air in the downdrafts and the turbulent statistics from a fast response anemometer.

REA combines fast response vertical anemometry to measure upward and downward air motions, with fast switching of intake air to isolate the air from the upward and downward motions. The scalar material carried in the isolated upward and downward moving air is then accumulated in separate reservoirs. And the scalar concentrations in the reservoirs are measured with the available slow response instrumentation. The REA technique uses a mathematical approach similar to eddy covariance (BOWLING ET AL., 1998) and allows the sampling of air at only one height making it simpler to operate and maintain than the MBR flux techniques (COBOS ET AL., 2002).

The University of Connecticut relaxed eddy accumulation system was deployed to quantify the mercury flux over a mixed hardwood forest in rural Northeast Connecticut. This system included REA measurements of Hg and latent heat fluxes, Figure 1. Co-located EC instrumentation provided independent latent and sensible heat measurements. REA flux calculations are made following BUSINGER AND ONCLEY (1990). Measurements were made over the winter of 2003-2004 when the forest was leafless.



**Figure 1.** Air flow path diagram of the University of Connecticut's REA system; a – high speed sampling valve, b – particle filters, c – high speed zero air valve, d – 2l pressure perturbation tanks, e – two way valves, f – three way valve, MFM – mass flow meter, Rh/T – relative humidity temperature enclosure.

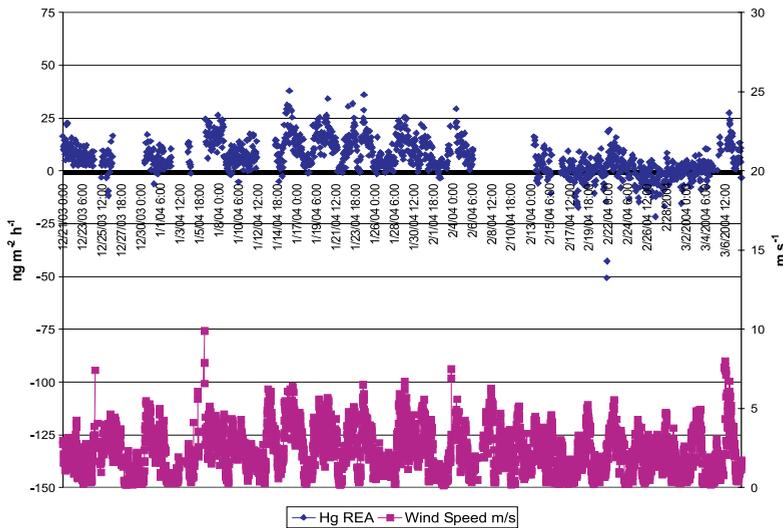
## RESULTS AND DISCUSSION

REA latent heat and Hg flux measurements were taken simultaneously throughout the measurement period. A running calibration was then performed by correlating the REA latent heat flux to the EC latent heat flux.

Net Hg fluxes for the winter of 2003-2004 ranged from a maximum rate of  $37.97 \text{ ng m}^{-2} \text{ h}^{-1}$  (evasion) to a minimum rate of  $-50.56 \text{ ng m}^{-2} \text{ h}^{-1}$  (gaseous deposition) with a small net positive flux over the entire measurements period. Hg evasion from the forest was at its highest preceding and follow-

ing most precipitation events **during times of high wind speed** (Figure 2). Net Hg deposition events occurred primarily when a fresh snow covered the ground.

Wintertime net emissions peaked during the month of January. January 2004 was cold with temperature rarely reaching above 0 °C with frequent snow events. However, January also had periodic high-sustained winds lasting several days (Figure 2).



**Figure 2.** Hg flux (blue diamonds) and the wind speed (purple squares) at the height of the measurement from 21 December 2003 to 8 March 2004

## CONCLUSIONS

Our measurements show that magnitude and direction of the wintertime mercury flux over a mixed hardwood forest can be accurately measured with the REA system. Wintertime measurements show fluxes from the forest increase with increased wind intensity, typically observed with the passing of storms. Deposition events were measured almost exclusively during snow events when the

open path sonic anemometer and krypton hygrometer were not compromised by accumulation of water on the sensor heads. The single remaining problem with the system is that the 3D sonic anemometer does not function properly during most precipitation events due to water or ice accumulating on the sensor heads. Thus our net flux accumulated over the season is likely overestimated due to poor sampling during times of the largest deposition events.

**REFERENCES**

- BUSINGER, J. A. AND ONCLEY (1990): Flux measurements by conditional sampling; *J. Atmos. Oceanic Technol.* 7, pp. 349-35.
- PIRRONE, N., COSTA, P., PACYNA, J. M., AND FERRA, R. (2001): Mercury emissions to the atmosphere from natural and anthropogenic sources in the Mediterranean region; *Atmospheric Environment* 35, pp. 2997-3006.
- LINDBERG, S. E., HANSON, P. J., MEYERS, T. P., AND KIM, K.-H. (1998): Air/surface exchange of mercury vapor over forests-the need for a reassessment of continental biogenic emissions; *Atmospheric Environment* 32, pp. 895-908.
- COBOS, D. R., BAKER, J. M. AND NATER, E. A. (2002): Conditional sampling for measuring mercury vapor fluxes; *Atmospheric Environment*, Vol. 36, pp. 4309-4321.
- GILLIS, A. AND MILLER, D. R. (2000): Some potential errors in the measurement of mercury gas exchange at the soil surface using a dynamic flux chamber; *The Science of the Total Environment*, Vol. 260, pp. 181-189.
- BOWLING, D. R., TURNIPSEED, A. A., DELANY, A. C., BALDOCCHI, D. D., GREENBERG, J. P. AND MONSON, R. K. (1998): The use of relaxed eddy accumulation to measure biosphere-atmosphere exchange of isoprene and other biological trace gases; *Oecologia* 116, pp. 306-315.

# A model for natural emissions of Mercury in the Northeast, United States

JESSE O. BASH, DAVID R. MILLER, PATRICIA BRESNAHAN, HUGO THOMAS

Department of Natural Resource Management and Engineering, University of Connecticut, Storrs CT, USA, E-mail: jesse.bash@uconn.edu

**Abstract:** Current mercury emission inventories typically include anthropogenic emissions only and neglect the contribution of natural emissions and re-emissions. Estimates of this component of the mercury cycle are on the order of 25 to 50 percent of the total mercury emissions. A model to estimate the natural emissions of mercury has been developed, the Mercury (Hg) Surface Interface Model (HgSIM). HgSIM is based on recent publications on mercury emissions and models and is driven using modeled meteorological data using one-hour time steps. The emissions over land are modeled as a function of the land cover, evapotranspiration, and temperature. The emissions over water are modeled as a function of the concentration gradient in air, the mixing of the air and water, and the temperature.

**Key words:** Surface Flux, Emissions Model, Transpiration, Natural mercury emissions, Air quality model

## INTRODUCTION

The processes leading to atmospheric mercury dispersion are governed by the industrial use of elemental mercury ( $\text{Hg}^0$ ) and combustion in the form of anthropogenic emissions and the emissions from natural surfaces. The emissions of  $\text{Hg}^0$  from contaminated surfaces have long been known. However, elemental mercury is readily re-emitted from natural surfaces due to its high vapor pressure (LINDBERG ET AL., 1998). Recent estimates have indicated that the contribution of natural Hg emissions to the global Hg pool is roughly equal to the anthropogenic emissions (PIRRONE ET AL., 2001). This paper describes a model of these natural mercury emissions.

## METHODS

Natural  $\text{Hg}^0$  emissions were modeled using a numerical model parameterized using fifth-generation NCAR/Penn State Mesoscale Model (MM5) meteorological data and the EPA's Biogenic Emissions Inventory Version 2 (BEIS2) land cover data. Natural mercury emissions were categorized into three sources based on the mechanism of the emissions for the given land cover types. The modeled domain covered the northeast United States and southeast Canada using 2500, 36 km on a side square grids.

## Air-Water Flux

The air water flux of mercury is driven by the equilibrium between the vapor and aqueous phases of  $\text{Hg}^0$ , which is governed by the concentration gradient and the turbulent diffusion coefficient modeled after WANNINKHOF (1992).

## Canopy Emissions

Recent studies have indicated that  $\text{Hg}^0$  in soil water is taken up by vegetation during the transpiration processes, transported through the xylem stream and emitted into the atmosphere along with the water vapor (LINDBERG ET AL., 1998). Thus, emissions from vegetation are modeled as a linear function of evapotranspiration. Evapotranspiration was modeled using the Penmann-Monteith model as described in CAMPBELL AND NORMAN (1998). Canopy conductance was modeled according to STEWART (1988).

## Soil Emissions

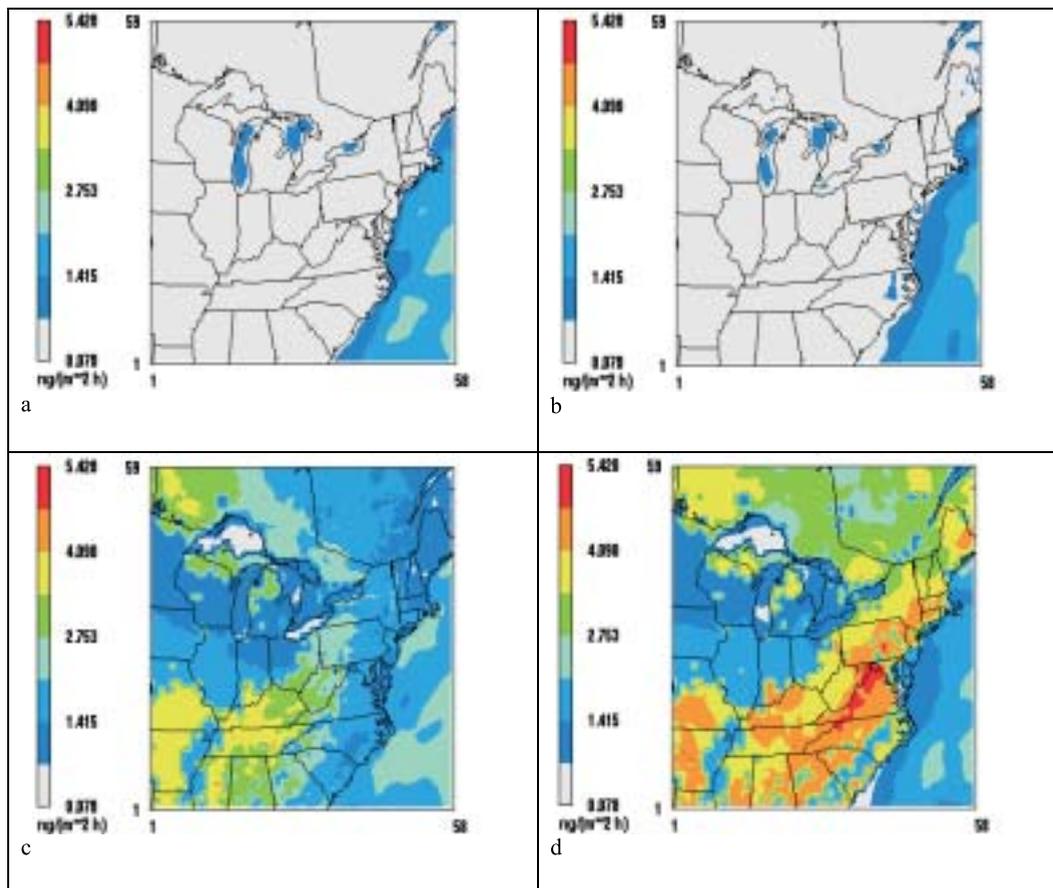
Emissions of  $\text{Hg}^0$  from soil surfaces are believed to be dependent on the soil water content, surface temperature, and solar radiation (CAPRI AND LINDBERG, 1998). However, insufficient measurements have been made to determine an analytical relationship for  $\text{Hg}^0$  emissions from soils, but empirical relationships between temperature and emissions have been described (XU ET AL., 1999).

Therefore the net soil flux was modeled as a function of soil temperature by a linear relationship between the log of the net emission rate and the soil surface temperature, as described in CAPRI AND LINDBERG (1998).

## RESULTS

HgSIM was run for a two-week simulation period from July 6<sup>th</sup> 1997 to July 19<sup>th</sup> 1997. The total emission calculated for the two-week period for the entire domain was 2101.5 kg. The HgSIM model predicted a spatially averaged daily maximum emission rate of mercury from vegetation of  $4.4 \text{ ng m}^{-2} \text{ h}^{-1}$ , a daily maximum average emission rate from soil of  $2.3 \text{ ng m}^{-2} \text{ h}^{-1}$  and a daily maximum average positive flux of mercury from surface waters of  $2.7 \text{ ng m}^{-2} \text{ h}^{-1}$ . The maximum fluxes for all three pathways occurred in the early to late afternoon and the minimum values,  $\sim 0 \text{ ng m}^{-2} \text{ h}^{-1}$  for all three modeled pathways, occurred in the early to mid-morning.

Figure 1 maps the mercury flux spatial and time variability across the computational domain. The maximum and minimum terrestrial emissions corresponded with the maximum and minimum ambient temperatures respectively. The highest overall rate of emissions came from the southern portion of the modeled domain. However, during the afternoon peak, the spatial variability of  $\text{Hg}^0$  fluxes for terrestrial systems was at its maximum in the northern parts of the domain. Over the two week simulation the highest total natural emissions were  $820 \text{ ng m}^{-2}$  from the Atlantic Ocean off the southeast US coastline and the lowest total natural emissions were  $74 \text{ ng m}^{-2}$  in the urban areas with little vegetation cover around Washington D.C.



**Figure 1.** Modeled natural mercury emissions at Eastern Standard Time (EST) a. 2400, b. 0600, c. 1200, and d. 1800

## CONCLUSIONS

HgSIM modeled mercury fluxes are highly variable in both time and space. The spatial variations in the fluxes are due to the land use parameterization and the gradients in meteorological parameters over the large domain. Temporal variations occur on both a diurnal cycle and a larger synoptic cycle as weather systems pass over the modeled regions.

The average vegetation emissions rates for forested regions were roughly twice that of the soil or water emission rates during times

of peak transpiration. However, the vegetation and soil emissions exhibit a strong diurnal pattern with lower emissions at night while the emissions from water do not. Therefore, the total emissions from the water over the two-week period were roughly equal to that of vegetation emission from heavily forested areas. Emissions from soils below forest canopies contributed about 20 % to 25 % of the total forest emissions. In agricultural regions, direct emissions from soils were the largest source contributing up to 75 % of the total terrestrial emissions in these locations.

This study showed that the spatial variability in mercury flux across the region was extreme and that spatially distributed models are the most feasible way to integrate over large regions.

This study showed higher Hg fluxes in the southern portion of the modeled domain,

which had higher heat energy loads available to vegetation canopies. This implies that the warmer climates are able to re-cycle mercury faster the cooler northern climates and warming of the northern regions could substantially increase the world wide biogenic Hg fluxes.

## REFERENCES

- LINDBERG, S. E. (1998): Air/surface exchange of mercury vapor over forests-The need for a reassessment of continental biogenic emissions; *Atmospheric Environment*, Vol. 32, pp. 895-908.
- CARPI, A. AND LINDBERG, S. E. (1998): Application of a teflon\TM dynamic flux chamber for quantifying soil mercury flux: tests and results over background soil; *Atmospheric Environment*, Vol. 32, pp. 873-882.
- XU, X., YANG, X., R. MILLER, D., HELBLE, J. J. AND CARLEY, R. J. (1999): Formulation of bi-directional atmosphere-surface exchanges of elemental mercury; *Atmospheric Environment*, Vol. 33, pp. 4345-4355.
- CAMPBELL, G. S., NORMAN, J. M. (1998): *An Introduction to Environmental Biophysics*; Springer-Verlag, New York.
- STEWART, J. B. (1988): Modeling surface conductance of pine forest; *Agriculture and Forest Meteorology*, Vol. 43, pp. 19-35.
- WANNINKHOF, R. (1992): Relationship between wind speed and gas exchange over the ocean; *Journal of Geophysical Research*, Vol. 97, pp. 7373-7382.
- HANSON, P. J., LINDBERG, S. E., TABBERER, T. A., OWENS, J. G. AND KIM, K.-H. (1995): Foliar exchange of mercury vapor: Evidence for a compensation point; *Water, Air and Soil Pollution*, Vol. 80(1-4), pp. 373-382.
- PIRRONE, N., COSTA, P., PACYNA, J. M., AND FERRARA, R. (2001): Mercury emissions to the atmosphere from natural and anthropogenic sources in the Mediterranean region; *Atmospheric environment*, Vol. 35, pp. 2997-3006.

## **Contribution of mercury from national antropogenic emissions, natural sources and atmospheric long range transport in Norway**

TORUNN BERG, EIRIK FJELD, BRIT-LISA SKJELKVILLE & EILIV STEINNES

**Abstract:** The environmental loadings of national Norwegian mercury emissions compared to the loadings of atmospheric long range transported mercury and mercury in natural background have been estimated. Data used have been the Norwegian participation in EMEP, data from Norwegian monitoring programmes on mercury in mosses, soil and sediments, in addition to official Norwegian emission data for mercury. The results show that atmospheric long range transport to Norway are somewhat larger than the national Norwegian emissions of mercury. The results also show that there are still communities in Norway where the mercury loadings are so high that the environment can be affected.

**Key words:** mercury, loading, Norway

## Four years measurements of Mercury Depletion Events (MDEs) at Ny-Ålesund, Svalbard

T. BERG<sup>1</sup>, K. ASPMO<sup>1</sup>, E. BAHLMANN<sup>2</sup>, C. BANIC<sup>3</sup>, J. DEARY<sup>3</sup>; A. DOMMERGUE<sup>4</sup>, R. EBINGHAUS<sup>2</sup>, C. FERRARI<sup>4</sup>, G. GUEHENEUX<sup>4</sup>, P-A- GAUCHARD<sup>4</sup>, K. GLRDFELDT<sup>5</sup>, M. LANDIS<sup>6</sup>, O. MAGAND<sup>4</sup>, J. MUNTHE<sup>7</sup>, N. PIRRONE<sup>8</sup>; F. PLANCHON<sup>4</sup>, S. SEKKESĆTER<sup>1</sup>, J. SOMMAR<sup>5</sup>, F. SPROVIERI<sup>8</sup>, A. STEFFEN<sup>3</sup>, R. STEVENS<sup>6</sup>, C. TEMME<sup>2</sup>, A. URBA<sup>9</sup>, A-K VALDAL<sup>1</sup>, I. WANGBERG<sup>7</sup>,

<sup>1</sup>Norwegian Institute for Air Research, P. Box 100, N-2027 Kjeller, NORWAY.

E-mail: torunn.berg@nilu.no.

<sup>2</sup>GKSS-Forschungszentrum Geesthacht GmbH, Germany. <sup>3</sup>Environment Canada (MSC), Toronto, Canada. <sup>4</sup>CNRS, Grenoble, France. <sup>5</sup>University of Gothenburg, Sweden. <sup>6</sup>US EPA, US. <sup>7</sup>IVL Swedish Environmental Research Institute, Sweden. <sup>8</sup>CNR-Institute for Atmospheric Pollution, Rende, Italy. <sup>9</sup>Institute Physics, Lithuania

**Abstract:** Development and some highlights from four years “Mercury Depletion Event (MDE) Campaigns” at Ny-Ålesund, Svalbard (78°54’N, 11°53’E) where research groups from all together eight countries have participated are presented. The purpose of this effort was to provide further quantitative information on mercury in different environmental compartments including air, snow, ice cores and seawater during polar spring and extend the database of MDEs. To contribute to the knowledge, we have conducted time-resolved speciated determination of mercury in the atmosphere (GEM, RGM, PM) and snow (total mercury) at two altitudes (474 and 12 m a.s.l.). At the sea level gas-transfer experiments over snow and sea surfaces have been conducted. The observations have been analysed using meteorological and remote-sensing data.

**Key words:** Atmospheric mercury, mercury depletion events, Svalbard

### INTRODUCTION

The discovery of the mercury depletion events at Alert in the Canadian Arctic (SCHROEDER ET AL., 1998) initiated a lot of activities on atmospheric mercury in polar regions. At Ny-Ålesund the first Tekran 2537A was installed at the Zeppelin mountain in February 2000. Since then spring cam-

paigns have been carried out every year: in 2000 and 2001 with only Norwegian scientists, in 2002 with participation of Swedish, Norwegian, Lithuanian and Canadian groups and in 2003 with participation of more than 20 scientists from six countries (Norway, Canada, France, Germany, Italy, US). The following presentation gives a summary of the results from these campaigns.

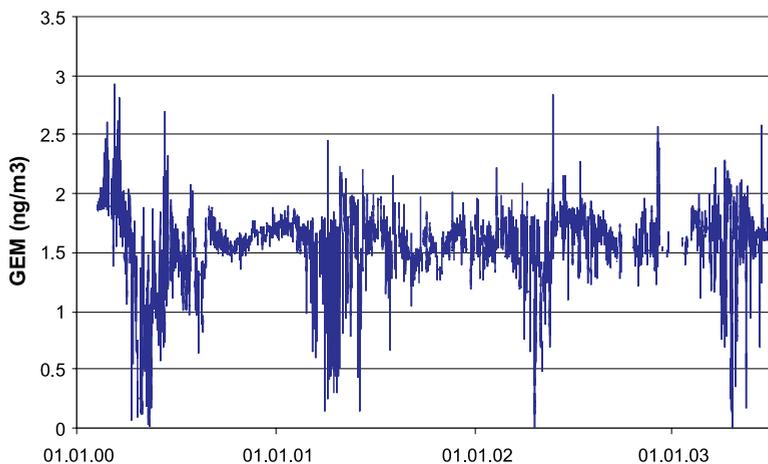


Figure 1. Time series of hourly average values for GEM, Zeppelin, 2000-2003.

## MAIN RESULTS

### MDEs:

MDEs are taking place every spring at Ny-Åesund (Fig. 1). Normally mid-April – mid-May is the period with most frequent MDEs. Results from the campaigns indicate that there are different types of depletion events with varying characteristics. Different environmental and meteorological conditions yield a different distribution of mercury (SOMMAR ET AL., 2003; STEFFEN ET AL., 2004). Some the MDEs seem to be locally generated whereas others are the result of atmospheric long-range transport of depleted air masses. This conclusion has been supported by comparison of BrO columns with mercury data (WANGBERG ET AL., 2003; SOMMAR ET AL., 2004).

### Mercury species:

Reactive gaseous mercury (RGM) and particulate mercury (PM) in general anticorrelate with GEM, but the concentrations of RGM and PM vary in different MDEs. Sometimes the PM is highest, some times the RGM is

highest. During other MDEs RGM and PM are similar. The observed variability in RGM and PM may be linked to the overall behaviour of particulate matter during depletion events. Measurements performed at Ny Åesund have shown that the number of particles smaller than ~0.3 micrometers decrease when ozone and mercury concentrations decrease. Larger particles seem to increase during such events (GAUCHARD ET AL., 2004). The size distribution of particles containing mercury is not known but it is likely that the gas-particle processes involved (e.g., adsorption of RGM on aerosols) is affected both by the number of particles available and the size distribution.

### Two elevations:

The Zeppelin station (474 mas) is situated over or at least at the top of the marine boundary layer. GEM levels during depletion events at 12 m a.s.l and Zeppelin are comparable (BERG ET AL., 2003A; SOMMAR ET AL., 2004; TEMME ET AL., 2004). Considerable concentration differences between the stations were often observed prior to depletions, and a much higher variance was observed

at 12 m a.s.l. after MDEs (SOMMAR ET AL., 2004). The vertical spatial gradient in GEM and its temporal development is likely to be due to re-emission of mercury from the snow surface, an effect that is enhanced by restricted mixing of air on a micrometeorological scale.

#### **Surface snow:**

Enhanced concentrations of Hg in surface snow are clearly evident throughout the MDE period at Zeppelin. A ten-fold increase in the concentrations is seen from winter to spring (BERG ET AL., 2003b). During spring 2002 time series of total mercury presents a moderate maximum during the major MDE and becomes highly episodic during the minor events with peaks as high as 77 ng L<sup>-1</sup>. The highest values were obtained during one of the MDEs, in conjunction with snowfall. The sample from the Zeppelin station was collected before the snowfall started and contained small amounts of mercury. The sample at 12 m a.s.l. was collected approximately one hour after the snowfall started and contained high amounts of mercury (~15-fold increase) (SOMMAR ET AL., 2004). Hence, this observation clearly indicates that the mercury arrived with the snow. Methyl-Hg was consistently undetectable (<0.06 ng L<sup>-1</sup>) during the campaign 2002 (SOMMAR ET AL., 2004).

#### **Flux measurements:**

During spring an accumulation of GEM was generally observed in the air passing through the DFC, corresponding to mid-day peak emissions of up to 70 ng m<sup>-2</sup> h<sup>-1</sup> (SOMMAR ET AL., 2004). Elevated fluxes were observed contiguous to enhanced deposition events during the MDEs. The average DFC-flux obtained was ~8 ng m<sup>-2</sup> h<sup>-1</sup>. Late September

flux measurements on snow showed no reemission at all, but barely detectable deposition corresponding to 0.23 ng m<sup>-2</sup> h<sup>-1</sup> (concentration differences as low as ~0.05). The vertical two level GEM measurements over snow generally displayed very small concentration differences (<0.1-0.2 ng/m<sup>3</sup>) during spring 2002. However, during one event, solid evidence for photo-stimulated emissions of Hg<sup>0</sup>(g) from the snow pack was obtained. The GEM gradient represents 9 h following a snowfall during which a large increase in Hg-tot was observed in consecutive samples. The seawater in Kongsfjorden was supersaturated with respect to dissolved gaseous mercury (DGM) during measurements in early May 2002. The concentration of DGM in the surface water showed a pronounced daily variation well correlated with solar radiation. Hence, it seems like a significant part of the oxidised mercury deposited onto snow and water surfaces is quickly re-emitted back to the atmosphere as elemental mercury (SOMMAR ET AL., 2004).

#### **Temporal trend:**

No temporal trends have been seen in the GEM level measured at the Zeppelin station since 1994 (BERG ET AL., 2004). The measurements were carried out using manual methods during 1994-1999. From 2000 a Tekran 2537 A have been used. This is also in accordance with results from

#### **Modelling:**

A study was performed in order to assess whether Hg emitted from anthropogenic sources in Europe could be transported to and deposited in the Arctic (BERG ET AL., 2001). It was concluded that this was not a major pathway as the concentrations of Hg species in the Arctic atmosphere were indistinguish-

able from the global background. Thus, to assess the impact of anthropogenic Hg emissions on the Arctic ecosystems, the global cycling of Hg including air-surface exchange has to be taken into account.

## Acknowledgments

The Norwegian research has been funded by the Norwegian Research Council and the Norwegian State Pollution Authority. Special thanks go to Norwegian Polar Institute, Alfred Wegner and CNR Italy for their support and hospitality at Ny-Ålesund.

## REFERENCES

- ASPMO, K., BANIC, C., BERG, T., EBINGHAUS, R., FERRARI, C., GAUCHARD, P.-A., STEFFEN, A. AND TEMME, C. (2004): *ICMGP*; Ljubljana, Slovenia, June 27 – July 2, 2004.
- BERG, T., BARTNICKI, J., MUNTHE, J., LATTILA, H., HREHORUK, J. AND MAZUR, A. (2001): Atmospheric mercury species in the Arctic: Measurements and modelling; *Atmospheric Environment* 35, pp. 2569-2582.
- BERG, T., SOMMAR, J., WÄNGBERG, I., GLRDFELDT, K., MUNTHE, J. AND SCHROEDER, W. H. (2003A): Arctic mercury depletion events at two elevations as observed at the Zeppelin Station and Dirigibile Italia, Ny-Ålesund, spring 2002; *J. Phys. IV France* 107, pp. 151-154.
- BERG, T., SEKKESĆTER, S., STEINNES, E., VALDAL, A. AND WIBETOE, G. (2003b): Arctic springtime depletion of mercury in the European Arctic as observed at Svalbard; *Sci. Total Environ.* 304, pp. 43-51.
- BERG, T., KALLENBORN, R. AND MANŘ, S. (2004): Temporal trends in atmospheric heavy metal and organochlorine concentrations at Zeppelin, Svalbard; *Arctic, Antarctic, and Alpine Research* Vol. 2, Nr. 2, May 2004 (in press).
- GAUCHARD ET AL. (2004): Atmospheric particle evolution during Hg depletion events in Ny-Ålesund, Svalbard in April-May 2003; *ICMGP*, Ljubljana, Slovenia, June 27 – July 2, 2004.
- SCHROEDER, W. H., ANLAUF, K., BARRIE, L. A., LU, J. Y., STEFFEN, A., SCHNEEBERGER, D. R., BERG, T. (1998): Arctic springtime depletion of mercury. *Nature* 394, pp. 331-332.
- SOMMAR, J., WÄNGBERG, I., BERG, T., GLRDFELDT, K., MUNTHE, J., RICHTER, A., URBA, A., WITTROCK, F. AND SCHROEDER, W. H. (2004): Circumpolar transport and air-surface exchange of atmospheric mercury at Ny-Ålesund (79°N), Svalbard, spring 2002; *Atmospheric Chemistry and Physics Discussions* (in press).
- STEFFEN, A., ASPMO, K., BANIC, C., BERG, T., EBINGHAUS, R., FERRARI, C., GAUCHARD, P.-A. AND TEMME, C. (2004): Characterizing Mercury Depletion Events in Ny-Ålesund, 2003; *ICMGP*, Ljubljana, Slovenia, June 27 – July 2, 2004.
- TEMME, C., ASPMO, K., BAHLMANN, E., BANIC, C., BERG, T., DOMMERGUE, A., EBINGHAUS, R., FERRARI, C., GAUCHARD, P.-A., MAGAND, O., PIRRONE, N., PLANCHON, F., SPROVIERI, F. AND STEFFEN, A. (2004): Repeatability and reproducibility of data from different groups and locations in Ny-Ålesund during the Hg-campaign 2003; *ICMGP*, Ljubljana, Slovenia, June 27 – July 2, 2004.
- WÄNGBERG, I., SOMMAR, J., BERG, T., GLRDFELDT, K. AND MUNTHE, J. W. H. (2003): Interpretation of Mercury Depletion Events Observed at Ny-Ålesund, Svalbard During Spring 2002; *J. Phys. IV France* 107, pp. 1353-1356.

## Biogeochemical Overview of Mercury Cycling in the Venice Lagoon (2001-03)

NICOLAS S. BLOOM<sup>1</sup>, LIGIA M. MORETTO<sup>2</sup> AND PAOLO UGO<sup>2</sup>

<sup>1</sup>Frontier Geosciences, 414 Pontius North Seattle, WA 98109 USA nicolasb@nickslab.org

<sup>2</sup>Universita Ca'Foscari, S. Marta, 2137 Venezia 30123, Italy moretto@unive.it

**Abstract:** Mercury and CH<sub>3</sub>Hg were measured in the sediments, waters, suspended matter and biota of the Venice Lagoon, in 5 seasonal campaigns between winter of 2001 and spring of 2003. These data show that the lagoon, which was contaminated with up to 300,000 kg of Hg, largely from two chlor-alkali plants in the 1950's to 1980's, is now only moderately enriched with Hg, but over a very extensive area. This is the result of massive redistribution of sediments in this highly energetic system. The continuous re-suspension of sediments, combined with rapid tidal flushing results in the Lagoon being a major net exporter of Hg (1,100 kg) and CH<sub>3</sub>Hg (5.6 kg) to the Adriatic Sea.

**Key words:** Mercury, Speciation, Biogeochemistry, Venice Lagoon

### INTRODUCTION

The Venice Lagoon (Figure 1) encompasses 540 km<sup>2</sup>, of which about 13 % is described as salt marsh ecosystems (CRITTO AND MARCOMINI, 2001). Having an average depth of only 1.1 m and a tidal cycle that often exceeds that, a large fraction of the lagoon is alternately submerged and re-emerged on a daily basis. Although many chemical industries are located on the western shore of the Lagoon, it is likely that the largest source of Hg is the mercury-cell chlor-alkali complex, which operated largely without pollution control equipment from 1951 until 1988. The circulation properties of the Lagoon confine the majority of the pollution to its northern half. Because of the diversion of river inputs, large-scale re-suspension, and exaggerated tidal flow caused by the deepening of channels for ship traffic, the Lagoon is now a net exporter of sediments to the Adriatic sea,



Figure 1. Map of the Venice Lagoon. Location of historic chlor-alkali discharges indicated by (★).

losing 1.1 million m<sup>3</sup>, or 0.2 cm yr<sup>-1</sup> (DAY ET AL., 1995). Although researchers have known for some time that Hg was a major contaminant of concern in the Lagoon (CRITTO AND MARCOMINI, 2001), there had not yet been a comprehensive study of its biogeochemical cycle. As a result of studies initiated in 2001 by the University of Venice and Frontier Geosciences, we have recently been able to fill in many of the gaps in the story of Hg contamination of the Lagoon. In this paper, focussing on the Lagoon-wide mass balance and comparison to other similar sites around the world, we will briefly summarize our findings for Hg and CH<sub>3</sub>Hg, the first ever collected using ultra-clean sampling techniques. Much greater detail can be found by reference to the original publications, which were excerpted for this summary (BLOOM ET AL., 2004a,b; BLOOM ET AL., 2003A,B; MORETTO ET AL., 2003).

## RESULTS AND DISCUSSION

Samples were collected and filtered using established ultra-clean techniques (BLOOM, 1995), and analyzed for Hg species using cold vapour atomic fluorescence spectrometric (CVAFS) detection (BLOOM AND FITZGERALD, 1988). Total Hg was quantified after BrCl oxidation, using SnCl<sub>2</sub> reduction and dual gold amalgamation prior to the CVAFS step (BLOOM AND CRECELIUS, 1983). CH<sub>3</sub>Hg was determined with aqueous ethylation, purging onto Carbotrap<sup>TM</sup>, and then isothermal GC-CVAFS detection (LIANG ET AL., 1994). An evaluation of the over 1,000 data points generated (BLOOM ET AL., 2004a) indicated that almost all individual points were precise (relative replicate differences <10 %), and accurate (recoveries of 80-120 %), and virtually all fell well above the method detection limits (approximately 0.2 ng L<sup>-1</sup> for Hg and 0.01 ng L<sup>-1</sup> for CH<sub>3</sub>Hg).

Location	N	Mean [Hg], ng L <sup>-1</sup>		Reference
		Total	Methyl	
Venice urban canals	40	94 ± 19	0.28 ± 0.04	Bloom et al., 2004a
Venice north wetlands	16	29 ± 9	0.21 ± 0.05	Bloom et al., 2004a
Venice industrial canals	8	27 ± 6	0.09 ± 0.03	Bloom et al., 2004a
Venice north open water	23	15 ± 3	0.07 ± 0.01	Bloom et al., 2004a
Venice south open water	10	3.1 ± 0.5	0.03 ± 0.00	Bloom et al., 2004a
Lavaca Bay, Texas	15	47 ± 14	0.30 ± 0.07	Bloom et al., 2004b
Tropical Brasil Lagoons	8	12 ± 6	0.10 ± 0.04	Bloom et al., 2004b
San Francisco Bay	28	9.0 ± 6.8	0.05 ± 0.04	Choe et al., 2003a,b
Gulf of Trieste	<i>nr</i>	5.9	0.04	Horvat et al., 2001
Hong Kong Harbor	6	1.6 ± 0.3	< 0.02	Bloom et al., 2004b
Elliott Bay, Seattle	2	0.6 ± 0.1	0.03 ± 0.01	Bloom et al., 2004b
Adriatic Sea	<i>nr</i>	0.2	0.03	Horvat et al., 2001

**Table 1.** Comparison of the average unfiltered Hg speciation in various regions of the Venice Lagoon to other estuarine and lagoon systems.

Flow	Type	Hg flux, kg yr <sup>-1</sup>	
		Total	Methyl
<b>Inflows</b>	Resuspension (north lagoon)	1,051	1.8
	Resuspension (south lagoon)	41	0.1
	Adriatic Sea inflow (total)	308	1.9
	Industrial discharges	36	0.4
	Rivers	13.2	0.22
	Precipitation	9.4	0.04
	Venezia canals	11.9	0.03
	<b>TOTAL INPUTS</b>	<b>1,471</b>	<b>4.4</b>
<b>Outflows</b>	Adriatic Sea outflow (north lagoon)	1,243	5.9
	Adriatic Sea outflow (South lagoon)	175	1.5
	Gaseous Hg evasion	4.2	0.00
	Seafood removal	0.29	0.19
	<b>TOTAL OUTPUTS</b>	<b>1,422</b>	<b>7.5</b>
<b>Net</b>	<b>EXPORT TO ADRIATIC SEA</b>	<b>1,114</b>	<b>5.6</b>

**Table 2.** Mercury and methylmercury mass balances for the Venice Lagoon (2002-2003), as summarized from Bloom et al., 2004a.

Hg ranges from about 1–2 ng L<sup>-1</sup> at the Lido entrance to the Adriatic, to 5-20 ng L<sup>-1</sup> within the main body of the northern Lagoon. The less contaminated southern reaches of the Lagoon were not studied as intensively, but found to contain only 1–3 ng L<sup>-1</sup> Hg. Up to 50–200 ng L<sup>-1</sup> Hg were observed in the industrially impacted areas and urban canals. Most Hg was from re-suspended sediments, as levels are strongly correlated with TSS in this shallow lagoon. Dissolved Hg concentrations were narrowly constrained to the range of approximately 0.5-3 ng L<sup>-1</sup>. CH<sub>3</sub>Hg ranged from about 0.02-0.4 ng L<sup>-1</sup> in unfiltered samples and 0.005 to 0.2 ng L<sup>-1</sup> in the dissolved fraction. Surface (0-3 cm) sediments varied from about 0.5 to 2.5 µg g<sup>-1</sup> dry basis, with 0.1-0.3 % of that methylated. CH<sub>3</sub>Hg levels were about three times higher during the spring and summer, compared to winter (BLOOM ET AL., 2004a,b). The Lagoon appears to be moderately, but extensively contaminated by Hg, showing concentrations of both

Hg and CH<sub>3</sub>Hg higher than those reported in other coastal harbors and lagoons (Table 1), but spread over a much wider area. The impact of the past direct chlor-alkali discharges is diffused throughout the system by an array of re-suspension pathways, but may ultimately be mitigated by rapid tidal flushing.

Using all of the data collected together with literature values for mass fluxes we were able to construct well-constrained mass balances for the Lagoon (Table 2). This balance shows that a large amount of Hg circulates through the Lagoon, although only about 5 % represents new contamination. Rather, almost the entire system mass balance is made up of the cycling of previously contaminated sediments, which were estimated to contain a total of 200,000 to 300,000 kg of anthropogenic Hg. Because of the high degree of anthropogenically mediated sediment re-suspension, combined with the large tidal currents, approximately 1,100 kg of Hg and

5.6 kg of CH<sub>3</sub>Hg is exported to the Adriatic sea each year, making the Venice Lagoon perhaps its second largest source of Hg, after the Isonzo River, which drains the Hg mining areas of Idria, Slovenia. The impact of the Lagoon sediments may be even more dramatic, however, as the Hg adsorbed to the organic fraction of the sediments is likely to be more bioavailable (BLOOM ET AL., 2003c) than the cinnabar-bound Hg derived from the mining areas.

## CONCLUSIONS

Since the Second World War, the Venice Lagoon has been highly contaminated by anthropogenic mercury, which is adsorbed to and transported with the sediments. As a

result of extremely high levels of anthropogenically mediated sediment re-suspension, the Hg contamination has been both diluted and spread over an extensive area, primarily of the northern basin (about 250 km<sup>2</sup>). Given the extensive prevalence of highly productive intertidal wetlands, it was not surprising to find significant levels of Hg methylation, especially as the Lagoon warms up in the late spring and early summer. Overall, mass balance calculations show that due to export of re-suspended sediments, the Lagoon is a major net exporter of Hg and CH<sub>3</sub>Hg to the Adriatic Sea. The 1,100 kg of Hg exported each year appears to only be exceeded by the outflow of the highly Hg contaminated Isonzo River (1,500 kg yr<sup>-1</sup>), which drains the historic Hg mining region of Slovenia.

## REFERENCES

- BLOOM, N. S., MORETTO, L. M., SCOPECE, P., AND UGO, P. (2004a): *Mar. Chem.* (in press).
- BLOOM, N. S., MORETTO, L. M., AND UGO, P. (2004b): *Limnol. Oceanogr.* Vol. 49, pp. 367-375.
- BLOOM, N. S., MORETTO, L. M., AND UGO, P. (2003a): In: *Proceedings of the 7<sup>th</sup> International Conference on the Biogeochemistry of Trace Elements, Volume I*, (G. R. GOBRAN AND NICHOLAS LEPP, Eds.), pp. 20-21.
- BLOOM, N. S., MORETTO, L. M., AND UGO, P. (2003b): *Geochim. Cosmochim. Acta* Vol.67, pp. A-41.
- BLOOM, N., PREUS, E., KATON, J. AND HILTNER, M. (2003c): *Anal. Chim. Acta* Vol. 479, pp. 233-248.
- BLOOM, N. S. (1995): *Env. Lab.* March/April, pp. 20-26.
- BLOOM, N. S AND FITZGERALD, W. F. (1988): *Anal. Chim. Acta.* Vol. 208, pp. 151-161.
- BLOOM, N. S AND CRECELIUS, E. A. (1983): *Mar. Chem.*, Vol. 14, pp. 49-59.
- CHOE, K-Y., GILL, G. A., AND LEHMAN, R. (2003a): *Limnol. Oceanog.*, Vol. 48, pp. 1535-1546.
- CHOE, K-Y., AND GILL, G. A. (2003b): *Limnol. Oceanog.*, Vol. 48, pp. 1547-1556.
- CRITTO, A. AND MARCOMINI, A. (2001): *Rischio ecologico e inquinamento chimico lagunare*, Liberia Editrice Cafoscarina, Venezia, Italy.
- DAY, J. W., ARE, D., RIMONDO, A., SCARTON, F., AND CECCONI, G. (1995): *Consorzio Venezia Nuova, Quaderni Trimestrali*, Venezia, pp. 24-34.
- HORVAT, M., KOTNKI, J., FAJON, V., LOGAR, M., ZVONARIC, T. AND PIRRONE, N. (2001): *RMZ-Materials and Geoenvironment*, Vol. 48, pp 241-252.
- LIANG, L., BLOOM, N.S, AND HORVAT, M. (1994): *Clin. Chem.* Vol. 40/4, pp 602-607.
- MORETTO, L., BLOOM, N., SCOPECE, P. AND UGO, P. (2003): *J. Phys. IV France*, Vol. 107, pp. 887-890.

## Monitoring of mercury in water, sediment, and aquatic biota to assess responses to changing atmospheric emissions

R. A. (DREW) BODALY<sup>1</sup>, DAVID P. KRABBENHOFT<sup>2</sup>,  
MICHAEL C. NEWMAN<sup>3</sup> AND JAMES G. WIENER<sup>4</sup>

<sup>1</sup>Freshwater Institute, Fisheries and Oceans Canada,  
501 University Crescent, Winnipeg, MB, Canada R3T 2N6

<sup>2</sup>U. S. Geological Survey, Water Resources Division,  
8505 Research Way, Middleton, WI, USA 53562

<sup>3</sup>College of William and Mary, Virginia Institute of Marine Science, Department of Environmental  
Sciences, Route 1208 Greate Road, Gloucester Point, VA, USA 23062-1346

<sup>4</sup>University of Wisconsin – La Crosse, River Studies Center,  
1725 State Street, La Crosse, WI, USA 54601

**Abstract:** Mercury is an important contaminant of concern throughout the world and levels in the environment remain problematic. Many agencies in North America and Europe are considering new regulations that will reduce atmospheric emissions. Evaluation of the effectiveness of emission controls will require accurate methods of documenting responses to changes in mercury loadings from atmospheric deposition. A workshop was convened in September 2003 to determine a framework for monitoring Hg in watersheds and airsheds, in waters and sediments, in aquatic biota, and in terrestrial wildlife. The objectives of this workshop were to (1) identify attributes of indicators that would be useful for discerning trends in the concentration of Hg or MeHg in water, sediment and aquatic biota, (2) critically evaluate and rank candidate indicators that would be most useful in trend-monitoring programs for Hg or MeHg, (3) identify ancillary data needs and possible confounding factors that should be considered or documented, to ensure the defensible application and interpretation of the indicators in a trend-monitoring program, and (4) identify the environmental settings (e.g., water-body type and geographic location) that would be most sensitive for detecting short-term changes in atmospheric deposition of Hg. We report the workshop recommendations pertaining to monitoring of mercury in water, sediment, and aquatic biota. The selection of indicators was guided by required and desirable criteria to ensure that the indicators are useful, relevant, and possess sufficient discriminatory or diagnostic attributes to detect a signal (change in Hg deposition) above the background noise (variation in Hg concentration or MeHg bioaccumulation attributable to other factors). Criteria for indicators for monitoring waters and sediments are that water provides a direct exposure route to pelagic organisms whereas sediments smooth and integrate benthic exposure and deposition rates over longer time scales. A sampling design for monitoring water and sediment should stratify by water body type, and include Mercury Deposition Network sites, replicate sampling, and collection of ancillary data. Criteria for indicators for monitoring aquatic biota include relevance to public and ecological health and the development of policy, the need to standardize procedures for sample collection and analysis and reporting of results, the presence of historical data, and the recognition of confounding factors and co-variables. Candidate organisms should be evaluated with respect to criteria including wide geographic range, importance in the trophic transfer of

MeHg, knowledge of feeding ecology and trophic position, rapid response time (3-5 years) to changes in Hg loadings, and the possibility of non-intrusive sampling methods. It is important to integrate the monitoring of Hg in waters, sediments and aquatic biota with modeling needs. Many anthropogenic and natural factors, independent of the bulk loading of Hg from atmospheric deposition, can strongly influence the concentrations and trends of Hg in aquatic biota and in water and sediments. Our ability to discern trends in MeHg or Hg concentrations in aquatic biota and other media will depend on knowledge of the influence of such factors on the concentration of Hg in water and sediment and the bioaccumulation of MeHg.

# Modelling Mercury in the Connecticut River Basin Airshed

PATRICIA BRESNAHAN

**Abstract:** The Atmospheric Resources Laboratory at the University of Connecticut is using the USEPA Models III system in a Linux cluster to model the atmospheric transport and transformation of mercury in Northeast North America. The air quality model CMAC with mercury chemistry included is the basic program. This paper describes the model performance on multiprocessor computer systems. It also presents simulations demonstrating the spatial and time variability of mercury in atmosphere and deposition to the Connecticut River Basin.

**Key words:** deposition, Models III, variability

## Problems Associated with Spatial Extrapolation of Springtime Mercury Deposition to Polar Regions

STEVEN BROOKS<sup>1</sup> & STEVEN LINDBERG<sup>2</sup>

<sup>1</sup> National Oceanic and Atmospheric Administration, Atmospheric Turbulence and Diffusion Division, 456 S. Illinois Ave, Oak Ridge, TN 37830 USA, e-mail: steve.brooks@noaa.gov

<sup>2</sup> Oak Ridge National Laboratory, Environmental Science Division, Oak Ridge, TN US, e-mail: sll@ornl.gov

**Abstract:** Schroeder et al. (1998, Nature) first reported springtime episodic gaseous elemental mercury (GEM or Hg<sub>0</sub>) depletions based on ground measurements of air at Alert, Canada. Since then these events have proven to be widespread in the Arctic occurring every springtime at Alert, Barrow, Ny Ålesund, and Station Nord. At Barrow these events have been linked with the near-surface air formation of reactive mercury (Hg(II)) in the gas form (RGM), fine particulate form (FPM), and the accumulation of total mercury in the snowpack (~100 ng/L just prior to melt). This transport of Hg via atmospheric conversion, to deposition, to bio-available forms is likely the predominate pathway for mercury into Arctic biota.

For the first time, we have spatially extended the Barrow measurements by conducting two weeks of concurrent measurements roughly 350 km upwind of Barrow on the multiyear sea-ice edge.

At the US Navy Applied Physics Laboratory Ice Station (APLIS) 2003 atop multiyear sea-ice in the Beaufort Sea, we measured mercury speciation in the near surface air, and monitored total mercury in the local snow and ice surfaces. These measurements add to the growing database of polar mercury depletion events. Further, the upwind location from Barrow provided a two week glimpse into the mercury chemistry of airmasses traversing this region of the Arctic.

Our mercury measurement sensors consisted of Tekran models 2537a/1130/1135 for the determination of GEM, RGM, and FPM, respectively. Airmass trajectories were computed using the National Oceanic and Atmospheric Administration HYSPLIT model. Snow samples and ice samples were collected from the upper surface (~5cm) using clean techniques.

Measurements at the ice station began on March 30, 2003 at Latitude 73.03N and Longitude 148.07W (364 km NE of concurrent measurements at Barrow, Alaska), and ended on April 14, 2003 at 73.42N and 149.91W (341 km NE of Barrow). The total station drift was 73 km to the NW.

Airmass movement in this region is dominated by flow from the North (termed the Siberian Express) which, around the latitude of Barrow, takes on the counter-clockwise (towards the West) circulation of the persistent Aleutian Low. Trajectory computations during the measurement period showed that airmasses over the ice station predominately headed towards Barrow, and on two occasions, the model showed airmasses following a exact line between the Ice station and Barrow.

The Ice Station site experienced episodic mercury depletion events of similar character to typical Barrow measurements, but with some notable differences. Compared to Barrow, the Ice station average GEM was similar, average RGM was similar, average FPM was much higher and, total Hg in the surface snow and ice was less.

Taken as a whole, this suggests that the more compact snowpack and snow-free ice at the Ice station, with less wind forced ventilation, does not deposit reactive gaseous mercury as effectively from the air (lower deposition velocity). The reactive gaseous mercury remaining in the near surface air has more time to adhere to airborne particulates to form enhanced concentration of FPM, explaining the higher FPM concentrations and the lower snowpack Hg.

Ice station depletion events were not of coincident timing or duration, to the concurrent Barrow monitoring, even when modeling showed that an air mass had transected both sites. This suggests that depletion events are forced by very local conditions (i.e. local refreezing of leads).

Episodic mercury depletion events ~340 km upwind of Barrow, Alaska appear to be decoupled from the concurrently measured events at Barrow. While of similar character, the upwind Ice station site saw higher fine particulate mercury levels in the near surface air, and lower Hg levels in the surface snow. This suggests that; Mercury depletion events are driven by local conditions. Following a depletion, gaseous elemental mercury levels in the near surface air are replenished to ambient levels within hours. And, that the physical characteristics of the surface (wind scoured sea-ice and a compacted snowpack) are likely the critical factors controlling the deposition rate of reactive gaseous mercury and the partitioning of reactive gaseous mercury and fine particulate mercury in the near surface air.

**Key words:** Arctic, deposition, Sea-ice

## Aqueous reduction of $\text{Hg}^{2+}$ to $\text{Hg}^0$ by $\text{HO}_2$ in the CMAQ-Hg model

O. RUSSELL BULLOCK, JR.

NOAA Air Resources Laboratory (on assignment to the U.S. Environmental Protection Agency, Office of Research and Development), U.S. EPA Mail Drop E243-03, Research Triangle Park, NC, 27711, USA, e-mail: bullock.russell@epa.gov

**Abstract:** Numerical models of atmospheric mercury are formulated based on the current understanding of mercury chemistry in air and in atmospheric water. Recent evidence that significant reduction of  $\text{Hg}^{2+}$  by reaction with  $\text{HO}_2$  may not actually occur in natural atmospheric water has obvious implications for the modeling of atmospheric mercury, the seriousness of which has been investigated in the context of the Community Multi-scale Air Quality (CMAQ) model. A published rate constant of  $1.1 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$  for the aqueous reduction of  $\text{Hg}^{2+}$  by  $\text{HO}_2$  was used in the mercury version of the CMAQ model (CMAQ-Hg) that was previously tested for its agreement to observed measurements of mercury wet deposition in the United States. A modeling analysis has now been conducted to investigate the effect of removing this controversial reaction from the CMAQ-Hg model. The results show more mercury wet deposition, thus reducing the low bias previously found from the base model configuration. However, other sources for this low bias have also been identified. An examination of mercury concentrations in precipitation brings into question the apparent model improvement and highlights the need for confident determination of chemical kinetic modeling parameters.

**Key words:** atmospheric, mercury, modeling, chemistry, uncertainty

### INTRODUCTION

A recent study of the potential for aqueous reduction of  $\text{Hg}^{2+}$  species by  $\text{HO}_2/\text{O}_2^-$  under atmospheric conditions described in GLRDFELDT (2003) has concluded that the reaction is not thermodynamically favored. The formation of  $\text{Hg}^0$  observed during an earlier study of the reaction described in PEHKONEN (1998) was probably due to photo-reduction of  $\text{Hg}^{2+}$  complexed with oxalate used to produce  $\text{HO}_2/\text{O}_2^-$ . The study concluded that the aqueous phase reduction of  $\text{Hg}^{2+}$  species by  $\text{HO}_2/\text{O}_2^-$  should not be included in models describing the atmospheric

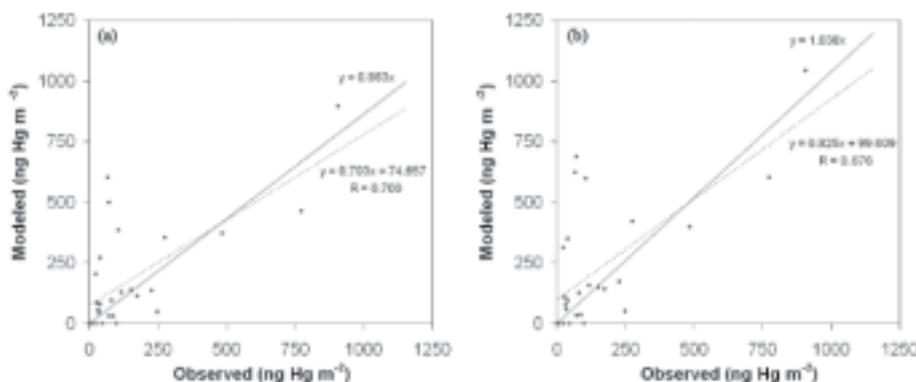
transport and transformation of mercury. Because this controversial reaction is currently included in the special version of the Community Multi-scale Air Quality (CMAQ) model developed at the U.S. Environmental Protection Agency to simulate atmospheric mercury, a study was conducted to determine the importance of the reaction in the model's simulation of mercury in cloud water and its subsequent effects on the simulation of total mercury wet deposition as compared with observations from the Mercury Deposition Network (MDN) (VERMETTE, 1995).

The mercury version of the CMAQ model (CMAQ-Hg) was previously applied to assess the model's accuracy based on weekly wet deposition measurements from the MDN during two separate 4-week periods in 1995 as described in BULLOCK (2002). The model currently simulates in its cloud-water chemical model the reduction of all aqueous  $\text{Hg}^{2+}$  species by  $\text{HO}_2$  using a rate constant of  $1.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  from PEHKONEN (1998) based on the assumption that some chloride is present in the cloud water. This rate constant has not changed in the CMAQ-Hg model since the study in BULLOCK (2002). However, a few minor changes have since been made to the standard CMAQ codes and to mercury-specific parts of the model to improve numerical accuracy, whereby the model's ability to reproduce observed mercury wet deposition has improved slightly. To investigate the importance of this reaction in the full-scale CMAQ-Hg model, the test period of 4 April – 2 May 1995 previously applied in BULLOCK (2002) was simulated once again, this time with the model rate constant for the aqueous reduction of  $\text{Hg}^{2+}$  by  $\text{HO}_2$  set to zero. Changes in simulated wet deposition of total mercury due to

removal of the reaction from the model were analyzed and compared against the same set of MDN observations previously used in BULLOCK (2002).

## RESULTS AND DISCUSSION

As expected, elimination of the  $\text{HO}_2$  reaction resulted in increased simulated wet deposition of mercury during all weekly periods of observations at all MDN sites. However, these increases were highly variable and ranged from 3.3 % to 110.1 %. The mass-weighted average change in simulated wet deposition for all MDN observation periods was 23.9 %. Fig. 1 shows analyses of modeled versus observed mercury wet deposition from the base CMAQ-Hg model and from the test version without the  $\text{HO}_2$  reaction. The model correlation to wet deposition observations dropped slightly with the elimination of the  $\text{HO}_2$  reaction. Where the normal CMAQ-Hg simulation showed a Pearson correlation coefficient of  $R = 0.700$ , the test simulation showed a value of  $R = 0.676$ . BULLOCK (2002) reported a value of  $R = 0.657$  for the base model before program-



**Figure 1.** Scatter plots of the observed versus modeled wet deposition of mercury: (a) from the base CMAQ-Hg model; (b) from the CMAQ-Hg model without the  $\text{HO}_2$  reaction

ming improvements were made to increase numerical accuracy.

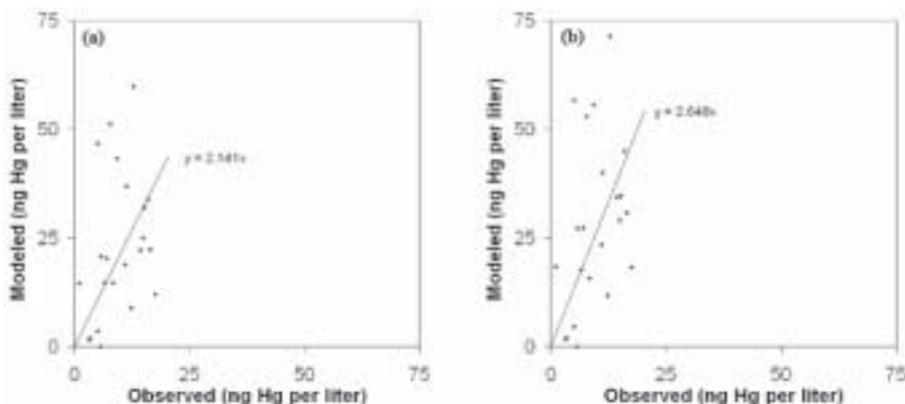
Removing the aqueous HO<sub>2</sub> reaction negated slightly over half of the improvement achieved through these coding modifications, but neither effect was highly significant. Removing the HO<sub>2</sub> reaction did improve the slope of the standard least-squares regression for mercury wet deposition from 0.703 to 0.825, but the associated zero intercepts for the regression increased from 74.66 to 99.61 ng(Hg) m<sup>-2</sup>. The slope of the zero-intercept least-squares regression increased from 0.863 to 1.038 with the elimination of the HO<sub>2</sub> reaction.

The apparent improvement in CMAQ-Hg model results with the HO<sub>2</sub> reaction removed may be somewhat misleading. The analysis in BULLOCK (2002) has shown that the low bias in simulated mercury wet deposition from the base CMAQ-Hg model is attributable to an even stronger low bias in the precipitation amount simulated by the model used to define meteorology for CMAQ simulations. Fig. 2 shows analyses of modeled versus observed Hg concentration in precipi-

tation with and without the HO<sub>2</sub> reaction in the CMAQ-Hg model. The mercury concentrations in precipitation simulated by the base model are already too high in most instances. Thus, the 23.9 % increase in total mercury wet deposition observed in this study from the elimination of the HO<sub>2</sub> reaction in CMAQ-Hg may in fact be a significant model adjustment in the wrong direction. Bullock (2002) showed that the base CMAQ-Hg model was simulating much higher mercury concentrations than were observed for the lighter-intensity precipitation events during the spring 1995 test period.

## CONCLUSIONS

The reduction of aqueous Hg<sup>2+</sup> species to Hg<sup>0</sup> by reaction with HO<sub>2</sub> is an important factor in the amount of mercury contained in cloud water and deposited in precipitation as simulated by the CMAQ-Hg model based on the chemical kinetics information available as of 2002. New information suggesting that this reaction may not be important in the real atmosphere causes obvious concern among the developers of the CMAQ-Hg model and



**Figure 2.** Scatter plots of the observed versus modeled concentrations of Hg in precipitation: (a) from the base CMAQ-Hg model; (b) from the CMAQ-Hg model without the HO<sub>2</sub> reaction.

other models that also simulate this reaction. These numerical models are a synthesis of our current understanding of atmospheric mercury behavior and general atmospheric transport and deposition processes. It is widely acknowledged that our scientific understanding of atmospheric mercury remains incomplete. Numerical modeling is continually used to test our understanding by comparing process simulations against available measurements. However, the degrees of freedom inherent in the system being modeled are numerous, as are the state variables not measured due to sampling costs or the lack of appropriate methods. Thus, modeling alone cannot be used to define the true nature of any specific state variable such as the rate of a particular chemical reaction. This model sensitivity study has demonstrated that

comprehensive atmospheric mercury models like the CMAQ-Hg model must be based on accurate reaction rate determinations from laboratory studies. Otherwise, the development and evaluation of deterministic air-quality models will remain a difficult and potentially confusing endeavor.

## DISCLAIMER

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency (EPA) and has been developed as part of an interagency agreement with the National Oceanic and Atmospheric Administration (NOAA). It has been subject to review by both EPA and NOAA, and has been approved for publication, although it may not necessarily reflect official Agency policy.

## REFERENCES

- BULLOCK, O. R., JR. & BREHME, K. A. (2002): Atmospheric mercury simulation using the CMAQ model: formulation description and analysis of wet deposition results; *Atmos. Env.*, Vol. 36, pp. 2135-2146.
- GŁRDFELDT, K. & JONSSON, M. (2003): Is bimolecular reduction of Hg(II) complexes possible in aqueous systems of environmental importance; *J. Phys. Chem. A*, Vol. 107, No. 22, pp. 4478-4482.
- PEHKONEN, S. O. & LIN, C.-J. (1998): Aqueous photochemistry of mercury with organic acids; *J. Air & Waste Man. Assoc.*, Vol. 48, pp. 144-150.
- VERMETTE, S., LINDBERG, S., BLOOM, N. (1995): Field tests for a regional mercury deposition network - sampling design and preliminary test results; *Atmos. Env.*, Vol. 29, pp. 1247-1251.

## Modeling the Atmospheric Transport and Deposition of Mercury to the Great Lakes

MARK COHEN

**Abstract:** To effectively address mercury pollution issues in the Great Lakes, it is important to know the relative importance of different sources of the contamination. This model-based analysis attempts to provide estimates of such source-receptor information.

A special version of the NOAA HYSPLIT\_4 model has been developed and used to estimate the atmospheric fate and transport of mercury in a North American modeling domain. The model is a three-dimensional Lagrangian puff model, with detailed simulation of dispersion, deposition, and chemical transformation processes for atmospheric mercury. Spatial and chemical interpolation procedures were used to expand the HYSPLIT\_4 modeling results to provide detailed source-receptor information.

Overall simulation results include the following: (a) transfer coefficient maps, showing the propensity of mercury of different forms [Hg(0), RGM, and Hg(p)] emitted throughout the model domain to atmospherically wet and dry deposit into each of the Great Lakes; (b) comparison of simulated and measured ambient concentrations and deposition fluxes at monitoring sites for model evaluation purposes; (c) estimates of the contribution of each of the 107,000 sources in a 1996 anthropogenic U.S./Canadian emissions inventory to atmospheric mercury deposition to the Great Lakes (and other receptors); (d) maps summarizing the source-receptor relationships for each lake; (e) information on the amount of mercury contributed to each lake from different distance ranges away from the lake and from different source categories; and (f) overall budgets for the atmospheric fate of emitted mercury of different forms.

While there are uncertainties in the emissions inventories and in the simulation of mercury's atmospheric fate and transport, model results were found to be reasonably consistent with wet deposition measurements in the Great Lakes region and with independent measurement-based estimates of deposition to Lake Michigan. The spatial patterns of source contributions to atmospheric mercury deposition were different for each lake, but sources up to 2000 km away from the Great Lakes contributed significant amounts of mercury. While there were significant contributions from incineration and metallurgical sources, coal combustion was generally found to be the largest contributor to atmospheric mercury deposition to the Great Lakes.

**Key words:** source-receptor, atmospheric model, Great Lakes

## Sequential Two-Photon LIF detection of Hg<sup>0</sup> and RGM

DEANNA DONOHOUE, DIETER BAUER, AND ANTHONY J. HYNES

Division of Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Science/University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149, USA;  
E-mail: ddonohoue@rsmas.miami.edu

**Abstract:** In an effort to understand the atmospheric distribution of gas phase elemental mercury, we have developed a sequential two-photon laser induced fluorescence (LIF) detection system for elemental mercury (Hg<sup>0</sup>) and reactive gaseous mercury (RGM). The sensitivity and time resolution associated with the configuration of the instrument will be discussed.

**Key words:** mercury detection, laser-induced fluorescence, RGM.

### INTRODUCTION

Mercury (Hg) is a known toxin. Understanding the atmospheric and biospheric interactions of mercury is essential in assessing both the ecological and health risks associated with the pollutant. Recent observations in the Arctic<sup>(1, 2)</sup> suggest that under certain conditions gas phase halogen chemistry may play a role in the fast atmospheric transformation of Hg<sup>0</sup>. An atmospheric transformation of mercury will impact the rates and mechanisms of deposition and re-emission. The most substantial challenge to evaluating the possibility of an atmospheric transformation of mercury is the slow time response of conventional methods for determining Hg<sup>0</sup> and RGM concentrations. The ability to monitor both the Hg<sup>0</sup> and RGM concentrations on a time scale that is fast compared to changes in environmental conditions, such as solar radiation, is critical to evaluating the potential role of rapid gas phase chemistry in the biogeochemical cycling of mercury. One novel system, which could provide the sen-

sitivity and the time resolution necessary for these measurements is a sequential two-photon LIF detector.

Sequential two-photon LIF involves the sequential excitation of two atomic transitions followed by detection of the emission from a third. This technique is extremely specific and precludes detection of anything other

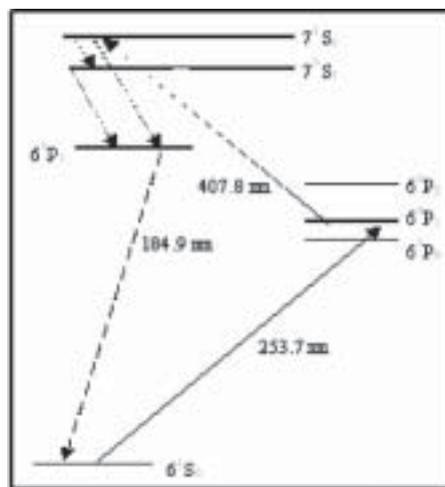


Figure 1. Excitation scheme for 2-photon LIF

than the species of interest. We have demonstrated the feasibility of a sequential two-photon laser induced fluorescence (LIF) system for the detection of  $\text{Hg}^0$ <sup>[3, 4]</sup>. A frequency doubled tunable dye laser is used to generate the initial excitation, the  $6^3\text{P}_1$ - $6^1\text{S}_0$  transition at 253.7 nm. This is followed by excitation of the  $7^1\text{S}_0$ - $6^3\text{P}_1$  transition at 407.8 nm, which is generated by a second dye laser. The  $7^1\text{S}_0$  level can be quenched or radiate to the  $6^1\text{P}_1$  level and the subsequent fluorescence at 184.9 nm from the  $6^1\text{P}_1$ - $6^1\text{S}_0$  transition is observed using a solar blind photomultiplier.

## RESULTS AND DISCUSSION

### Detection of $\text{Hg}^0$ :

Our lab-based study evaluated a sequential two-photon LIF system for applications in field measurements, in order to answer the pressing questions concerning the gas phase transformation of mercury. Our laser-based system has both the high sensitivity and temporal resolution required. The detection limit of the system is  $0.4 \text{ ng m}^{-3}$  when averaged for 1s with a repetition rate of 10 Hz. If the sample time is increased to 10s the detection limit is reduced to  $0.1 \text{ ng m}^{-3}$ . These results show that our system offers similar sensitivity to the Tekran 2537A with an increased time resolution of more than two orders of magnitude. This improved time resolution means it may be possible to apply sequential two-photon LIF detection as a sensor for micrometeorological techniques, such as eddy-correlation. Subsequent efforts have focused on the development of a more compact field instrument and investigation of the use of gold amalgamation prior to detection.

### Detection of RGM:

By coupling sequential two-photon LIF and KCl denuder sampling it is possible to determine atmospheric concentrations of RGM. The LIF system is limited to detection of  $\text{Hg}^0$ . However, RGM from ambient air can be collected on a KCl denuder and subsequently decomposed and desorbed as  $\text{Hg}^0$ . In an air or  $\text{N}_2$  based system, like the system employed for the detection of  $\text{Hg}^0$ , the detection sensitivity of the two-photon system is limited by the quenching of the excited states of mercury. By introducing an inefficient quencher, such as argon, as the bath gas, the sensitivity of the mercury detection is increased. Therefore, we can directly observe  $\text{Hg}^0$ , which decomposed and desorbs from the KCl denuder.

We sampled ambient air for 5 hours on a KCl denuder with a sample flow rate of  $10 \text{ L min}^{-1}$ . The KCl denuder was then flushed with argon at a slow flow rate of 200 sccm and heated to  $500 \text{ }^\circ\text{C}$ . The evolving  $\text{Hg}^0$  was detected by the LIF system and LIF area was plotted vs. time (Figure 2). This is the first direct observation of the evolving  $\text{Hg}^0$  from a KCl denuder. From this data we determined that sequential two-photon LIF is an effective detector of RGM in the atmosphere when coupled with KCl denuders. The reported 5-hour sample had a S/N ratio of 10/1; therefore it should be possible to detect RGM from KCl denuders that have been sampled for 30 min. This detection sensitivity could be enhanced by preconcentration of the evolving  $\text{Hg}^0$  on gold tubes, thereby further decreasing the necessary denuder sampling time. Another interesting result of this work is that the RGM is released from the denuder within the first 3 min. This is important because current sampling proce-

dures require a 20 min sample desorption step. This result indicate that this desorption step could be reduced without impacting the efficiency of the denuder.

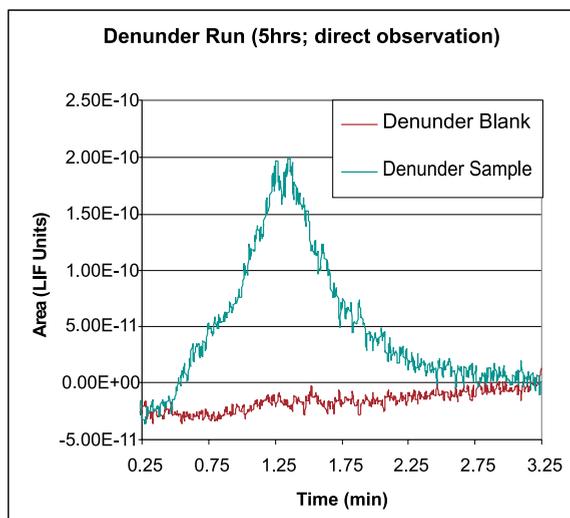


Figure 2. 5 hour denuder sample, Sample flow rate = 10 L min<sup>-1</sup>

## CONCLUSIONS

Sequential two-photon LIF offers a sensitive and specific method for the detection of Hg<sup>0</sup> and RGM at ambient levels. The challenge is to produce an instrument that is reasonably compact and that can be deployed for field measurements.

## REFERENCES

- [1] SCHROEDER, W. H., ANLAUF, K. G., BARRIE, L. A., LU, J. Y., STEFFEN, A., SCHNEEBERGER, D. R. AND BERG, T. (1998): Arctic springtime depletion of mercury; *Nature* 394, 331-332.
- [2] LINDBERG, S. E., BROOKS, S., LIN, C. J., SCOTT, K. J., LANDIS, M. S., STEVENS, R. K., GOODSITE, M. AND RICHTER, A. (2002) Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise; *Environ. Sci. Technol.* 36, 1245-1256.
- [3] BAUER, D., CAMPUZANO-JOST, P., HYNES, A. J. (2002): Rapid, ultra-sensitive detection of gas phase elemental mercury under atmospheric conditions using sequential two-photon laser induced fluorescence; *J. Environ. Monitor.* 4, 339-343.
- [4] BAUER, D., D'OTTONE, L., CAMPUZANO-JOST, P., HYNES, A. J. (2003): Gas phase elemental mercury: a comparison of LIF detection techniques and study of the kinetics of reaction with the hydroxyl radical; *J. Photoch. Photobio. A* 157, 247-256.

# Seasonal Behavior of Atmospheric Mercury Species in Polar Regions

RALF EBINGHAUS & CHRISTIAN TEMME

Institute for Coastal Research, GKSS Research Centre, Max-Planck-Str. 1, D-21502 Geesthacht, Germany; E-mail: ralf.ebinghaus@gkss.de

**Abstract:** Atmospheric Mercury Depletion Events (AMDEs) during polar springtime have been experimentally observed in the Arctic and in the Antarctic. During these events Hg(0) and ozone concentrations are significantly depleted and well correlated, whereas concentrations of ionic mercury species (RGM) simultaneously increase. During Antarctic summer however, we frequently observed decreasing Hg(0) concentrations along with simultaneous increases in RGM as well as ozone levels.

**Key words:** Atmospheric mercury, Speciation, Arctic, Antarctica, Mercury depletion events, AMDE

## INTRODUCTION

Atmospheric Mercury Depletion Events (AMDEs) have been observed in the Arctic as well as in the Antarctic (SCHROEDER ET AL., 1998; EBINGHAUS ET AL., 2002). A possible explanation for AMDEs may involve chemical or photochemical oxidation of Hg<sup>0</sup> to Hg<sup>2+</sup> by reactive halogen species [resulting either in particle-associated mercury (Particulate-Phase Mercury: PM) and/or RGM species]. This is accompanied by significantly enhanced deposition fluxes of mercury leading to unequivocally increased input of atmospheric mercury into the polar ecosystem. AMDEs in the north and south polar regions are strongly correlated with tropospheric ozone depletions. Polar mercury and ozone depletions coincide with simultaneous increases in tropospheric BrO<sup>?</sup> mixing ratios during spring as shown by differential optical absorption spectroscopy measurements from the ground and from satellite borne instruments.

For the atmospheric deposition, its mechanism and environmental impact the speciation of mercury

plays a key role. In this work we present concentration data of different atmospheric mercury species and indications for a variety of dynamic species transformations of atmospheric mercury during different seasons and in different hemispheres (Arctic spring and Antarctic spring and summer).

First results from an Arctic international field study in Ny Åesund, Spitsbergen (78°55'N, 11°90' E) are presented, showing that strong AMDEs of Gaseous Elemental Mercury (GEM) concentrations occurred during Arctic springtime 2003. Supplementary data were obtained during Antarctic spring giving experimental evidence for AMDEs and Australian summer respectively, where AMDEs normally do not occur.

## RESULTS AND DISCUSSION

### Annual time series of GEM at an Antarctic coastal site (Neumayer / 70°39'S, 8°15'W)

The results of GEM measurements and ground-level ozone concentrations for the

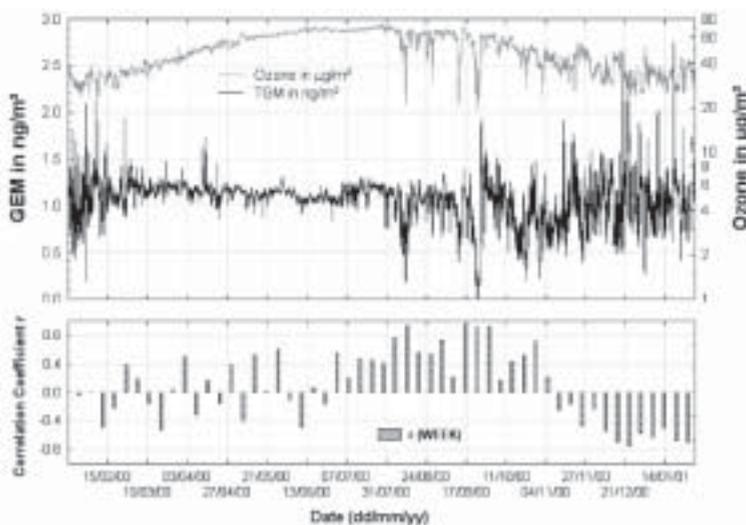
time period January 2000 to January 2001 are presented in Figure 1. The arithmetic mean of all GEM measurements between January 2000 and January 2001 was  $(1.06 \pm 0.24)$   $\text{ng m}^{-3}$  whereby the complete data set conform only broadly to a normal distribution.

The GEM concentration data shown in Figure 1 can briefly be characterised for three different time periods:

1. Between January and February 2000, and December to February 2000/01, GEM concentrations were highly variable [ $(1.04 \pm 0.28)$   $\text{ng m}^{-3}$ ]. During this time period, GEM and ozone concen-

trations are frequently negatively correlated (see next chapter)

2. Between March and July 2000 the GEM concentrations remained at a fairly constant level of  $(1.15 \pm 0.08)$   $\text{ng m}^{-3}$  while ozone concentrations constantly increased
3. Between August and November 2000 several simultaneous depletion events of surface-level GEM and ozone were detected with minimum daily average GEM concentrations of about  $0.1$   $\text{ng m}^{-3}$ . The arithmetic mean during MDE's was calculated with  $(0.96 \pm 0.28)$   $\text{ng m}^{-3}$ .



**Figure 1.** Annual time series of 1-h averaged atmospheric mercury and ozone concentrations and their weekly mean correlation coefficient ( $r$ ) measured at the Antarctic coastal site Neumayer.

### Mercury species concentrations during Antarctic summer

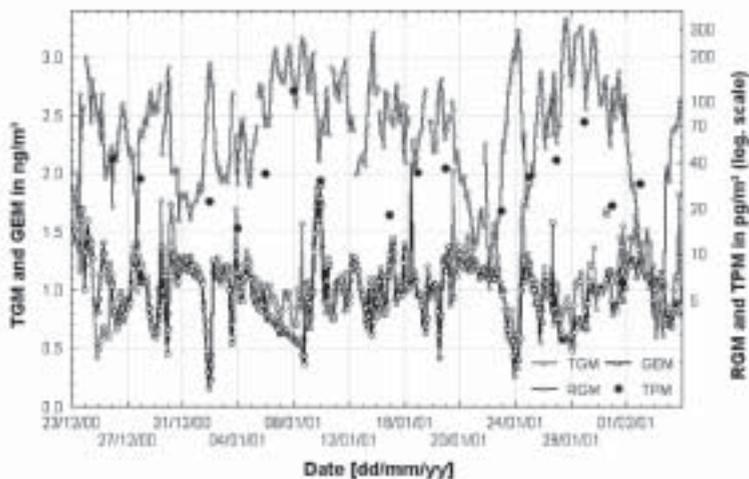
The Antarctic measurements reported here comprise a comprehensive dataset of different atmospheric mercury species carried out at research station Neumayer during Australian summer 2000/01.

GEM concentrations measured during the time period December 23, 2000 to February 5, 2001 represent typical southern hemispheric background values with a mean of  $(1.1 \pm 0.3)$   $\text{ng m}^{-3}$ . However, GEM concentrations during sunlit summer period varied more than during the dark winter months and decrease to concentrations  $< 0.3$   $\text{ng m}^{-3}$ . RGM concentrations varied between

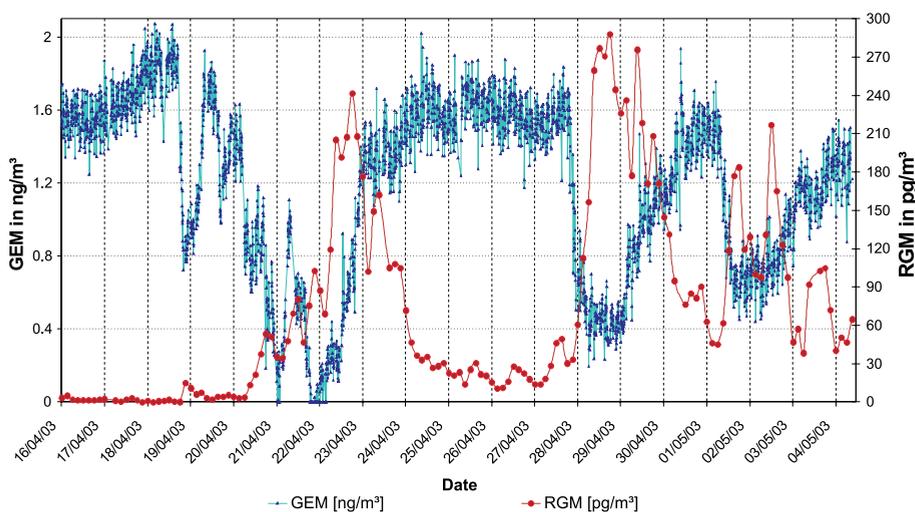
5  $\text{pg m}^{-3}$  to maximum levels of more than 300  $\text{pg m}^{-3}$ . In contrast to AMDEs during polar springtime a negative correlation with surface-level ozone concentrations during Antarctic summer was observed. The reaction mechanism could be explained by a gas-phase oxidation of elemental mercury by potential atmospheric oxidants such as hydroxyl radicals (TEMME ET AL., 2003).

### Mercury species concentrations during Arctic springtime

Strong Atmospheric Mercury Depletion Events (AMDEs) of Gaseous Elemental Mercury (GEM) concentrations occurred during Arctic springtime 2003 at Ny Llesund, Spitsbergen (78°55'N, 11°90'E) as shown in



**Figure 2.** Atmospheric mercury species concentrations at Neumayer Station between 23<sup>rd</sup> of December 2000 and 05<sup>th</sup> of February 2001. TGM, RGM and GEM levels are 2-hourly mean concentrations. TPM concentrations were obtained from 48-h integrated samples.



**Figure 3.** Atmospheric mercury species concentrations at Ny Llesund, Spitsbergen during April and May 2003.

Figure 3. Simultaneously Reactive Gaseous Mercury (RGM) concentrations increased by a factor of 10 to 20 to more than  $250 \text{ pg m}^{-3}$  during several AMDEs which were also associated with ground-level ozone depletions.

## CONCLUSIONS

AMDEs were observed during springtime at coastal Arctic and Antarctic stations. In both locations GEM concentrations were strongly correlated with ground-level ozone concentrations. It is hypothesized that Br atoms and/

or BrO radicals are involved in an autocatalytic chemical chain reaction which destroys ozone. The concurrent depletion of atmospheric boundary layer mercury (at times up to an altitude of  $\approx 1 \text{ km}$ ) is conceivably due to a reaction between gaseous elemental mercury and BrO free radicals.

In contrast, during Antarctic summer ozone concentrations were negatively correlated with GEM concentrations. Although  $\text{Hg}(0)$  must be oxidized to RGM species this reaction does not lead to a net-destruction of ozone as shown for springtime AMDEs.

## REFERENCES

- SCHROEDER, W. H., ANLAUF, K. G., BARRIE, L. A., LU, J. Y., STEFFEN, A., SCHNEEBERGER, D. R. & BERG, T. (1998): Arctic springtime depletion of mercury; *Nature*, Vol. 394, pp. 331-332.
- EBINGHAUS, R., KOCK, H. H., TEMME, C., EINAX, J. W., LOEWE, A. G., RICHTER A., BURROWS, J. P. & SCHROEDER, W. H. (2002): Antarctic springtime depletion of atmospheric mercury; *Environmental Science and Technology*, Vol. 36, pp. 1238-1244.
- TEMME, C., EINAX, J. W., EBINGHAUS, R. & SCHROEDER, W. H. (2003): Measurements of atmospheric mercury species at a coastal site in the Antarctic and over the south Atlantic Ocean during polar summer; *Environmental Science and Technology*, Vol. 37, pp. 22-31.

## Speciated Hg Measurements at a Rural Site Near Atlanta, GA, USA

E. S. EDGERTON<sup>1</sup>, J. J. JANSEN<sup>2</sup> & B. E. HARTSELL<sup>3</sup>

<sup>1</sup>ARA, Inc., 410 Midenhall Way, Cary, NC, 27513, USA, e-mail: ericedge@gte.net

<sup>2</sup>Southern Company, Birmingham, AL, USA, e-mail: JJJansen@southernco.com

<sup>3</sup>ARA, Inc., 720 Ave. F, Ste. 104, Plano, TX, 75074, USA, e-mail: hartsell@gte.net

**Abstract:** Recent inventories of atmospheric Hg emissions show that anthropogenic sources are important on local, regional and perhaps even global scales. As important as the magnitude of emissions is their chemical form. Elemental Hg has a long atmospheric lifetime (approx. 1 year) and is therefore broadly dispersed from the point of emission. Reactive gaseous Hg (RGM), on the other hand, is removed from the atmosphere much more quickly (atmospheric lifetime several days) and thus has a more localized range of influence than elemental Hg. Coal fired power plants (CFPPs) are recognized as a major source of atmospheric Hg. The form of Hg in CFPP emissions is a complex function of fuel composition, combustion characteristics and pollution control technology, but is generally considered to be about two-thirds RGM, one-third elemental Hg and less than a few percent particulate Hg.

The purpose of this research is to elucidate Hg speciation in coal-fired power plant (CFPP) plumes opportunistically observed at a rural research site., during a 2-year study period.

The experimental approach is to make continuous (60-minute resolution, or better) measurements of elemental Hg, RGM, and particulate Hg at a research site located approximately 60 km WNW of downtown Atlanta. Simultaneous measurements of tracer species (NO<sub>y</sub>, CO and SO<sub>2</sub>) and meteorological variables permit identification of episodes when the site is influenced by CFPP emissions. Back trajectory analysis (HY-SPLIT) and hourly CEM data are then used to identify the CFPP and to estimate transit time from the CFPP to the research site.

Statistically significant relationships were observed between RGM and SO<sub>2</sub> in CFPP plumes, however, substantially less RGM was observed than expected, based on coal analysis and estimated partitioning between elemental Hg and RGM. Analysis of roughly 2 dozen plume events showed RGM/SO<sub>2</sub> ratios between 10 percent and 50 percent of expectation. Episodes occurred without precipitation indicating that wet deposition could not account for the difference. Model investigations (see Seigneur abstract) all indicate that dry deposition could not account for differences. Results suggest significant errors and uncertainties in Hg partitioning estimates for CFPP emissions.

**Key words:** RGM, power plant plumes, atmospheric Hg

## Elemental Hg Measurements in Atlanta, GA, USA: Evidence for Mobile Sources?

ERIC EDGERTON & JOHN JANSEN<sup>1</sup>

<sup>1</sup>Southern Company, 600 18th Street N, 35203, Birmingham, USA

**Abstract:** Semi-continuous (1-hour integrated) speciated Hg measurements were made over a 2-year period at a research site located 4 km NW of downtown Atlanta, GA, USA. Measurements were performed using a Tekran 2537A analyzer equipped with 1130 and 1135 modules for reactive and particulate Hg, respectively. Ancillary measurements included continuous or semi-continuous surface meteorology, trace gases ( $O_3$ , CO,  $SO_2$ , NO,  $NO_2$ ,  $NO_y$ ,  $HNO_3$ ) fine particle mass and composition. Trace gas ratios  $CO/NO_y$  and  $SO_2/NO_y$  were used to identify periods when the data were influenced by mobile and coal-burning point sources, respectively. Mean Hg(0) concentrations for the 2-year period were  $1.8 \text{ ng/m}^3$ , or very similar to that for a rural site 55 km NW of the city ( $1.7 \text{ ng/m}^3$ ). Time series data show occasional peaks in Hg(0), sometimes exceeding  $5 \text{ ng/m}^3$ , or several times assumed hemispheric background. Excursions occurred at night during the winter and early spring, and when surface winds were very light ( $<0.5 \text{ mps}$ ). Inspection of trace gas data showed that excursions coincided with high concentrations of CO and  $NO_y$ . Regressions of Hg(0) vs. CO were found to be highly significant, with slopes ranging from  $0.4 \text{ ng/m}^3/\text{ppm}$  to  $1.6 \text{ ng/ml/ppm}$ , suggesting a mobile source for Hg. Using a carbon content of 83 % for gasoline and diesel fuel, regression slopes imply Hg content of motor vehicle fuel in the range of 14-54 ng/kg. Observations also show that Hg(0)/CO regression slopes increase from winter through spring; that is, with surface temperature. This raises the possibility that evasion may also be contributing to Hg(0) excursions. The full presentation will attempt to differentiate between evasion and mobile sources of Hg(0) in Atlanta.

**Key words:** Hg(0), mobile sources, evasion

## Speciated Hg Measurements at an Industrial and a Near-Coastal site in the Southeastern U.S.

ERIC EDGERTON & JOHN JANSEN<sup>1</sup>

<sup>1</sup>Southern Company, 600 18th Street N, 35203, Birmingham, USA

**Abstract:** Continuous, speciated Hg measurements are needed to understand sources, sinks and transformations of atmospheric mercury. This presentation will analyze recent speciated Hg data from a suburban site on the outskirts of Pensacola, FL (OLF) and an urban site in Birmingham, AL (BHM). OLF is located near the Gulf coast and, hence, opportunistically observes air parcels which have had significant residence time over the Gulf of Mexico as well as the U.S. landmass. Several industrial facilities, a paper mill and a power plant are also located within 20 km of the site. BHM is in a residential-industrial area about 5 km NW of downtown Birmingham. Numerous steel mills, coking facilities, pipe plants and power plants are in and around the city. Both sites are equipped with Tekran 2537A analyzers and 1130/1135 modules for semi-continuous (1-hour average) speciation of Hg(0), RGM and TPM. Other measurements include continuous (typically 1-minute average) surface meteorology, trace gases (CO, SO<sub>2</sub>, NO, NO<sub>2</sub>, NO<sub>y</sub>, HNO<sub>3</sub>, O<sub>3</sub>) and fine particle mass and composition. Early results show contrasts and similarities between the two sites. At OLF, mean Hg(0) concentrations are relatively invariant and near the hemispheric average of 1.7 ng/m<sup>3</sup>. At BHM, Hg(0) exhibits frequent sharp excursions (possibly from local industrial sources) and a mean concentration about 50 % higher than OLF. Overnight excursions of Hg(0), in association with elevated CO, also suggest possible mobile or area sources. RGM at both sites is characterized by brief spikes almost invariably associated with local sources. TPM, in contrast, is rarely above detection limit at either site and bears no clear association with any local source(s). The full presentation will analyze the first 6 months of data from these sites and attempt to derive local source signatures for Hg(0), RGM and TPM.

**Key words:** mercury speciation, mobile sources, industrial sources

# Atmospheric Mercury Emissions from Substrate and Fumaroles associated with two Hydrothermal Systems in the Western United States

MARK A. ENGLE<sup>1</sup>, MAE SEXAUER GUSTIN<sup>1</sup>, FRASER GOFF<sup>2</sup>, CATHY J. JANIK<sup>3</sup>,  
DALE A. COUNCE<sup>2</sup>, & JAMES J. RYTUBA<sup>3</sup>

<sup>1</sup>Nat. Res. and Env. Sci., University of Nevada, Reno, NV 89557, USA

<sup>2</sup>EES-6, Los Alamos National Lab, Los Alamos, NM 87545, USA

<sup>3</sup>US Geological Survey, Menlo Park, CA 94025, USA

**Abstract:** We quantified atmospheric Hg emissions from soils and fumaroles at two magma driven hydrothermal systems: Lassen Volcanic Center, CA (LVC) and Yellowstone Caldera, WY (YC). Mercury emissions from substrates and thermal features at LVC were estimated at 12.5 to 28.0 kg yr<sup>-1</sup> (10.3-19.0 kg yr<sup>-1</sup> from substrates [dominantly from background areas] and 2.2-8.9 kg yr<sup>-1</sup> from thermal features). At YC total emissions were estimated at 18.5-64.2 kg yr<sup>-1</sup>. Emission of Hg from soils in acidically altered areas were the dominant source (17.7-47.3 kg yr<sup>-1</sup>). This research demonstrates that emissions from hydrothermal features in volcanic areas are significant natural sources of Hg.

**Key words:** air-surface exchange; mercury; flux; geothermal; hydrothermal

## INTRODUCTION

Despite significant progress characterizing atmospheric mercury (Hg) emissions from natural systems there are still some data gaps on emissions from specific sources. One of these is Hg emission from substrate and fumaroles associated with active hydrothermal systems. In an attempt to reduce this data gap, this project focused on quantifying Hg emissions from two types of hydrothermal systems.

The Lassen Volcanic Center (LVC) (637 km<sup>2</sup>), located at the southern end of the Cascade mountain range in northern California, last erupted in 1917 and is a product of subduction-related volcanism. The

Yellowstone Caldera (YC), Wyoming, USA, a 2,294 km<sup>2</sup> volcanic complex that formed during the last 0.6 Ma, has an active hydrothermal system that is driven by magmas evolved from an underlying mantle hotspot. Both systems contain one or more high-temperature, liquid-dominated reservoirs ( $\geq 250$  °C) and localized vapor-dominated zones.

At all locations, mercury fluxes were measured using established flux chamber methods, along with a suite of environmental parameters. Fumarole gas samples, collected using KOH-filled double-port evacuated flasks or a Lumex Zeeman Atomic Absorbance Spectrometer (Lumex), were taken from representative thermal sites in each study area.

## RESULTS AND DISCUSSION

### *Lassen Volcanic Center:*

Over the last 2 years, 192 Hg flux measurements at 31 sampling points have been made at representative areas including: areas distal to thermal features and hydrothermal alteration (background data), areas of fossil hydrothermal alteration (hydrothermally active in the past), and hydrothermally active areas at LVC.

Summarized results from Hg flux measurements are presented in Table 1. Background and altered areas had similar Hg fluxes and Hg substrate concentrations and were combined for analysis. Average fluxes for each sampling point ranged from  $-80.1$  to  $42.8 \text{ ng m}^{-2} \text{ h}^{-1}$  for background and fossil alteration areas and  $16.2$  to  $103 \text{ ng m}^{-2} \text{ h}^{-1}$  for thermally active areas. Highest fluxes were associated with areas of thermal activity.

Regression analysis was used to determine environmental parameters that were best correlated with Hg fluxes. Measured parameters included: soil temperature, air temperature, relative humidity, light intensity, and Hg concentration of the substrate beneath the flux chamber. Of these, the natural log of Hg concentration in the substrate (soil) was

found to be the most predictive, although the correlation is not particularly strong ( $r^2 = 0.26$ ,  $p < 0.01$ ). Using individual flux measurements from background and fossil alteration areas a significant correlation between light and Hg flux was observed ( $r^2 = 0.45$ ,  $p < 0.01$ ). Concentrations in the substrate for these areas were low ( $<100 \text{ ppb}$ ) and thus were not a significant factor driving flux.

Using this correlation between light and Hg flux at background and fossil alteration areas and 24-hour average light intensity data collected at 2 sites in LVC near the autumn equinox, area Hg emissions were estimated. Emissions were then adjusted by assuming that no emission occurs from background/altered sites during snow cover ( $\sim 7$  months a year) and 30 % of the annual deposited atmospheric Hg is re-emitted (and subtracted from our estimates; using Hg deposition network [MDN] data). In thermally active areas, the mean and median of the fluxes were scaled up to the area impacted by thermal features. This calculation assumed that no snow accumulated in thermal areas and that daily variations in flux are small. These initial results suggest that Hg emissions from natural substrates in LVC are  $\sim 10.4$ - $19.1 \text{ kg yr}^{-1}$  and that  $>98$  % of these emissions are from

**Table 1.** Results from Hg soil flux measurement in the Lassen Volcanic Center. \*Adjusted for re-emitted Hg from atmospheric deposition and lack of emission due to snow cover.

Area	Flux $\text{ng m}^{-2} \text{ hr}^{-1}$	number of sample locations	Area $\text{km}^2$	Emission* $\text{kg yr}^{-1}$
Background and fossil alteration	mean +/- std. dev. 10.2 +/- 23.7 median 10.5	27	637	10.1 18.9
Thermally active	mean +/- std. dev. 57.5 +/- 44.6 median 55.5	4	0.44	0.22 0.21

background and fossil alteration areas. The lack of contribution from soil emission from thermally active areas is due to their small proportion of the total study area (<1 %). Emissions from background and fossil alteration areas at Lassen were elevated relative to other background areas, especially given the low Hg concentration in the substrate. This may be a result of elevated Hg concentrations at depth and/or regionally elevated heatflow is producing elevated emissions throughout the study area.

To determine atmospheric emissions from thermal features, 19 Lassen fumaroles were sampled for Hg using KOH-filled evacuated flasks. Initial results from 3 flasks indicate Hg:CO<sub>2</sub> range from 1:1.0-5.0 x 10<sup>8</sup>. These were applied to the annual CO<sub>2</sub> emission budget from Lassen thermal features of 3.5 x 10<sup>7</sup> kg yr<sup>-1</sup> (ROSE AND DAVISSON, 1996) to provide a roughly estimated emission of 2.2 to 8.9 kg Hg yr<sup>-1</sup> from thermal features.

#### *Yellowstone Caldera:*

During the autumn of 2003, 550 Hg fluxes at 151 sampling locations in 13 areas were measured across YC. Locations were classified based on the type or lack of hydrothermal alteration present: unaltered (background), neutral alteration (areas where neu-

tral pH hydrothermal fluids typically precipitate silica and travertine), and acidic alteration (areas where acidic hydrothermal fluids have leached out and converted rocks to clay minerals and other low pH phases). Unlike LVC, most of the altered areas are thermally active. For data analysis, flux measurements for each sampling point were averaged from 1-100 individual flux measurements taken at that location. Additional measurements obtained north of the caldera by Abbott et al. (this volume).

Results from YC are presented in Table 2. Fluxes were highest in the areas of acidic alteration, followed by neutral alteration, and the lowest fluxes from the unaltered areas.

Statistical regression analysis was applied to determine possible relations between Hg flux and other parameters using data for each alteration type. This analysis provided poor results for single predictors ( $r^2 = 0.082-0.28$ ,  $p > 0.05$ ). Because of the lack of statistical strength of individual predictor variables at YC, mean and median fluxes for each alteration area were applied and scaled up as a first estimate (Table 2). For background areas, it was assumed that no flux occurred during the snow season (November-April). Re-emitted (assumed 30 %) Hg derived from atmospheric deposition using MDN data was

**Table 2.** Results from Hg soil flux measurement in the Yellowstone Caldera. \*Adjusted for re-emitted Hg from deposition and lack of emission due to snow cover.

Area	Flux ng m <sup>-2</sup> hr <sup>-1</sup>	number of sample locations	Area km <sup>2</sup>	Emission* kg yr <sup>-1</sup>
Background and fossil alteration	mean +/- std. dev. 10.2 +/- 23.7 median 10.5	27	637	10.1 18.9
Thermally active	mean +/- std. dev. 57.5 +/- 44.6 median 55.5	4	0.44	0.22 0.21

also subtracted from emissions for all areas. Emissions from neutrally and acidically altered generally overlie hydrothermal systems and thus effects from snow were ignored. These preliminary Hg emission estimates range from 18.4-63.2 kg yr<sup>-1</sup> and suggest that the largest source of Hg emissions from substrate in the caldera (75- 96 %) occur from acidically altered areas.

Our initial estimates suggested that very high loads of Hg were being emitted from YC fumaroles. Mud Volcano (MV) is the dominant vapor-dominated system in the caldera and was selected as the primary focus of this investigation. Mercury concentrations in fumaroles at MV ranged from 722 to 29,970 ng m<sup>-3</sup> (mean = 8,324 ng m<sup>-3</sup>, median = 1,302 ng m<sup>-3</sup>; n=4) as determined by a Lumex Hg analyzer. These mean and median concentrations were applied to the CO<sub>2</sub> emission estimates from fumaroles at MV by Werner et al. (2000) of 2.4 x 10<sup>8</sup> to 4.0 x 10<sup>9</sup> mol yr<sup>-1</sup> to derive rough estimates of 0.10 to 1.07 kg of Hg per year. This suggests that Hg emissions from fumaroles may be a fairly small source of atmospheric mercury relative to emissions from substrates at YC.

## CONCLUSIONS

Results from this paper demonstrate that Hg emissions from both soils and fumaroles in hydrothermal systems are significant natural sources of atmospheric Hg and their emissions are similar to those of "fossil" hydrothermal systems (2.4-110 kg yr<sup>-1</sup>) from which fluxes have been scaled (GUSTIN, 2003). Mer-

cury emissions from soils at LVC were estimated at 10.3-19.0 kg yr<sup>-1</sup> (dominantly from background areas) with an additional output of 2.2-8.9 kg yr<sup>-1</sup> from fumaroles. At Yellowstone, the dominant source of Hg emissions appears to be from soils in acidically altered areas (17.7-47.3 kg yr<sup>-1</sup> of the 18.5-64.2 kg yr<sup>-1</sup> emitted from all sources). These estimates also suggest that the much smaller LVC emits 1.5 to 2.5 times more Hg per unit area than YC. This variation in Hg emissions between the study areas reflects the different geologic and geochemical environments at these volcanic centers.

## Acknowledgements

The research was funded by EPA STAR grant R82980001 and EPRI. We would like to acknowledge the National Park Service, Mike Abbott (INEEL), Nancy Hinman (U Montana), and the UNR team (Tony Giglini, Ben Hatchett, Melissa Markee, and Richard Zehner). We would also like to thank the USGS for use of a Tekran Hg analyzer.

## REFERENCES

- GUSTIN, M. S. (2003): Are mercury emissions from geologic sources significant? A status report; *Sci. Total Env.*, Vol. 304, No. 1-3, New York.
- ROSE, T. P. & DAVISSON, M. L. (1996): Radiocarbon in hydrologic systems containing dissolved magmatic carbon dioxide; *Science*, Vol. 273, No. 5280, pp. 1367-1370, Washington.
- WERNER, C., BRANTLEY, S. L. & BOOMER, K. (2000): CO<sub>2</sub> emissions related to the Yellowstone volcanic system 2. Statistical sampling, total degassing, and transport mechanisms; *J. Geophys. Res.*, Vol. 105, No. B5, pp. 10831-10846, Washington.

## Investigation of the effect of tropospheric oxidants on Hg emissions from substrates

MARK A. ENGLE<sup>1</sup>, MAE SEXAUER GUSTIN<sup>1</sup>, STEVE E. LINDBERG<sup>2</sup>, & ALAN W. GERTLER<sup>3</sup>

<sup>1</sup>Nat. Res. and Env. Sci., Univ. of Nevada, Mail Stop 370, Reno, NV 89557, USA; E-mail: engle@unr.nevada.edu

<sup>2</sup>Env. Sci. Div., Oak Ridge National Lab., Oak Ridge, TN 37831, USA

<sup>3</sup>Div. Atmos. Sci., Desert Research Institute, Reno, NV 89512, USA

**Abstract:** This paper describes experiments investigating the effect of atmospheric oxidants, specifically O<sub>3</sub>, on Hg emission from a variety of Hg-bearing substrates. Substrates with Hg(II) as the dominant Hg phase demonstrated a 1-3 order of magnitude increase in elemental Hg (Hg<sup>0</sup>) flux and a 1.5- to 10-fold increase in reactive gaseous mercury (RGM) flux in the presence of O<sub>3</sub> (up to 69 ppb) relative to oxidant-free air. In contrast, Hg<sup>0</sup> fluxes from two Hg<sup>0</sup>-amended substrates decreased 40-93 % during exposure to O<sub>3</sub> relative to oxidant-free air. RGM fluxes from the latter increased immediately after exposure to O<sub>3</sub> but then decreased quickly. Specific chemical mechanisms that produced these trends are not well understood and we speculate that increased emissions of Hg<sup>0</sup> and RGM from substrates in the presence of O<sub>3</sub> may be a result of physical displacement from the substrate surface by O<sub>3</sub> and possible heterogenous formation of RGM. Inhibition of Hg<sup>0</sup> emission from Hg<sup>0</sup>-amended substrates may occur through heterogenous oxidation of Hg<sup>0</sup> to the much less volatile HgO species via reaction with O<sub>3</sub>.

**Key words:** air-surface exchange, ozone, mercury, reactive gaseous mercury

### INTRODUCTION

Mercury emissions from natural substrates typically exhibit a diel pattern that correlates with light intensity (GUSTIN ET AL., 2002) and temperature (POISSANT ET AL., 1999). However, ZHANG AND LINDBERG (1998) observed strong diel cycles of gaseous elemental Hg (Hg<sup>0</sup>) emission from soil samples during exposure to ambient air in a dark, constant temperature laboratory environment but were unable to explain the mechanism involved. They suggested interaction with an unknown chemical substance in ambient air. During laboratory experiment similar to Zhang and Lindberg's, we observed several large pulses

of Hg<sup>0</sup> emission from a sample of mine tailings that correlated strongly ( $R^2=0.98$ ;  $p<0.05$ ) with concentrations of O<sub>3</sub> in the incoming ambient air. Fluxes of reactive gaseous mercury (RGM) also appeared to vary with O<sub>3</sub> concentrations. These initial results initiated further study on the effects of O<sub>3</sub> and other atmospheric oxidants on controlling atmospheric Hg emissions substrates.

In this laboratory study, seven substrate samples were exposed to oxidant free air (cleaned air), O<sub>3</sub> enriched (50 ppb) cleaned air, and ambient air (0 to 70 ppb O<sub>3</sub>). Fluxes of RGM and Hg<sup>0</sup> from each substrate were measured during 24-hour air exposures. The

experiments were conducted in a temperature-controlled environment in the absence of light to minimize effects from other factors that control Hg emissions. Hg(II)- and Hg<sup>0</sup>-bearing substrates were used in this study and are described below:

*Hg(II)-bearing substrates:*

Oklahoma Soil: (OK) Clay-rich soil (5 ppb Hg) from south-central Oklahoma.

Bessel Mill Tailings: (BMT) Mercury-contaminated mine tailings from the Carson River Superfund site, Nevada (347,000 ppb Hg).

Washington Hill Prospect Waste: (WHP) Naturally Hg-enriched mine waste from a Mo-W porphyry deposit in western Nevada (229,000 ppb Hg).

HgCl<sub>2</sub>-amended sand: (HgCl<sub>2</sub> sand) Clean sand (Fisher brand) amended with HgCl<sub>2</sub> solution (313 ppb Hg).

HgS-amended sand: (HgS sand) Clean sand amended with HgS<sub>(s)</sub> (24,400 ppb Hg).

*Hg<sup>0</sup>-amended substrates:*

Hg<sup>0</sup>-amended Pyramid Lake Sand: (PLS) Sand from Pyramid Lake, Nevada rich in feldspar, muscovite, biotite, and quartz amended with Hg<sup>0</sup>.

Hg<sup>0</sup>-amended sand: (Hg<sup>0</sup> sand) Clean sand (quartz-dominated) amended with Hg<sup>0</sup>.

## RESULTS AND DISCUSSION

Results from experiments are summarized in Table 1. Data are corrected for system blanks and fluxes were calculated based on subtraction of Hg<sup>0</sup> and RGM in incoming ambient air from that in the chamber divided by the surface area of the substrate in the chamber times the flow rate of the air moving through the chamber.

**Table 1.** 24-hour average +/- standard deviation Hg<sup>0</sup> and RGM fluxes (ng m<sup>-2</sup> h<sup>-1</sup>) from substrates during exposure to different air sources. \*Indicates fluxes are significantly larger than fluxes for the same substrate in cleaned air (p<0.01). †Indicates fluxes are significantly smaller than fluxes for the same substrate in cleaned air (p<0.01). O<sub>3</sub> concentrations in ambient air ranged from 0 to 69 ppb with 24-hour average concentrations ranging from 19 to 42 ppb.

Substrate	Hg <sup>0</sup> flux in cleaned air	Hg <sup>0</sup> flux in O <sub>3</sub> -enriched air	Hg <sup>0</sup> flux in ambient air	RGM flux in cleaned air	RGM flux in O <sub>3</sub> -enriched air	RGM flux in ambient air
<i>Hg(II)-bearing substrates</i>						
OK	8.3 +/- 27.8	40.5 +/- 27.2*	--	7.89 +/- 4.28	15.1 +/- 3.88*	--
WHP	76.7 +/- 59.3	3216 +/- 1068*	3820 +/- 882*	0.28 +/- 0.33	11.0 +/- 2.42*	29.4 +/- 4.25*
HgCl <sub>2</sub> sand	343 +/- 233	1490 +/- 348*	1790 +/- 685*	174 +/- 123	669 +/- 125*	600 +/- 112*
HgS sand	-3.8 +/- 156	1632 +/- 257*	1600 +/- 315*	7.52 +/- 3.13	66.3 +/- 16.6*	67.6 +/- 0.55*
BMT	605 +/- 151	5946 +/- 2653*	37200 +/- 10500*	4.35 +/- 0.50	5.72 +/- 0.55*	23.9 +/- 4.78*
<i>Hg<sup>0</sup>-amended substrates</i>						
PLS	72830 +/- 16810	17410 +/- 10230†	--	13.6 +/- 2.11	19.0 +/- 2.73*	--
Hg <sup>0</sup> sand	200730 +/- 8060	14460 +/- 30840†	119030 +/- 63640†	7.07 +/- 2.11	5.17 +/- 4.08	11.7 +/- 1.76*

*Emissions from Hg(II)-bearing substrates :*

All Hg(II) containing substrates showed a significant ( $p < 0.01$ ) increase in  $\text{Hg}^0$  and RGM emissions during exposure to  $\text{O}_3$ -enriched air relative to cleaned air. Exposure of the substrates to near constant concentrations of  $\text{O}_3$  (50 ppb) produced an immediate large pulse of both  $\text{Hg}^0$  and RGM. Fluxes of  $\text{Hg}^0$  then asymptotically declined to a lower but still elevated flux while RGM fluxes either continued to increase slightly throughout the rest of the run or decreased asymptotically. Elemental mercury emissions increased by 1-3 orders of magnitude and RGM emissions increased by factors of roughly 1.5 to 10 (24-hour averages). Mercury flux from substrate samples exposed to ambient air also exhibited significant ( $p < 0.01$ ) increases relative to cleaned air, except for fluxes from the OK sample which were too small to separate from incoming Hg concentrations. Increases in  $\text{Hg}^0$  and RGM emissions followed temporal patterns of  $\text{O}_3$  concentrations in the incoming ambient air (regression relationships were significant at  $p < 0.01$  for all substrates except for the HgS-amended sand). Better correlations were observed between  $\text{O}_3$  and  $\text{Hg}^0$  emissions from the natural substrates and may be related to increased  $\text{O}_3$  reactivity with Al- and Fe-bearing minerals absent in the amended substrates.

*Emissions from Hg<sup>0</sup>-amended substrates:*

Unlike the Hg(II)-bearing substrates,  $\text{O}_3$  decreased Hg emissions from both  $\text{Hg}^0$ -amended substrates by 40-95 % in both  $\text{O}_3$ -enriched air and ambient air relative to cleaned air [ $p < 0.01$ ]; only  $\text{Hg}^0$  sand was exposed to ambient air]. During exposures of the substrates to  $\text{O}_3$ -enriched air,  $\text{Hg}^0$  concentrations inside the reaction chamber

dropped off asymptotically while RGM emissions showed an immediate pulse in emission followed by an asymptotic decrease. During ambient air exposure of  $\text{Hg}^0$  sand,  $\text{Hg}^0$  fluxes decreased with increasing  $\text{O}_3$  concentrations ( $R^2 = 0.71$ ,  $p < 0.01$ ). RGM fluxes positively followed temporal patterns of  $\text{O}_3$  concentration.

These results demonstrate that  $\text{O}_3$  in ambient air controls  $\text{Hg}^0$  and RGM emissions from substrate and the magnitude of influence is proportional to the  $\text{O}_3$  concentration. For Hg(II)-amended substrates, increased emissions of  $\text{Hg}^0$  with  $\text{O}_3$  are thought to be a result of physical displacement of  $\text{Hg}^0$  from the substrate surface. RGM emitted in response of  $\text{O}_3$  exposure, could be formed from homogeneous gas-phase oxidation of  $\text{Hg}^0_{(g)}$  or heterogenous reactions on the substrate surface. Experiments to test the potential for homogenous gas-phase reaction between  $\text{Hg}^0_{(g)}$  and  $\text{O}_3$  failed to produce RGM, demonstrating that this is not the source of increased RGM air concentrations in the Hg(II)-bearing substrate experiments. Rather, the increased RGM concentrations are hypothesized to be due to 1) physical displacement of the RGM on the soil by  $\text{O}_3$  or other oxidants or; 2) heterogenous oxidation of  $\text{Hg}^0$  on the substrate surface and subsequent emission. The exact chemical reaction for RGM formation is unknown. Inhibition of  $\text{Hg}^0$  emission from  $\text{Hg}^0$ -amended substrates in the presence of  $\text{O}_3$  is likely a result of heterogenous oxidation of  $\text{Hg}^0$  to  $\text{HgO}$ ;  $\text{HgO}$  is  $\sim 10^{11}$  times less volatile than  $\text{Hg}^0$ . The pattern of a pulse of RGM release followed by rapid decline of RGM emission from  $\text{Hg}^0$ -amended substrates in the presence of  $\text{O}_3$  is not well understood.

## CONCLUSIONS

Results from this work demonstrate that atmospheric oxidants appear to control Hg emissions from substrates. Speciation of the Hg in the substrate sample appears to influence the net affect, with Hg(II)-bearing substrates emitting significantly more Hg<sup>o</sup> and RGM in the presence of O<sub>3</sub> and Hg<sup>o</sup> emissions from Hg<sup>o</sup>-amended substrates being strongly inhibited by O<sub>3</sub>. RGM emissions from Hg<sup>o</sup>-amended substrates exhibit an initial increase in emission followed by an asymptotic decrease in the presence of O<sub>3</sub>.

Potential implications of this are related to increasing concentrations of atmospheric oxidants, such as O<sub>3</sub>, over the last 100 years as a result of human activity. Because most soil-bound Hg is thought to be in the Hg(II) state (ANDERSSON, 1979), results from this study suggest that increased oxidant emissions could produce a net increase in Hg<sup>o</sup> and RGM emissions from natural substrates.

## REFERENCES

- ANDERSSON, A. (1979): Mercury in soils; In *The biogeochemistry of mercury in the environment* (J. NRIAGU, Ed.), pp. 79-112, Amsterdam.
- FITZGERALD, W. F., ENGSTROM, D. R., MASON, R. P., AND MATER, E. A. (1998): The case for atmospheric mercury contamination in remote areas; *Env. Sci. Tech.*, Vol. 32, No. 1, pp. 1-7, Washington.
- GUSTIN, M. S., BIESTER, H. & KIM, C. S. (2002): Investigation of the light-enhanced emission of mercury from naturally enriched substrates; *Atm. Env.*, Vol. 36, No. 20, pp. 3241-3254, Amsterdam.
- POISSANT, L., PILOTE, M. & CASIMIR, A. (1998): Mercury flux measurements in a naturally enriched area: Correlation with environmental conditions during the Nevada Study and Tests of the Release of Mercury from Soils (STORMS); *J. Geophys. Res.*, Vol. 104, No. D17, pp. 21845-21858, Washington.
- ZHANG, H. & LINDBERG, S. E. (1998): Processes influencing the emission of mercury from soils: a conceptual model; *J. Geophys. Res.*, Vol. 104, No. D17, pp. 21889-21896, Washington.

Subsequent deposition of the released Hg is also likely to occur with increasing oxidants in the atmosphere. This would cause an increase in the rate of global Hg cycling and could contribute to observed elevated Hg concentrations observed in long-term Hg records that are typically attributed to a contemporaneous increase in Hg emission from industrial sources (FITZGERALD ET AL., 1998). This previously unrecognized process has important implications for proposed effective strategies to reduce atmospheric Hg deposition and impacts.

## Acknowledgements

Funding for this project was provided by the U.S. Environmental Agency Program STAR grant #R82980001. A Tekran 1130 mercury speciation unit was borrowed from the U.S. Dept. of Energy and the O<sub>3</sub> generator was made available by the Division of Atmospheric Sciences at the Desert Research Institute.

## Modern and Historic Atmospheric Mercury Fluxes in Northern Alaska: Global Sources and Arctic Depletion

DANIEL R. ENGSTROM<sup>1</sup>, WILLIAM F. FITZGERALD<sup>2</sup>, CARL H. LAMBORG<sup>3</sup>,  
CHUN-MAO TSENG<sup>4</sup>, & PRENTISS H. BALCOM<sup>2</sup>

<sup>1</sup>St. Croix Watershed Research Station, Science Museum of Minnesota, Marine on St. Croix, MN 55047 USA; E-mail: dengstrom@smm.org

<sup>2</sup>Department of Marine Sciences, University of Connecticut, Groton, CT USA

<sup>3</sup>Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA USA

<sup>4</sup>National Center for Ocean Research, National Taiwan University, Taipei, Taiwan

**Abstract:** We reconstruct from lake-sediment archives atmospheric Hg deposition to Arctic Alaska over the last several centuries and constrain a contemporary lake/watershed mass-balance with real-time measurement of Hg fluxes in rainfall, runoff, and evasion. Results indicate that (1) anthropogenic Hg impact in the Arctic is of similar magnitude to that at temperate latitudes; (2) whole-lake Hg sedimentation determined from 55 <sup>210</sup>Pb-dated cores from the five small lakes demonstrates a 3-fold increase in atmospheric Hg deposition since the advent of the Industrial Revolution, (3) due to high soil Hg concentrations and relatively low atmospheric deposition fluxes, erosional inputs to these lakes is more significant than in similar temperate systems, (4) volatilization accounts for about 20 % of the Hg losses (evasion and sedimentation), and (5) another source term is needed to balance the evasional and sedimentation sinks. This additional flux, though small and non-dramatic, is comparable to direct atmospheric Hg deposition. It may be due to some combination of springtime Arctic depletion and more generalized deposition of reactive gaseous Hg species. As the degree of secular change in these cores is similar to that from other remote sites at lower latitudes, we conclude that if this unknown flux term represents the impact of springtime depletion, that this phenomenon was active to some extent in the pre-industrial past.

**Key Words:** Arctic depletion, lake sediments, deposition, historic trends, soils

# First Mercury Determination in Snow from high-mountain Sites in the Siberian Altai and Swiss Alps as Reflection of Present Atmospheric Concentrations of Hg

STELLA EYRIKH<sup>1,2</sup>, MARGIT SCHWIKOWSKI<sup>1</sup>, HEINZ W. GÄGGELER<sup>1</sup>,  
LEO TOBLER<sup>1</sup> AND TATYANA PAPINA<sup>2</sup>

<sup>1</sup> Paul Scherrer Institut, 5232 Villigen PSI, Switzerland, e-mail: stella.eyrikh@psi.ch

<sup>2</sup> IWEP, SB RAS, 1 Molodezhnaya St., 656038 Barnaul, Russia

**Abstract:** High-altitude mountain glaciers are well suited as paleoarchives which allow to estimate the historical and present-day atmospheric emission of air pollutants both on a global and local scale. The Altai mountain region (Russia) is especially interesting for Hg, since it's located close the large Hg mine in Aktash (one of largest Hg producers in the USSR) and to the sources of air pollution in East Kazakhstan and South Siberia during Soviet Union times. Thus, local, regional and long-range transport is supposed to contribute to Hg contamination in this area. The preliminary data is the first data on Hg levels in snow ever obtained for the Altai region. The Hg concentrations in the snow pit (0.8-1.4 ng/l) and in the firn core (most values are around 1.2-1.8 ng/l) from Belukha glacier (3896 m asl) are comparable with those (1.5 - 2 ng/l) determined in snow from the Jungfrauoch (3500 m asl, Swiss Alps) and Hg levels reported for the snow from French Alps. The similar Hg levels found in high-alpine snow in Central Asia and in Europe indicate that present-day Hg level in the Altai region is determined mostly by long-range transport and global emissions of Hg.

**Key words:** Hg in snow, Altai, Swiss Alps, high-mountain glaciers, CV ICP-MS.

## INTRODUCTION

Many studies have been conducted on Hg in water and other compartments of environment in recent years. With regard to ice and snow much less work has been performed. Most of it concerns the Hg behavior in fresh snow, processes of transformation of different Hg forms and historical records of Hg occurrence in remote areas (Greenland, Arctic and Antarctic)<sup>[1,2]</sup>. Regarding the Hg content in mid- and low-latitude glaciers, which are also suitable as paleoarchives of natural and anthropogenic Hg emissions, only scarce information is available<sup>[3,4]</sup>. The Altai mountain region

is interesting for a Hg study because it might be influenced by Hg emissions from the industry in East Kazakhstan and Southwest Siberia and also by local Hg pollution from the Aktash smelter and natural mercury deposits (one of the major in Russia). The aim of our study is to establish the analytical method using ICP-MS equipped with a Hydrogen Generator and to apply this method to samples of snow and ice from the Altai to assess the present and historical air pollution level. Here we present preliminary results obtained from the analysis of present snow layers from the Altai and the Alps and of a 6 m firn core from Belukha glacier. This firn core at this site covers the period of ~ 1995 to 2000.

## EXPERIMENTAL PART

The Altai mountain region is located on the border between East Kazakhstan, Southwest Siberia, Northwest China, and West Mongolia. The Altai belongs to the large Kuznetsk-Altai mercuriferous belt stretching along the South of Siberia. One of the major Hg mines is operated in Aktash.

Our studies were conducted in the Altai Mountains in July 2000, where a 6 m firm core was drilled and snow samples were collected from a 1.5 m deep snow pit on the Belukha glacier (3896 m asl, 28 samples) and from a 0.7 m snow pit on the Aktru glacier (3150 m asl, 7 samples). Snow samples were also collected from a 1.3 m snow pit on the high-mountain site Jungfrauoch (3500 m asl, 68 samples) in the Swiss Alps. Samplings and analysis were carried out following recommendation of a protocol for ultra-clean work. All samples were transported frozen to PSI and kept in frozen condition until

analysis. The firm core was cut into 3.5 cm segments resulting in 152 samples. Snow and ice samples for Hg determination were acidified with ultra-pure  $\text{HNO}_3$  and melted at room temperature inside a clean bench<sup>[5]</sup>.

The precleaning procedure and types of sample containers were tested both with standard solutions and with real snow samples from the Alps. Depending on the type of container and the precleaning procedure, the concentration of Hg in samples can increase more than two-fold. Containers “drying” (after precleaning treatment) that is commonly used for other trace metal analysis was found unsuitable for Hg analysis. Containers must be kept filled with acidified MQ-Water before use. Referring to<sup>[6]</sup> PFA is the best suited material of fluorinated polymers for extreme trace metal analysis. Nevertheless we found that high-density polyethylene (HDPE) material is also quite suitable for storage and Hg analysis after appropriate pretreatment.



**Figure 1:** Map of the Altai mountain region, showing the locations of Belukha and Aktash mine

## ANALYTICAL TECHNIQUE

Hg was determined by inductively coupled plasma mass spectrometry ICP-MS (ELEMENT, Finnigan MAT) with a Hydrogen Generator having a membrane gas-liquid separator. The potential of this technique for Hg determination was studied with Hg standard solutions and snow samples. Results presented in this work are operationally defined as “reactive mercury”, i.e. the fraction of Hg which is easily reducible by  $\text{SnCl}_2$  (Hg in ionic or weakly bonded form). The detection limit of the method, calculated as 3- $\sigma$  the standard deviation of the blank, is 0.4 ng/L (for 20 blank samples). The reproducibility of the analysis is 3-6 %.

## RESULTS AND DISCUSSIONS

The stability of Hg solutions during storage and the influence of acid concentration on the Hg signal were tested. Hg concentrations in standard and blank solutions kept at room temperature and at 4 °C for 17 days and 1.5 month showed almost full loss of Hg even from acidified standard solutions (in the con-

centration range 3-100 ng/l). The loss was most pronounced for Hg solutions with low acid concentrations. Blank solutions showed that the Hg content in nitric acid is relatively low and that there is no contamination from laboratory air during long-time storage.

Hg solutions are usually stabilized by acidification with  $\text{HNO}_3$ . The acid concentration should be optimized for best stabilization of Hg in solution and for ICP-MS analysis to avoid influence of acidity on the plasma. A strong dependence of the obtained Hg signal on the acid concentration was observed, as shown in Fig. 2.

The intensity of the Hg signal increased steadily until acid concentrations of 0.5 to 1N  $\text{HNO}_3$ , where it became sufficiently stable. Thus, we consider 0.7N  $\text{HNO}_3$  as optimal acid concentration.

Instrumental conditions and measurement parameters of the ICP-MS were optimized for Hg analysis: speed of peristaltic pump 600  $\mu\text{L}/\text{min}$ ; washing time 2 minutes. The sensitivity for Hg ranged from 120 000 to 200 000 cps/100 ng/l.

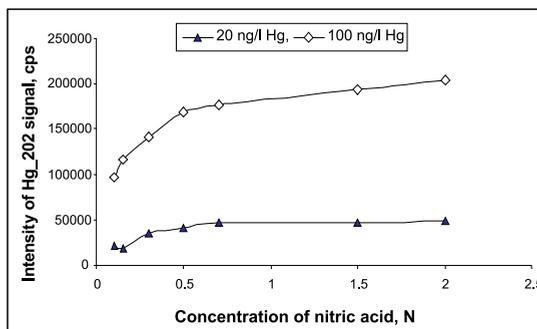
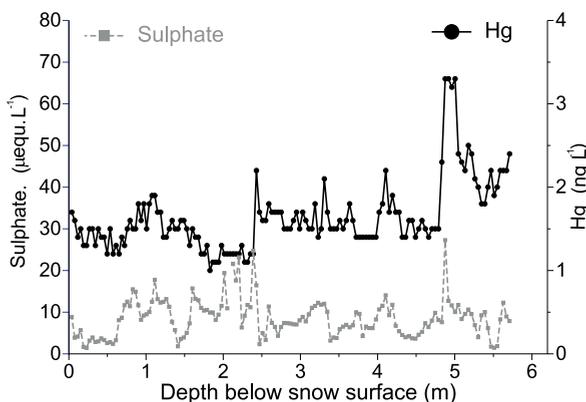


Figure 2: Dependence of  $^{202}\text{Hg}$  signal on  $\text{HNO}_3$  concentration.

**Table 1.** Comparison between mercury concentrations in snow and ice from different sites

Sample site	Object	Hg total, ng/l	Hg reactive, ng/l
Aktru glacier (Altai 3150 m) <sup>[7]</sup>	snow pit		3.6 - 4.4
Belukha glacier (Altai, 3895 m) <sup>[7]</sup>	snow pit		0.8 - 1.4
	firm core		1 - 3.3
Jungfrauoch (Swiss Alps, 3450 m) <sup>[7]</sup>	snow pit	1.5 - 2	1 - 1.5
Mont Blanc (French Alps, 250-2100 m) <sup>[3,9]</sup>	snow	13 - 130	< DL (0.8 ng/l)
	ice core	0.86-5.8	0.2 - 1.8
Upper Fremont glacier (USA, 4100 m) <sup>[4]</sup>	ice core	3 - 21	
Rawson lake (Ontario) <sup>[8]</sup>	surface snow	0.95 - 9.31	
Central Greenland (1949-1989) <sup>[1]</sup>	ice		<0.05 - 2.0

**Figure 3:** Concentration of Hg and sulfate in a firm core from Belukha glacier

The preliminary data are the first data on Hg levels in snow and ice ever obtained for the Altai region. They are compared with data from other sites in table 1.

The only Hg concentrations that were higher than background for remote areas were observed in the snow pit from Aktru glacier (3.6-4.3 ng/l), indicating an influence from the Hg mine in Aktash (70 km distance). The Hg concentrations in the snow pit (0.8-1.4 ng/l) and in the firm core (most values are around 1.2-1.8 ng/l) from Belukha glacier are similar to concentrations reported for Hg in snow of remote areas such as Central Greenland<sup>[1]</sup>. Low Hg concentrations were also determined in snow from the Jungfrau-

joch (Swiss Alps) which is in good agreement with results from the French Alps<sup>[3,9]</sup>.

The concentration of Hg in the 6 m firm core from Belukha is presented in Figure 3, along with the corresponding concentration of sulphate. Both trace species show comparable concentration fluctuations, which is expected because of joint atmospheric transport from the source areas to the remote glacier.

## CONCLUSIONS AND OUTLOOK

Since similar Hg levels were found in high-alpine snow in Central Asia and in Europe, long-range transport and global emissions

seem to determine the present-day Hg level in the Altai. However, historically, the local Hg contribution might have been more important. In 1970-80th the production of Hg in the Aktash smelter amounted to 120-130 t/year, a significantly larger production than in recent years. In addition an industrial activity in Former Soviet Union was more considerable in 20<sup>th</sup> century. In this work only a 6 m firm core was analyzed and

reactive Hg was determined there. Further work will include the analysis of an ice core obtained from the Belukha glacier in July 2001 and Hg<sub>tot</sub> and Hg<sub>R</sub> will be determined there. This ice core covers at least the last two centuries<sup>[10]</sup> and will allow reconstructing the past contribution of natural and industrial sources of atmospheric mercury contaminations in the Siberian Altai.

## REFERENCES

- [1] BOUTRON, C.F., VANDAL, G.M., FITZGERALD, W.F., FERRARI, C.P. (1998): A forty year record of mercury in central Greenland snow. *Geophys. Res. Lett.* 25, pp. 3315-3318.
- [2] LALONDE, J.D., POULAIN, A.J., AMYOT, M. (2002): The role of mercury redox reactions in snow on snow-to-air mercury transfer. *Environ. Sci. Technol.* 36, pp. 174-178.
- [3] JITARU, P., INFANTE, H.G., FERRARI, C.P., ET AL. (2003): Present century record of mercury species pollution in high altitude alpine snow and ice. *J. Phys. IV France*, 107, pp. 683-686
- [4] SCHUSTER, P. F., KRABBEHOFT, D., ET AL. (2002): Atmospheric mercury deposition during the last 270 years: a glacial ice record of natural and anthropogenic sources. *Environ. Sci. Technol.*, 36, pp. 2303-2310.
- [5] FERRARI, C.P., MOREAU, A.L. AND BOUTRON, C.F. (2000): Clean conditions for the determination of ultra-low levels of mercury in ice and snow samples. *Fresenius J. Anal. Chem.* 366, pp. 433-437.
- [6] ORTNER, H. M., XU, H.H., DAMEN, J., ET AL. (1996): Surface characterization of fluorinated polymers (PTFE, PVDF, PFA) for use in ultratrace analysis. *Fresenius J. Anal. Chem.* 355, pp. 657-664.
- [7] EYRIKH, S., SCHWIKOWSKI, M., ET AL. (2002): First mercury determination in snow and firn from high-mountain glaciers in the Siberian Altai by CVICP-MS. *J. Phys. IV France*, 107, pp. 431-434.
- [8] SAINT-LOUIS V.L., RUDD J.W., KELLY C.A. AND BARRIE L.A. (1995): Wet deposition of methyl mercury in Northwestern Ontario compared to other geographic locations. *Wat. Air Soil Pollut.*, 80, pp. 405-414.
- [9] FERRARI, C.P., DOMMERGUE, A., VEYSSEYRE, A., PLANCHON, F., BOUTRON, C.F (2002): Mercury speciation in the French seasonal snow cover. *The Science of the Total Environment* 287, pp. 61-69.
- [10] OLIVIER, S., SCHWIKOWSKI, M., BRÜTSCH, S., ET AL. (2003): Glaciochemical investigation of an ice core from Belukha glacier, Siberian Altai. *Geophys. Res. Lett.* 30 (19), 2019, doi: 10.1029/2003GL018290

## Comparison between flux chambers and Fick's law for dissolved gaseous mercury determinations in the water atmosphere interface

FADINI P. S.<sup>1</sup>, SILVA, L. A. S.<sup>1</sup>, SILVA, G. S.<sup>2</sup> AND JARDIM, W. F.<sup>3</sup>

<sup>1</sup>Faculdade de Química – CEATEC/PUC-Campinas; \*E-mail: psfadini@puc-campinas.edu.br.

<sup>2</sup>CEFET – Paraná.

<sup>3</sup>Instituto de Química – UNICAMP.

**Abstract:** DGM fluxes data propitiates a key indication about the tendency of the mercury stay in water column or be lost to the atmosphere. Fick's law and fluxes chambers can be used for this purpose, and in this study both techniques were used on the same samples from the Negro River Basin, in the Amazon region, Brazil, with mercury measurements carried out after pre-concentration in quartz gold-sand columns and detection by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS). Estimated values between less than +0.5 and +6.5 pmol m<sup>-2</sup> h<sup>-1</sup> were obtained using Fick's law and values between -20.7 and +32.7 pmol m<sup>-2</sup> h<sup>-1</sup> were measured using plexiglass flux chambers. Although different, the values obtained by both alternatives are closed in the sense of direction fluxes and consequently, in the indication of the water column permanence and bioaccumulation tendency.

**Key words:** mercury fluxes, DGM; Rio Negro

### INTRODUCITON

The global biogeochemical cycle of mercury is largely influenced by volatile species formed in the aquatic system called dissolved gaseous mercury (DGM). Studies carried out in the Great Lakes have shown that evasional fluxes of DGM can reach up to 50 % of the annual input to the system (FITZGERALD ET AL., 1991; WATRAS ET AL., 1994; MASON ET AL., 1997). The importance of DGM species in the mobilization of mercury at the air/water interface has also been investigated in many other freshwater bodies such as in the Arctic Lakes (AMYOT ET AL., 1997a), in the Everglades (ZHANG & LINDBERG, 2000), and in different coastal waters, including the Gulf of Mexico (AMYOT ET AL., 1997b), and in

Mediterranean seawaters (FERRARA ET AL., 2000). According to MASON ET AL. (1994), oceanic evasion of Hg(0) is estimated to be 10 Mmol/year, which accounts for 30 % of the total flux to the atmosphere.

Operationally defined, DGM comprehends all mercury species that can be amalgamated in gold traps after gas stripping from the water sample. Although that elemental mercury is the most important species in the DGM pool, monomethylmercury chloride and dimethylmercury may also contribute to this parameter. In natural water bodies, abiotic in situ formation of DGM is related to 3 major aspects: (a) the presence of a suitable substrate, Hg<sup>2+</sup> and other easily reducible mercury species (AMYOT ET AL., 1997c;

ROLPHUS & FITZGERALD, 2001); (b) intensity of solar light in the UV and visible range (AMYOT ET AL., 1997a; COSTA & LISS, 2000), and (c) some key physico-chemical parameters such pH and Dissolved Organic Carbon (Amyot et al., 1994). The biotic formation of DGM may also occur, and has also been observed at higher concentrations of suitable substrates (BARKAY ET AL., 1991).

Due to the low solubility of Hg(0), evasion is an important mechanism of mercury losses from water bodies. The amount of mercury in the water column has a direct influence on its production and accumulation in the biota, which is a serious public health concern. In this study, fluxes of Dissolved Gaseous Mercury (DGM) were estimated by Fick's law and measured with plexiglass fluxes chambers, in the Negro River Basin, Amazon, a basin characterized by black waters, showing high levels of dissolved organic carbon (up to 20 mgC L<sup>-1</sup>) and average pH around 4.5 with a atypical mercury oxidation mechanism sometimes observed during the day (FADINI & JARDIM, 2000a). Mercury fluxes were estimated using Henry's law after measuring DGM in the aqueous phase as well as gaseous mercury in the atmosphere by cold vapor atomic fluorescence spectrometry (CVAFS). Clean sampling techniques were used all the time as described elsewhere (FADINI & JARDIM, 2001). Polyethylene terephthalate (PET) bottles were used for sample collection and purge on the DGM determination (FADINI & JARDIM, 2000b).

## RESULTS AND DISCUSSION

Conversely under sub-saturation conditions of the water, fluxes are invasive, from the

atmosphere to the water. In this study, evasive fluxes were considered as positive (+) and invasive fluxes as negative (-). Fluxes directions and intensities determine the residence time of mercury in the water column and influence the bioaccumulation and biomagnification process across the food web. According the investigation development in the Negro River Basin, stimulation or inhibition of the Hg(0) formation can be the result of the oxidative hydrogen peroxide action or due to the reductive role of organic matter.

However, the exact flux measurement at the level of pmol m<sup>-2</sup> h<sup>-1</sup> (1 ng = 5 pmol), is not a trivial task. Fick's law and fluxes chambers can be used for this purpose, and in this study both techniques were used on the same samples from the Negro River Basin, in the Amazon region, with mercury measurements after pre-concentration in quartz gold-sand columns and detection by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS). Esti-

**Table 1.** Fluxes measurements with Fluxes Chambers and estimated with Fick's Law in black waters.

Fluxes Chambers (pmol m <sup>-2</sup> h <sup>-1</sup> )	Fick's Law (pmol m <sup>-2</sup> h <sup>-1</sup> )
- 15.1	< 0.5
- 0.60	< 0.5
+ 17.3	+ 1.8
+ 29.9	+ 6.5

**Table 2.** Fluxes measurements with Fluxes Chambers and estimated with Fick's Law in white waters.

Fluxes Chambers (pmol m <sup>-2</sup> h <sup>-1</sup> )	Fick's Law (pmol m <sup>-2</sup> h <sup>-1</sup> )
- 20.7	< 0.5
+ 29.5	1.6
+ 32.7	2.9
+ 8.2	0.9
-0.5	< 0.5

mated values between less than +0.5 and +6.5 pmol m<sup>-2</sup> h<sup>-1</sup> were obtained using Fick's law and values between -20.7 and +32.7 pmol m<sup>-2</sup> h<sup>-1</sup> were measured using plexiglass flux chambers. Results are summarized in Table 1 for black waters where mercury oxidation is observed during lighting periods and in Table 2 for white waters, where mercury reduction is observed under sunlight periods, as already described elsewhere (FADINI & JARDIM, 2000a).

With flux chambers it is possible to monitor negative fluxes better than by applying the Fick's Law. Although flux chambers and

Fick's Law results in different flux values, both showed a good agreement between flux directions, and both procedures can be used in the mercury redox cycle investigations and correlations with factors as pH, light intensity and dissolved organic carbon concentration, although the exact flux intensity determination is a very difficult task.

### Acknowledgements

The authors are grateful to FAPESP for the financial support (processes 01/10532-2 e 00/0517-1).

### REFERENCES

- AMYOT, M., MIERLE, G., LEAN, D. R. S. & MCQUEEN, D. J. (1997): Sunlight-induced formation of dissolved gaseous mercury in lake waters; *Environ. Sci. Technol.* 28, pp. 2366-2371.
- AMYOT, M., LEAN, D. R. S. & MIERLE, G. (1997a): Photochemical formation of volatile mercury in high Arctic lakes; *Environ. Toxicol. Chem.* 1, pp. 2054-2063.
- AMYOT, M., GILL, G. A. & MOREL, F. M. M. (1997b): Production and loss of dissolved gaseous mercury in coastal seawater; *Env. Sci. Technol.* 31, pp. 3606-3611.
- AMYOT, M., MIERLE, G., LEAN, D., MCQUEEN, D. J. (1997): *Geochim. Cosmochim. Acta* 61, p. 975.
- BARKAY, T., TURNER, R. R., VANDENBROOK, A. & LIEBERT, C. (1991): The relationships of mercury(II) volatilization from a freshwater pond to the abundance of *mer* genes in the gene pool of the indigenous microbial community; *Microbial. Ecol.* 21, pp. 151-161.
- COSTA, M. & LISS, P. (2000): Photoreduction and evolution of mercury from seawater; *Sci. Tot. Environ.* 261, pp. 125-135.
- FADINI, P. S. & JARDIM, W. F. (2000a): Dissolved gaseous mercury (DGM) fluxes in Negro River basin, Brazilian Amazon; In *11th International Conference on Heavy Metals in the Environment* (J. NRIAGU, Editor), contribution #1080. University of Michigan, School of Public Health, Ann Arbor, Michigan (CD-ROM).
- FADINI, P. S. & JARDIM, W. F. (2000b): Storage of Natural Water Samples for Total and Reactive Mercury Analysis in PET Bottles; *Analyst* 125, pp. 549-551.
- FADINI, P. S. & JARDIM, W. F. (2001): Is the Negro River Basin (Amazon) Impacted by naturally occurring mercury?; *Sci. Tot. Environ.* 275, pp. 71-82.
- FERRARA, R., MAZZOLAI, B., LANZILLOTTA, E., NUCARO, E. & PIRRONE, N. (2000): Temporal trends in gaseous mercury evasion from the Mediterranean seawaters; *Sci. Tot. Environ.* 259, pp. 183-190.
- FITZGERALD, W. F., MASON, R. P. & VANDAL, G. M. (1991): Atmospheric cycling and air-water exchange of mercury over midcontinental lacustrine regions; *Water, Air and Soil Pollut.* 56, pp. 745 - 767.

- MASON, R. P., FITZGERALD, W. F. & MOREL, F. M. M. (1994): The Biogeochemical cycling of elemental mercury – Anthropogenic influences; *Geochim. Cosmoc. Acta* 58, pp. 3191-3198.
- MANSON, R. P. & SULLIVAN, K. A. (1997): Mercury in Lake Michigan; *Environ. Sci. Technol.* 31, pp. 942-947.
- ROLPHUS, R. K. & FITZGERALD, W. F. (2001): The evasion and spatial/temporal distribution of mercury species in Long Island Sound, CT-NY; *Geochim. Cosmoch. Acta* 65, pp. 407-418.
- WATRAS, C. J., BLOOM N. S., HUDSON, R. J. M., GHERINI, S., MUNSON, R., CLAAS, S. A., MORRISON, K. A., HURLEY, J., WIENER, J. G., FITZGERALD, W. F., MASON, R. P., VANDAL, G., POWELL, D., RADA, R., RISLOV, R., WINFREY, M., ELDER, J., KRABBENHOFT, D., ANDREN, A. W., BARBIARZ, C., PORCELLA, D. B. & HUCKABEE, J. W. (1994): Sources and fates of mercury and methylmercury in Wisconsin lakes; In *Mercury Pollution: Integration and Synthesis* (WATRAS, C. J., HUCKABEE, J. W., Eds.), Lewis Publishers, Boca Raton, FL, 153.
- ZHANG, H. & LINDBERG, S. E. (2000): Air/water exchange of mercury in the Everglades I: the behavior of dissolved gaseous mercury in the Everglades Nutrient Removal Project; *Sci. Tot. Environ.* 259, pp. 123-133.

# Gaseous Mercury Exchange Rate between Air and Water Surface over Baihua and Hongfeng Reservoir, Guizhou, China

XINBIN FENG<sup>1,\*</sup>, WANG SHAOFENG<sup>1,2</sup>, LI ZHONGGEN<sup>1,2</sup>, HAIYU YAN<sup>1,2</sup>

<sup>1</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, P.R. China.

<sup>2</sup>Graduate School of the Chinese Academy of Sciences, Beijing 100039, P. R. China.

\* Corresponding author, E-mail: xinbin.feng@mail.gyig.ac.cn;

Telephone number: +86 851 5891356; fax number: +86 851 5891609.

**Abstract:** Mercury exchange between air and water surface is recognized to be one of the most important processes governing the biogeochemical cycling of mercury in aquatic system. Baihua Reservoir is seriously contaminated with mercury due to anthropogenic activities, while Hongfeng Reservoir does not receive any direct input of wastewater contaminated with mercury. Both reservoirs are alkaline because the bedrocks of their catchments are limestone and dolomite. In order to compare the differences in the biogeochemical cycling of Hg in these two reservoirs, we measured mercury exchange fluxes between air and water surface by using a quartz flux chamber method coupled with high time resolved atmospheric Hg analysis technique. Mercury evasion from water surface is the predominant process at both cold and warm sampling periods, though the average GM emission flux in warm season is significantly larger than that in cold season. The correlations between Hg exchange flux and meteorological parameters showed that mercury flux only correlated significantly with solar irradiation in warm season, and that it only correlated with wind speed in cold season on the other hand, which indicated that the driving force of Hg emission from water in different seasons differed significantly. In general, the emission rate of Hg from Baihua Reservoir is much larger than that from Hongfeng Reservoir.

**Key words:** TGM, exchange flux, reservoir, Guizhou, Alkaline reservoir.

## INTRODUCTION

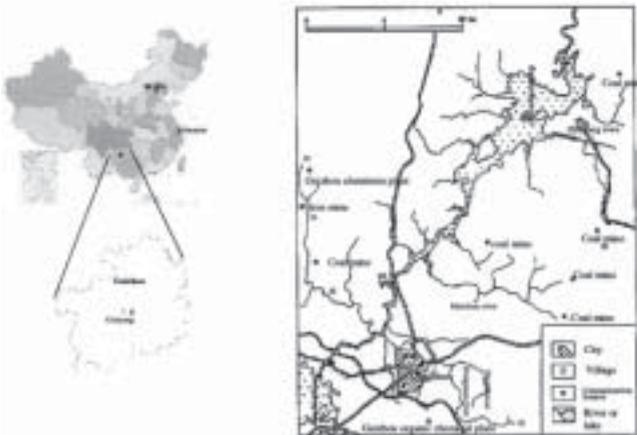
Baihua reservoir (26°35' -26°42' N, 106°27' -106°34' E) dammed in 1966 is situated at 16 km Northwest of Guiyang, the capital of Guizhou Province. Guizhou Organic Chemical Plant (GOCP), which is the only one in China that uses metallic mercury as a catalyst to produce acetic acid, is located at the upper reach of Baihua Reservoir (see Figure 1). GOCP went into operation in 1980, and

so far around 160 ton mercury has been consumed. From 1980 to 1985, the wastewater from GOCP was directly discharged into Dongmen river without any treatment, which seriously contaminated the surrounding environments including Baihua Reservoir. After 1985, a mercury removal device went into operation to prevent mercury discharging into Dongmen river. At present, total mercury concentrations in this river range from 250 to 1000 ng l<sup>-1</sup>. In addition, 7 small coal

mines, one iron mine and Guizhou Aluminum Plant are situated at the upper reaches of the reservoir, and these may also be mercury emission sources. Even though Baihua Reservoir is seriously contaminated in terms of mercury, so far no research related to mercury biogeochemical cycling in Baihua Reservoir has been conducted yet. The total water surface area of Baihua Reservoir is 14.5 km<sup>2</sup>, the average water depth is 12 m, and the average salinity and DOC concentrations are 0.2 ‰ and 0.3 mg l<sup>-1</sup>, respectively. Hongfeng reservoir established in 1960 with a surface area of 57.2 km<sup>2</sup> and a volume of 6.01×10<sup>8</sup> km<sup>3</sup> is located at the suburb of Guiyang city in Guizhou province where coal is the main energy source of industry and living. Hongfeng reservoir is a hyper-eutrophic and seasonal anoxic reservoir due to the contamination from domestic and industrial wastewaters, but so far no wastewaters with high Hg concentrations have been identified. The source of Hg pol-

lution to Hongfeng reservoir may be mainly come from deposition of the atmospheric mercury. Calcareously and sienna are dominant in drainage area and the bedrocks of the watershed of both reservoirs are limestone and dolomite.

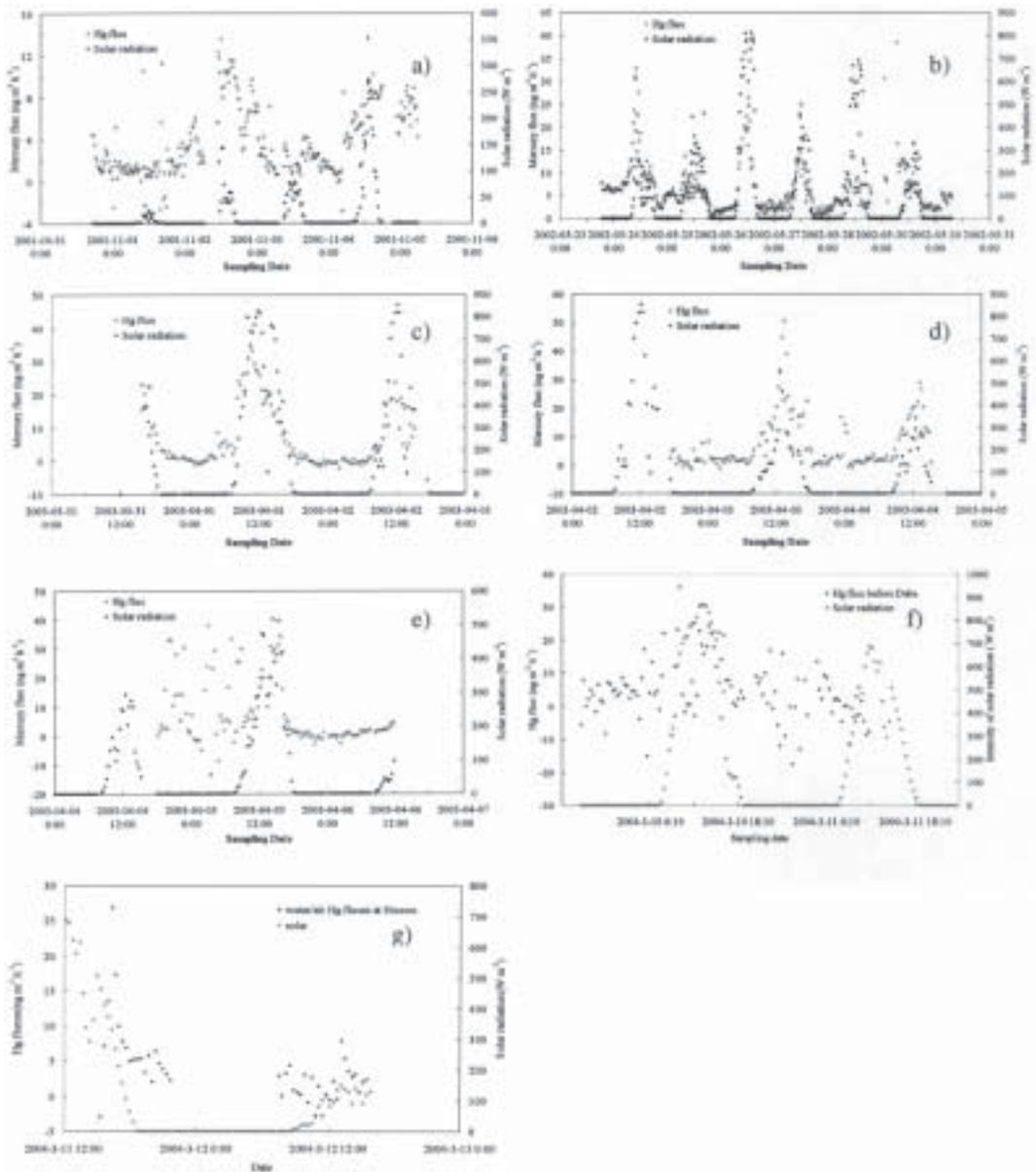
Three sampling sites were chosen in Baihua reservoir for Hg exchange fluxes measurement between air and water surface as shown in Figure 1. Three measurement campaigns were conducted. The first one representing the cold season was carried out from October 31 to November 4, 2001 at Matuo site, the second representing the warm season was performed from May 23 to 30, 2002, at Matuo site and the third representing the transition from the cold to the warm season was conducted from March 31 to April 6, 2003 at all 3 sampling sites. Two sampling sites were chosen in Hongfeng reservoir for Hg exchange fluxes measurement between air and water surface as shown in Figure 2.



**Figure 1.** Sampling locations for gaseous mercury exchange flux measurement over Baihua reservoir (\*). A: Matuo; B: Huaqiao; C: Daba.



**Figure 2.** Sampling locations over Hongfeng reservoir.



**Figure 3.** Relationships between Hg flux and solar irradiation at five sampling campaigns: a) October 31–November 05, 2001 at Matuo of Baihua reservoir; b) May 23–30, 2002 at Matuo of Baihua reservoir; c) March 31 to April 02, 2003 at Matuo of Baihua reservoir; d) April 02–04, 2003, at Huaqiao of Baihua reservoir; e) April 04–06, 2003 at Daba of Baihua reservoir; f) March 10 to 11, 2004 at Daba of Hongfeng reservoir; g) March 11 to 12 at Houwu of Hongfeng reservoir.

## RESULTS AND DISCUSSION

High temporal resolved Hg flux measurement results as well as solar irradiation are illustrated in Figure 3. At Daba measurement site of Baihua reservoir, short-term large variation of mercury flux events occurred between 18:00pm April 4 and 9:00 am April 5. This is obviously caused by the local mercury emission source that led elevated and rapidly varied TGM concentrations. Definitely mercury flux measured during that period of time using our method could not represent the true mercury flux values. It points out that our DFC method is not applicable to measure mercury flux between air and water/soil surface when irregularly large short-term TGM fluctuation occurs due to local mercury emissions. At all sampling campaigns, mercury flux significantly positively correlated with solar irradiation with linear correlation coefficients of 0.38 ( $p < 0.01$ ) at Matuo site of Baihua reservoir in cold campaign in 2001, of 0.57 ( $p < 0.01$ ) at Matuo site of Baihua reservoir in May 2002 campaign, of 0.82 ( $p < 0.01$ ) at Matuo site of Baihua reservoir in March-April 2003 campaign, of 0.91 ( $p < 0.01$ ) at Huaqiao site of Baihua reservoir in April 2003 campaign, of 0.87 ( $p < 0.01$ ) at Daba of Baihua reservoir in April 2003 campaign, of 0.47 ( $p < 0.01$ ) at Daba of Hongfeng reservoir in March 2004 campaign, and of 0.43 ( $p < 0.01$ ) at Houwu of Hongfeng reservoir in March 2004 campaign, respectively. This observation agrees well with previous studies (e.g., POISSANT AND CASIMIR, 1998; GLRDFELDT ET AL., 2001; FENG ET AL., 2002).

## CONCLUSIONS

The surface water of both Baihua reservoir and Hongfeng reservoir are a strong local atmospheric emission source at all seasons. Sunlight induced reduction of divalent mercury to  $Hg^0$  is the predominant process of DGM formation in surface water of Baihua reservoir, and the process is very fast. Compared to Baihu reservoir, mercury emission rate from water surface from Hongfeng reservoir is much slower.

## Acknowledgements

This work was financially supported by Chinese Academy of Sciences through "Hundred Talent Plan" and CAS innovation project (KZCX2-105), and by Chinese Natural Science Foundation (40173037).

## REFERENCES

- FENG, X. B., SOMMAR, J., GLRDFELDT, K., LINDQVIST, O. (2002): Exchange flux of total gaseous mercury between air and natural water surfaces in summer season; *Science in China (Series D)*, Vol. 45, No. 3, pp. 211-220.
- GÄRDFELDT, K., FENG, X. B., SOMMAR, J., LINDQVIST, O. (2001): Total gaseous mercury exchange between air and water over lake and sea surfaces; *Atmospheric Environment*, Vol. 35, pp. 3027-3038.
- POISSANT, L., CASIMIR, A. (1998): Water-air and soil-air exchange rate of total gaseous mercury measured at background sites; *Atmospheric Environment*, Vol. 32, pp. 883-893.

## Atmospheric particles evolution during Hg depletion events

CHRISTOPHE P. FERRARI<sup>\*1,2</sup>, PIERRE-ALEXIS GAUCHARD<sup>1</sup>, AURÉLIEN DOMMERGUE<sup>1</sup>,  
OLIVIER MAGAND<sup>1</sup>, SONIA NAGORSKI<sup>1</sup>, CLAUDE F. BOUTRON<sup>1,3</sup>, CHRISTIAN TEMME<sup>4</sup>,  
ENNO BAHLMANN<sup>4</sup>, RALF EBINGHAUS<sup>4</sup>, ALEXANDRA STEFFEN<sup>5</sup>, CATHY BANIC<sup>5</sup>,  
KATRINA ASPMO<sup>6</sup>, TORRUN BERG<sup>6</sup>

<sup>1</sup>Laboratoire de Glaciologie et Géophysique de l' Environnement du CNRS,  
54 rue Molière, BP 96, 38402 Saint Martin d'Hères, France.

\*Corresponding author: Tel.: +33 4 76 82 42 00; fax: +33 4 76 82 42 01;  
E-mail: ferrari@lgge.obs.ujf-grenoble.fr

<sup>2</sup>Polytech' Grenoble, Université Joseph Fourier (Institut Universitaire de France),  
28 Avenue Benoît Frachon, BP 53, 38041 Grenoble, France.

<sup>3</sup>Unités de Formation et de Recherche de Mécanique et de Physique, Université Joseph Fourier  
(Institut Universitaire de France), BP 68, 38041 Grenoble, France.

<sup>4</sup>Institute for Coastal Research/Physical and Chemical Analysis,  
G.K.S.S. Research Centre Geesthacht, D-21502 Geesthacht, Germany.

<sup>5</sup>ir Quality Research Branch, Meteorological Service of Canada, Environment Canada,  
4905 Dufferin St., M3H 5T4-Toronto, Canada.

<sup>6</sup>Norwegian Institute for Air Research (NILU),  
Instituttveien 18, P.O. Box 100, N-2027, Kjeller, Norway.

**Abstract:** During a field experiment campaign in Ny-Alesund, Svalbard, atmospheric particles (sizes 0.3-0.5  $\mu\text{m}$ ; 0.5-1  $\mu\text{m}$ ; 1-5  $\mu\text{m}$ ; > 5 $\mu\text{m}$ ), elemental gaseous mercury, reactive gaseous mercury and ozone have been measured continuously for one month from April to May, 2003. The purpose was to study the atmospheric particle concentration evolution during successive Atmospheric Mercury Depletion Events (AMDEs) so as to better understand the origin of these phenomena. During some events, negative correlations between concentrations of atmospheric particles in the range of 0.5 - 5  $\mu\text{m}$  and concentrations of ozone and atmospheric mercury were observed. Other events were characterized by positive correlations between concentrations of particles in the range of 0.3 - 0.5  $\mu\text{m}$  and concentrations of ozone and mercury. Furthermore, particles have been measured in the surface snow samples collected during the whole campaign. Assuming that these phenomena imply either a chemical link either an association through transport, we studied air masses trajectories in order to clearly define the origin of these AMDEs.

**Key words:** AMDE, particles, snow, transport

# Hg deposition onto snow surface during Mercury Depletion Events in Ny-Alesund (Svalbard) from April to May 2003: Temporal and spatial evolutions.

## Evaluation of deposition and re-emission fluxes of Hg.

CHRISTOPHE P. FERRARI<sup>\*1,2</sup>, PIERRE-ALEXIS GAUCHARD<sup>1</sup>, AURÉLIEN DOMMERGUE<sup>1</sup>, OLIVIER MAGAND<sup>1</sup>, SONIA NAGORSKI<sup>1</sup>, CLAUDE F. BOUTRON<sup>1,3</sup>, CHRISTIAN TEMME<sup>4</sup>, ENNO BAHLMANN<sup>4</sup>, RALF EBINGHAUS<sup>4</sup>, ALEXANDRA STEFFEN<sup>5</sup>, CATHY BANIC<sup>5</sup>, KATRINA ASPMO<sup>6</sup>, TORRUN BERG<sup>6</sup>, FRÉDÉRIC PLANCHON<sup>7</sup>, CARLO BARBANTE<sup>7</sup>

<sup>1</sup>Laboratoire de Glaciologie et Géophysique de l' Environnement du CNRS, 54 rue Molière, BP 96, 38402 Saint Martin d'Hères, France.

\*Corresponding author: Tel.: +33 4 76 82 42 00; fax: +33 4 76 82 42 01; E-mail: ferrari@lgge.obs.ujf-grenoble.fr

<sup>2</sup>Polytech' Grenoble, Université Joseph Fourier (Institut Universitaire de France), 28 Avenue Benoît Frachon, BP 53, 38041 Grenoble, France.

<sup>3</sup>Unités de Formation et de Recherche de Mécanique et de Physique, Université Joseph Fourier (Institut Universitaire de France), BP 68, 38041 Grenoble, France.

<sup>4</sup>Institute for Coastal Research/Physical and Chemical Analysis, G.K.S.S. Research Centre Geesthacht, D-21502 Geesthacht, Germany.

<sup>5</sup>ir Quality Research Branch, Meteorological Service of Canada, Environment Canada, 4905 Dufferin St., M3H 5T4-Toronto, Canada.

<sup>6</sup>Norwegian Institute for Air Research (NILU), Instituttveien 18, P.O. Box 100, N-2027, Kjeller, Norway.

<sup>7</sup>Environmental Sciences Department, University of Venice, Calle Larga S. Marta, 2137, I-30123 Venice, Italy

**Abstract:** During a field experiment campaign in Ny-Alesund, Svalbard, for one month from April to May, 2003, snow surface samples were collected using ultra-clean procedures so as to avoid any contaminations. During this time period, snow was collected every day when there was no MDE and every 8-10 hours during MDE periods. The aim of this study was to determine the temporal evolution of Hg concentration in snow and also spatial differences in surface snow concentrations of Hg after analysis with Cold Vapor Atomic Absorption Spectrophotometry (CVAAS). Deposition fluxes of Hg have been calculated for each MDE so as to give a raw evaluation of Hg deposition flux to the snow pack in the Arctic. After each MDE, Hg concentrations in snow surface samples seemed to decrease indicating possible re-emission of Hg to the atmosphere by photoreduction processes. The re-emission fluxes have been evaluated after each MDE and integrated for the whole Arctic surface. Differences in these fluxes allow us to calculate the net balance of Hg affecting the snow pack, and then to have a better idea about the impact of MDE for Arctic ecosystems.

**Key words:** AMDE, snow, interstitial air, flux

# The Hg/<sup>210</sup>Pb Hypothesis: Apportioning Regional and Global Components of Current and Historical Hg Deposition

WILLIAM F. FITZGERALD<sup>1</sup>, DANIEL R. ENGSTROM<sup>2</sup>, CARL H. LAMBORG<sup>3</sup> & PRENTISS H. BALCOM<sup>1</sup>

<sup>1</sup>Dept. of Marine Sciences, University of Connecticut, Groton, CT USA;  
E-mail: wfitzger@uconnvm.uconn.edu.

<sup>2</sup>St. Croix Watershed Research Station, Science Museum of Minnesota,  
Marine-on-St. Croix, MN USA.

<sup>3</sup>Dept. of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution,  
Woods Hole, MA USA.

**Abstract:** In a paper published in 2001, Lamborg et al. reported good correlations between total Hg and the naturally occurring, particle-reactive radionuclide <sup>210</sup>Pb in rainwater from northern Wisconsin and the equatorial Atlantic Ocean. The precise cause of this correlation is not known, but suggests an analogy between the <sup>210</sup>Pb system (solid <sup>226</sup>Ra/gaseous <sup>222</sup>Rn/particulate <sup>210</sup>Pb/precipitation <sup>210</sup>Pb) and Hg chemistry in the atmosphere (gaseous Hg/gaseous Hg(II)/particulate Hg(II)/precipitation Hg(II)). The precipitation correlation of Hg and <sup>210</sup>Pb offers a hypothetical tool for discerning regional and global influences on local Hg depositional fluxes. This tool would take the form of Hg:<sup>210</sup>Pb ratios in precipitation from a variety of locations. Sites which receive little local/regional Hg should show Hg:<sup>210</sup>Pb ratio values similar to those observed at remote locations while sites that receive Hg deposition of a more localized nature should show greater ratio values. In effect, the application of <sup>210</sup>Pb as a normalizing tracer of particulate scavenging should remove the issue of site-to-site variation in climatology (rain depth, frequency, temperature, etc.) and permit direct comparison of sites from widely differing locations.

We are currently engaged in a test of this hypothesis. <sup>210</sup>Pb and Hg determinations in precipitation are being made at 8 locations in North America, many at Mercury Deposition Network sites. These collections will continue for about 2 years and yield an unprecedented set of Hg and <sup>210</sup>Pb comparisons. Concurrently, we are collecting and analyzing sediment cores from undisturbed lakes from continental upwind (southeast Alaska) and downwind (Newfoundland) locations to assess the impact of continental/regional-scale sources on the anthropogenic enhancement of Hg deposition in the last few centuries.

**Key words:** atmosphere, lead, deposition, sediments, precipitation

## INTRODUCTION

Knowledge of the behavior and fate of Hg in the atmosphere is increasing. However, assessment of natural and anthropogenic sources is uncertain, the mechanisms by which Hg is removed from the atmosphere

are not well constrained, and linkages between inputs of anthropogenic Hg, especially from the atmosphere, and the bioaccumulation MMHg in sensitive aquatic ecosystems has not yet been established. This project is addressing questions relating to natural and anthropogenic contributions from

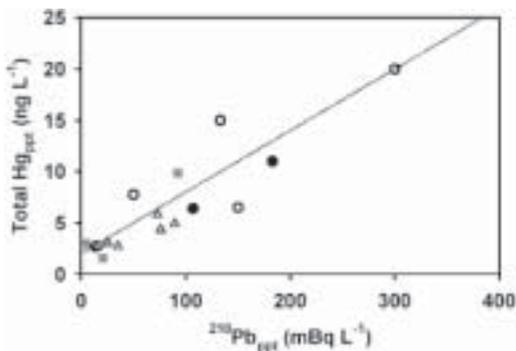
global and localized sources, the identification of Hg deposition with a regional origin (e.g., U.S.), and the examination of spatial and temporal trends (e.g., increases, declines) in atmospheric Hg deposition for predictive/modeling purposes. This research is focused on current measurement, reconstruction, quantification, and interpretation of the modern and historical variation in atmospheric Hg fluxes associated with the mid and sub-tropical latitudes of North America.

Our studies are taking place in the lacustrine environs of the Tongass National Forest of southeastern Alaska (June '03) and Deer Lake/Cornerbrook, Newfoundland (Sep. '04). This work is complemented by event-scale Hg and <sup>210</sup>Pb depositional investigations at the lake study-areas and other key geographic regions which display a range of variation in Hg deposition as determined from the Mercury Deposition Network (MDN). The regions include the West Coast North America, Mid-Continent U.S., East Coast North America, and the southeastern U.S. Our program benefits from the cooperation and assistance of interested colleagues associated with current operations and facilities (National Parks, and the MDN sites).

We are addressing the following hypotheses:

- 1) Atmospheric mercury deposition in southeastern Alaska can be viewed as an integrated sample of global Hg pollution in the Northern Hemisphere, and therefore represents a component of the Hg deposition experienced by sites closer to local and regional emission sources.
- 2) Atmospheric mercury deposition in Canada's maritime provinces is elevated above the northern hemispheric average by regional contributions from the industrialized Northeast/Midwest and can be separated into global and regional components by a comparison of sedimentary archives.
- 3) The linear correlation between Hg and <sup>210</sup>Pb found in rainwater from other remote and semi-remote locations (Lamborg, 2000; Figure 1) is observed in southeastern Alaska, and this behavior can be used to constrain the global-scale wet atmospheric flux of Hg to lakes and watersheds of temperate North America.
- 4) At less remote sites, enhanced atmospheric Hg deposition that is locally/regionally derived, is indicated by deviations from Hg and <sup>210</sup>Pb relationship observed in southeastern Alaska.
- 5) Sediment archives will show, when corrected for climatology using <sup>210</sup>Pb, that the Pacific and Atlantic seaboards of North America received equivalent preindustrial atmospheric Hg fluxes, and provide a baseline for assessing the global component of anthropogenic Hg deposition at any given locality.

This research should yield the high quality biogeochemical data needed for quantitative assessment of the scale and historical record of potentially enhanced atmospheric Hg deposition related to increased human-related Hg emissions over the past 150 years. This information will be especially useful in improving models of the global and regional biogeochemical and atmospheric cycling of Hg, and assessing the impact associated with atmospherically transported pollutant-derived Hg in the environment.



**Figure 1.** Hg/<sup>210</sup>Pb correlation in precipitation from Wisconsin (circles), South Atlantic (triangles) and from Arctic Alaska (squares). Adapted from LAMBORG (2000).

The project began with the establishment of <sup>210</sup>Pb collection capabilities at 7 MDN sites (Table 1). Two modified IVL, bulk deposition collectors (based on CHAZIN, 1995) were installed at these sites and samples are retrieved on the same schedule as the Hg samples. Some examples of the collectors can be seen at [www.teamhg.uconn.edu](http://www.teamhg.uconn.edu). <sup>210</sup>Pb radioactivity is determined indirectly by a spectrometry of the <sup>210</sup>Po progeny. Initially, however, Pb and Po are not at secular equilibrium, and therefore the samples must be held for about a year to allow sufficient Po “grow-in.” <sup>210</sup>Po is then determined by spontaneous plating onto a Ag disc (FLYNN, 1968;

BENOIT, 1988) after adding a <sup>209</sup>Po yield monitor to the sample. The <sup>210</sup>Pb activity is then inferred from the <sup>210</sup>Po/<sup>209</sup>Po activity ratio, the activity of the <sup>209</sup>Po spike and the <sup>210</sup>Po grow-in rate. At the 8<sup>th</sup> site, located in Glacier Bay National Park, we also installed the same ultraclean, automated Hg precipitation collector as is currently used at MDN sites (Loda Electronics; LINDBERG, 1995). Hg analyses are being performed at the Univ. of Connecticut.

The lakes cored during the summer of 2003 were all located in the Point Adolphus area on the northern end of Chichagof Island (part of the Tongass National Forest), across Icy Strait from Glacier Bay National Park and the town of Gustavus. Four remote lakes were sampled by Zodiac and using a piston-like gravity corer (HTH, Sweden). The cores were sectioned at high resolution (0.5-2 cm) soon after and are being processed, dated and analyzed for Hg. As with previous studies, we are selecting small headwater or kettle lakes with small watersheds and simple bottom morphometries. Lake sampling includes bottom mapping using a GPS equipped, recording sounder and GIS analysis of the lake watersheds. A comparable effort will take place in Newfoundland in the summer/fall

**Table 1.** Sites for <sup>210</sup>Pb and Hg collocated collection.

Site	MDN #	Description
Glacier Bay N.P., AK	---	Remote Northwest
Seattle, WA	WA18	Suburban Northwest
Marcell E.F., MN	MN16	Remote Midwest
Lamberton, MN	MN27	Agricultural Midwest
Cormack, NL	NF09	Remote Northeast
Acadia N.P., ME	ME96	Rural Northeast
ENRP Site, FL	FL34	Rural Southeast
Andytown, FL	FL04	Suburban Southeast

of 2004. As part of the dating process, the  $^{210}\text{Pb}$  content of the sediments is determined, also by a spectrometry of  $^{210}\text{Po}$  isolated by distillation (EAKINS, 1978). Sediment accumulation rates are calculated using the Constant Rate of Supply model (APPLEBY, 1978) which makes use of the total  $^{210}\text{Pb}$  inventory of the sediment core. Thus, we will have a good estimate of the long term, average  $^{210}\text{Pb}$  flux to the region which can be combined with the Hg: $^{210}\text{Pb}$  ratio to make additional, corroborative estimates of contemporary Hg fluxes.

Applying the relationship found in Lamborg, 2000 ( $[\text{Hg}] = [^{210}\text{Pb}] \times (0.06 \pm 0.01 \text{ ng mBq}^{-1}) + (2 \pm 2 \text{ ng L}^{-1})$ ) to the  $^{210}\text{Pb}$  flux implied by the inventory of cores analyzed from Glacier Bay (Flux =  $120 \pm 20 \text{ Bq m}^{-2} \text{ y}^{-1}$ ; rain depth 1.77 m) suggests a Hg deposition to the SE Alaska region of  $11 \pm 4 \text{ } \mu\text{g m}^{-2} \text{ y}^{-1}$ . Similarly, it is interesting to apply the Hg: $^{210}\text{Pb}$  relationship on a global-scale. The global flux of  $^{210}\text{Pb}$  from the atmosphere has been previously estimated to be about  $5 \times 10^{16} \text{ Bq y}^{-1}$  (TUREKIAN, 1977; PREISS, 1996), and annual precipitation flux about  $4.5 \times 10^{20} \text{ g y}^{-1}$  (GARRELS, 1971). Again applying the

empirical Hg: $^{210}\text{Pb}$  relationship to these values yields a global atmospheric Hg flux of about  $20 \pm 5 \text{ Mmole y}^{-1}$ , which is comparable to independent estimates (e.g., MASON, 1994).

### Acknowledgements

We thank the site operators: Bob Breen, Bob Brunette, Hazel Crocker, Art Elling, Lee Klosner, Mary Kralovec, Mark Kromer, Deacon Kyllander, Kirsi Longley, Nicholas McMillan, LaMoine Nickel, Emily Seger, Megan Vogt and Rusty Yerxa. Thanks to Steve Beauchamp, Bob Brunette, Larry Fink, David Manski, Rob Tordon, and Ed Swain for logistical help. Thanks also to Gaboury Benoit, Ken Buesseler, Ryan Porhola and TEMSCO Helicopters.

This work is supported by the U.S.E.P.A. STAR grant #R829796 and the WHOI Penzance Endowed Fund with site support from Acadia National Park, Environment Canada, Frontier Geosciences, Glacier Bay National Park and the South Florida Water Management District.

## REFERENCES

- APPLEBY, P. G. & OLDFIELD, F. (1978): The calculation of lead-210 dates assuming a constant rate of supply of unsupported  $^{210}\text{Pb}$  to the sediment; *Catena*, Vol. 5, pp. 1-8.
- BENOIT, G. & HEMOND, H. F. (1988): Improved methods for the measurement of  $^{210}\text{Po}$ ,  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$ ; *Limnology and Oceanography*, Vol. 33, No. 6, pp. 1618-1622.
- CHAZIN, J. D., ALLEN, M. K. & RODGER, B. C. (1995): Measurement of Mercury Deposition Using Passive Samplers Based on the Swedish (IvI)-Design; *Atmospheric Environment*, Vol. 29, No. 11, pp. 1201-1209.
- EAKINS, J. D. & MORRISON, R. T. (1978): A new procedure for the determination of lead-210 in lake and marine sediments; Vol. 29, pp. 531-536.
- FLYNN, W. W. (1968): The determination of low levels of polonium-210 in environmental materials; *Analytica Chimica Acta* 43, pp. 221-227.
- LAMBORG, C. H., FITZGERALD, W. F., GRAUSTEIN, W. C. & TUREKIAN, K. K. (2000): An examination of the atmospheric chemistry of mercury using Pb-210 and Be-7; *Journal of Atmospheric Chemistry*, Vol. 36, No. 3, pp. 325-338.
- LINDBERG, S. E. & VERMETTE, S. (1995): Workshop on sampling mercury in precipitation for the national atmospheric deposition program; *Atmospheric Environment* 29, pp. 1219-1220.
- MASON, R. P., FITZGERALD, W. F. & MOREL, F. M. M. (1994): The Biogeochemical Cycling of Elemental Mercury - Anthropogenic Influences; *Geochimica et Cosmochimica Acta*, Vol. 58, No. 15, pp. 3191-3198.
- PREISS, N., MÉLIÈRES, M.-A. & POURCHET, M. (1996): A compilation of data on lead 210 concentration in surface air and fluxes at the air-surface and water-sediment interfaces; *Journal of Geophysical Research*, Vol. 101, No. D22, pp. 28847-28862.
- TUREKIAN, K. K., NOZAKI, Y. & BENNINGER, L. K. (1977): Geochemistry of atmospheric radon and radon products; *Annual Review of Earth and Planetary Science* 5, pp. 227-255.

## Mercury and selenium levels in the atmosphere

M. C. FREITAS<sup>1</sup>, M. M. FARINHA<sup>1</sup>, M. G. VENTURA<sup>1</sup>, A. M. G. PACHECO<sup>2</sup>

<sup>1</sup>Reactor-ITN (Technological and Nuclear Institute), E.N. 10, 2686-953 Sacavém, Portugal;  
E-mail: cfreitas@itn.mces.pt

<sup>2</sup>CVRM-IST (Technical University of Lisbon), Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal;  
E-mail: apacheco@ist.utl.pt

**Abstract:** Vascular plants uptake mercury and accumulate it in the roots. Leaves are supposed to absorb volatilised elemental mercury. Thus airborne mercury seems to contribute significantly to the mercury contents in plants. Lichens are uptaking nutrients and pollutants directly from the atmosphere. In this work, mercury and selenium in *Parmelia sulcata* (Taylor) contents through Portugal mainland in 1993 are shown and compared. Mercury levels in airborne mercury are shown for a few sites in Portugal mainland, obtained in the last 10 years. It is known that selenium uptake is a form of protection of plants to excessive mercury availability. This was not evident from the results obtained for lichens. In airborne, selenium and mercury are emitted by the same source at one of the studied sites. Mercury and selenium were determined by instrumental neutron activation analysis.

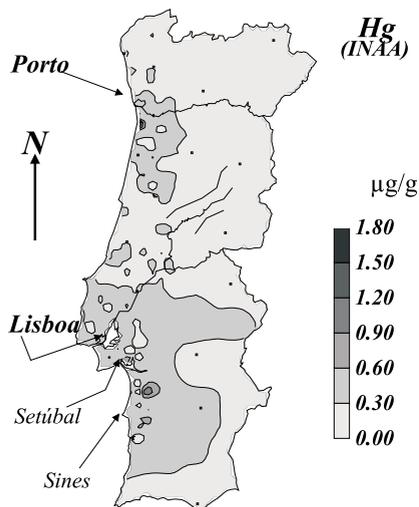
**Key words:** mercury, selenium, lichens, particulate matter

### INTRODUCTION

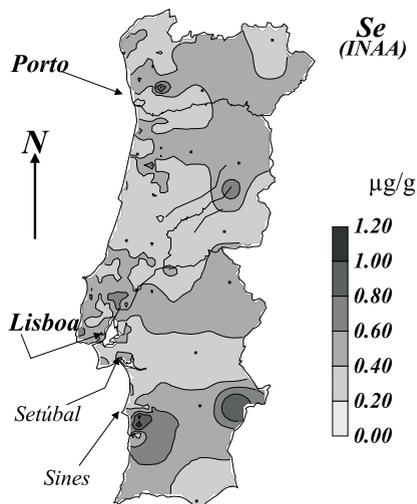
Mercury poisoning has become a problem of current interest as a result of environmental pollution on a global scale. Natural emission of mercury is an important component (still the major part) in the global mercury input. Anthropogenic mercury sources include agricultural soil sludge, fertilizers, chloroalkali industrial production, and coal combustion, among others. For evaluation of the levels of mercury either biomonitoring or airborne monitoring can be used. This work aimed at presenting a few data on Hg and Se in lichens and air particulate matter, obtained in Portugal in the last 10 years.

### RESULTS AND DISCUSSION

Figs. 1 and 2 show respectively the Hg and Se mapping, based on Hg and Se contents in native *Parmelia sulcata* (Taylor) collected through July and August 1993. The used grid followed 10 km x 10 km through the Atlantic Ocean coast and 50 km x 50 km through the interior of the country. Interpolation of the contents in the grid squares was based in  $1/r^3$  where  $r$  is the distance between two adjacent points. Mapping of Hg and Se as well as other chemical elements appeared in FREITAS (2000).



**Figure 1.** Distribution of Hg in *Parmelia sulcata* (Taylor) in Portugal collected in 1993. Hg was determined by instrumental neutron activation analysis (INAA).



**Figure 2.** Distribution of Se in *Parmelia sulcata* (Taylor) in Portugal collected in 1993. Hg was determined by instrumental neutron activation analysis (INAA).

**Table 1.** Hg concentrations (mean; maximal) in particulate matter below 2.5 µm, in ng.cm<sup>-3</sup>, as measured by INAA through Portugal since 1994.

Nearby coal power plants	Porto (1994/1995)
	0.97; 3.68
	Sines (1994/1995)
	2.34; 4.8
Nearby fuel power plants	Setúbal (1995/1996)
	0.17; 1.04
	Setúbal (1997/1998)
	0.33; 1.30
Far from power plants	Lisbon North (2002)
	0.065; 0.15
	Lisbon North (2003)
	0.079; 0.31

The Hg pattern put in evidence the influence of main industrial areas localized in Porto and Lisbon regions, spread over the interior of the country in a southwestern direction

due to the NW wind predominance. The Se pattern appeared by layers, with more concentrated spots near the coal power stations of Porto and Sines.

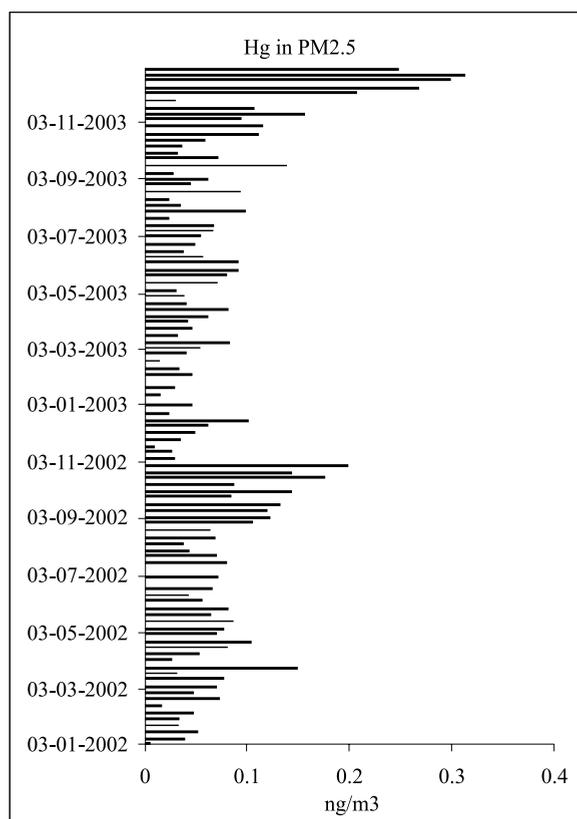
Table 1 presents Hg concentrations (mean and maximal values) in air particulate matter below  $2.5 \mu\text{m}$  (*i.e.*  $\text{PM}_{2.5}$ ) for a few sites in Portugal.  $\text{PM}_{2.5}$  was collected in a Gent sampler either for 24 h periods or some minutes out of the hour for 1 week.

The sites near coal power plants appeared with higher Hg concentrations than the other sites. The levels were quite low for the Lisbon northern area.

The individual values of the Hg concentrations for this area, shown in Fig. 2, put in evidence a seasonal influence on the Hg con-

centrations. These latter increase by the end of the year. As shown in FREITAS (2004) the Hg increase during winter concerned the northeastern wind predominance, which had as effect the reduction of the natural sea-spray and soil related chemical elements and the increase of the anthropogenic ones. The increase was particularly important for selenium in  $\text{PM}_{2.5}$  as shown in Freitas (2004). This might have occurred because Hg vapor phase could not be determined and usually accounts for over 90 % of the emitted mercury.

As mentioned above, in Portugal the industry concentrates in the Atlantic Ocean coast



**Figure 3.** Hg concentrations, in  $\text{ng}\cdot\text{cm}^{-3}$ , in Lisbon North during 2002 and 2003 (24h sampling/week).

and the predominant winds (NW) spread the pollutants towards the interior of the country. When the winds invert for an opposed direction (NE) it is possible to figure a realistic order of magnitude of the pollutants. This inversion occurs more during autumn and winter.

### Acknowledgements

This work was supported by the International Atomic Energy Agency and the Electricity of Portugal.

### REFERENCES

- FREITAS, M. C., REIS, M. A., ALVES, L. C. & WOLTERBEEK, H. TH. (2000): Nuclear analytical techniques in atmospheric trace element studies in Portugal; In *Trace elements – their distribution and effects in the environment*, (B. MARKERT AND K. FRIESE, Eds.), Amsterdam: Elsevier Science B.V. 2000, pp. 187-213.
- FREITAS, M. C., FARINHA, M. M., VENTURA, M. G., ALMEIDA, S. M., REIS, M. A. & PACHECO, A. M. G. (2004): Atmospheric Selenium in an Industrialized Area of Portugal; *J. Radioanal. Nucl Chem.* (in press).

## Contribution from biomass burning to global mercury budgets

HANS R. FRIEDLI<sup>1</sup> & LAWRENCE F. RADKE<sup>1</sup>

National Center for Atmospheric Research, P.O. Box 3000, Boulder, CO, 80307-3000, USA,  
e-mail: friedli@ucar.edu

**Abstract:** Burning of biomass samples from North American forests (boreal, temperate and Mediterranean) and from African savanna was investigated in small-scale (~0.5 kg) laboratory burns. Essentially all mercury was released during the flaming phase of the burn, mostly in form of gaseous elemental mercury (GEM), with particulate mercury (pHg) contributing up to 13% of the mercury released in the case of live conifer needles. The mercury content of the fuels reflected species- and life-cycle related differences: grasses and young leaves had lowest mercury content (<10 ng/g (dm)), while leaf litter contained up to 71 ng/g (dm) resulting from dry and wet deposition accumulated in the plant parts during their life cycle, followed by senescence. Aircraft measurements in the plumes of wildfires in temperate North American forests revealed the absence of ionic mercury (RGM) above detection limits, pHg at 2.5-13 %, remainder GEM, and emission factors (EF) with a broad range of (113+/-59) x10<sup>-6</sup> g Hg/kg fuel burnt. This value is much larger than the EF obtained for fuels burnt in the laboratory. The explanation for the excess mercury in wildfires is the contribution of the organic soil, which is often burnt to the mineral layer and is highly enriched in mercury (e.g. 300 ng/g (dm) in boreal forest samples). From the analysis of the distribution of mercury in live and dead vegetation and in the organic layers in a boreal forest it is evident that boreal forest soils contain a large fraction of the temporarily sequestered mercury. Global estimates of mercury release from biomass burning are still uncertain because of the wide range of EF, uncertain estimates for fuel consumption, large annual variability of biomass burning and the fact that biofuel emission estimates are not yet included. Our current estimate is 500+/-260 t/y or 8 +/- 4 % of the published annual mercury emissions. The resulting wet and dry redeposition of the emitted mercury has local (pHg) and global (GEM) impacts.

**Key words:** mercury speciation, biomass burning, budgets

## Mapping Errors of Mercury Source Emissions with Geostatistical Tools

G. GARRO<sup>1</sup>, S. CINNIRELLA<sup>1</sup> & N. PIRRONE<sup>1</sup>

<sup>1</sup>CNR-Institute for Atmospheric Pollution, 87036 Rende, Italy; E-mail: g.garro@cs.iiia.cnr.it

**Abstract:** Nowadays model complexity in terms of input data suggests the necessity of a complete and well structured database (DB). Within the construction process of a DB the check of data validity follows the collection of datasets. The above is more interesting when data gathered from different sources are considered. Also the integration of socio-economic evaluation stresses the importance of data integration for improving holistic analysis. The effort aimed to integrate and manage different data within a common database comply the requirements of the European Commission priorities to encourage the development of integrated and multi-compartment projects. Among these MERCYMS concerns the cycling of mercury in the Mediterranean environment. For the project purpose mercury emissions at point and non-point level were collected for Europe and Mediterranean countries.

This study illustrates the work done on 1995 and 2000 DB to detect errors in source emissions. After a preliminary check on displacement of emission sources, we use a probabilistic approach under the geostatistical analysis to obtain spatial distribution of error. Results show an elevated degree of uncertainties in few areas like Portugal and the East Europe. Finally a comparison of differences between the two DBs was assessed.

## Mercury speciation into tropospheric clouds

PIERRE-ALEXIS GAUCHARD<sup>†,\*</sup>, AURÉLIEN DOMMERGUE<sup>†</sup>, CHRISTOPHE P. FERRARI<sup>†,‡</sup>,  
LAURIER POISSANT<sup>§</sup> AND CLAUDE F. BOUTRON<sup>†,#</sup>

<sup>†</sup> Laboratoire de Glaciologie et Géophysique de l' Environnement du CNRS,  
54 rue Molière, BP 96, 38402 Saint Martin d'Hères, France.

<sup>‡</sup> Ecole Polytechnique Universitaire de Grenoble, Université Joseph Fourier,  
28 Avenue Benoît Frachon, BP 53, 38041 Grenoble, France.

<sup>§</sup> Service Météorologique du Canada, Processus des Toxiques Atmosphériques, Environnement  
Canada 105 rue McGill, Montréal, Québec H2Y 2E7

<sup>#</sup> Unités de Formation et de Recherche de Mécanique et de Physique, Université Joseph Fourier  
(Institut Universitaire de France), BP 68, 38041 Grenoble, France.

\*Corresponding author. Tel.: +33 4 76 82 42 00; fax: +33 4 76 82 42 01;  
E-mail: gauchard@lgge.obs.ujf-grenoble.fr

**Abstracts:** Mercury speciation into tropospheric clouds has been studied during a two months field experiment campaign at the meteorological station of the Puy De Dôme (France, 1465 m a.s.l., 45°46'N, 2°57'E). Gaseous Elemental Mercury (GEM), Reactive Gaseous Mercury (RGM) and Particulate Mercury (PM) have been measured by a complete speciation unit (Tekran, Canada) in the troposphere with and without clouds. Cloud water has also been sampled for inorganic mercury determination. Finally, some tests have been done to analyse mercury species in the interstitial phase of the cloud and to measure dissolved elemental mercury into the cloud water. These tests have been done using specific installations devoted to the study of the microphysics of clouds. Mercury speciation results as well as a discussion on competitive oxidation/reduction processes into cloud water will be presented in order to better understand the role of tropospheric clouds on the global Hg cycle.

**Key words:** tropospheric clouds, speciation, oxydo-reduction processes

## Sources of Atmospheric Mercury Impacting the North American Great Lakes

AMY GILDEMEISTER, GERALD KEELER & KHALID AL-WALI

**Abstract:** The Quantitative Transport and Bias Analysis (QTBA) model identified the most important source areas contributing to atmospheric mercury concentrations in the Lake Superior watershed, showing that contributions from both local sources and long-range transport from source regions as distant as the Gulf of Mexico resulted in elevated ambient mercury concentrations in the North American Great Lakes Region. The model combines data from the Hybrid Single Particle Lagrangian Integrated Trajectory (HY-SPLIT) model (used to calculate meteorological back-trajectories) with measured mercury concentrations and precipitation to calculate a two-dimensional transport probability distribution and estimate the potential for upwind sources to contribute to elevated mercury concentrations at the measurement sites. Hg concentrations were measured at three sampling sites in the North American Great Lakes region from January 1, 1998 through May 5, 1999. The QTBA model output was plotted onto a map of the Lake Superior basin using ArcView GIS. Possible sources of particulate, fine particulate ( $d < 2.5$   $\mu\text{m}$ ), elemental, and divalent mercury in the region were identified and included on the map. Northern Iowa, southeastern Minnesota, Wisconsin, and northern Illinois rely heavily on fossil fuel and waste incineration and made important contributions to the amount of particulate mercury in the North American Great Lakes. Another important source of particulate mercury was a large gold mine on the southern end of Lake Winnipeg in Ontario, Canada. Results of the size-fractionated particulate sampling reveal that there is a large fine fraction mercury contribution from across the entire US Great Lakes region, with an additional contribution from Thunder Bay, ON. The identified sources of vapor-phase mercury are areas in which there exist numerous industrial sources, coal fired power plants, and incinerators (e.g. Minneapolis MN, Chicago IL, and Gary IN).

**Key words:** mercury, transport, Great Lakes, model

## Urban Mercury Cycling: Differences between Urban and Rural Mercury Cycles Affecting the Deposition of Mercury in the North American Great Lakes Watershed

AMY GILDEMEISTER, GERALD KEELER & JOSEPH GRANEY

**Abstract:** Although there are many inherent differences between pollutant pathways in rural and urban environments, the impact that these differences may have on the environmental cycling of mercury in rural and urban areas of the North American Great Lakes basin has largely been ignored. To determine the impact of local sources on mercury cycling in an urban environment, dry deposition, wet deposition, and runoff were collected in southwest Detroit, MI from April through October of 1996. The sampling was conducted in a major industrialized area and was near coke refineries, smelters, and incinerators. It was determined that during the 1996 campaign, wet and dry deposition contributed approximately equal amounts to the overall mercury deposition in Detroit, with the monthly dry deposition ranging from 0.7-3  $\mu\text{g}/\text{m}^2$  and the wet deposition from 0.4-3.0  $\mu\text{g}/\text{m}^2$ . The amount of mercury measured per month in impervious surface runoff ranged from 0.7-6.0  $\mu\text{g}/\text{m}^2$ . Simultaneous collection of total particulate and fine fraction ( $d < 2.5 \mu\text{m}$ ) particulate mercury during the later part of the mercury deposition study indicates that, although the long-range transport of particulate mercury is associated with small, combustion-related particles, a significant percentage of the particulate mercury in an urban area is associated with coarse particles, thus enhancing the contribution of dry deposition mercury to total mercury deposition and subsequent runoff concentration. These data clearly demonstrate that it is critically important to evaluate the impact of the dry deposition of mercury on overall mercury deposition, particularly in urban areas or near combustion sources.

**Key words:** mercury, deposition, Great Lakes, urban

## Millennial-scale records of atmospheric mercury deposition in the Arctic of Canada from peat profiles

NICOLAS GIVELET<sup>1</sup>, FIONA ROOS-BARRACLOUGH<sup>2</sup>, MICHAEL E. GOODSITE<sup>3</sup> & WILLIAM SHOTYK<sup>4</sup>

<sup>1</sup>Institute of Geological Sciences, University of Berne,  
Baltzerstrasse 1-3, 3012, Berne, Switzerland, e-mail: givelet@geo.unibe.ch

<sup>2</sup>Institute of Geological Sciences, University of Berne,  
Baltzerstrasse 1-3, 3012, Berne, Switzerland

<sup>3</sup>Department of Chemistry, University of southern Denmark,  
Campusvej 55, 5230, Odense, Afghanistan

<sup>4</sup>Institute of Environmental Geochemistry, University of Heidelberg,  
INF 236, 69120, Heidelberg, Germany

**Abstract:** Because of the strong tendency of mercury to bioaccumulate in the food chain, one of the greatest challenges faced by environmental mercury research in the Arctic is to quantify the relative contribution of anthropogenic sources of mercury to the contamination of this environment, as anthropogenically elevated mercury deposition over the past 150 years in Arctic ecosystems is potentially a serious environmental problem. To determine the magnitude of this concern, it is necessary to quantify the natural “background” of atmospheric mercury deposition and its variation over a millennial-scale period of time. Geochemical studies of two peat hummocks from Bathurst Island, Nunavut reveal substantial inputs from soil dust (titanium), marine aerosols (bromine) and mineral-water interactions (uranium). Mercury, however, was supplied to these peat mounds exclusively by atmospheric deposition. Mercury concentration measurements and age dating of the peat profiles indicate rather constant natural “background” mercury flux of ca. 1 microgram per square meter per year from 5900 to 800 calibrated year BP. The values are well within the range of the Hg fluxes reported from other Arctic locations but also by peat cores from southern Canada which provide a record of atmospheric Hg accumulation extending back to eight thousand years. Thus, pre-anthropogenic Hg fluxes in the Arctic were not significantly different from atmospheric Hg fluxes in the temperate zone. In pre-industrial times, therefore, the High Arctic was no more important as a sink for global atmospheric mercury than the temperate zone. Therefore, other processes have to be invoked as chief mechanism for transferring atmospheric Hg to the Arctic environment, possibly made more efficient in recent years by environmental changes, resulting in the mercury contamination of the Arctic food chain.

**Key words:** Arctic, archive, Hg deposition flux

## Lidar Measurements of Mercury Emissions from the Idrija Mercury Mine

RASMUS GRÖNLUND<sup>1</sup>, HANS EDNER<sup>1</sup>, SUNE SVANBERG<sup>1</sup>, JOŽE KOTNIK<sup>2</sup> & MILENA HORVAT<sup>2</sup>

<sup>1</sup>Atomic Physics Division, Lund Institute of Technology, P.O. Box 118, 221 00 Lund, Sweden,  
e-mail: rasmus.gronlund@fysik.lth.se

<sup>2</sup>Jožef Stefan Institute, Ljubljana, Slovenija

**Abstract:** Mercury emission measurements from the Idrija mercury mine in Slovenia were performed during a late October campaign, where the DIAL (Differential Absorption Lidar) technique was used to map mercury concentrations and attempts were made to quantify the total mercury flux from the most contaminated area, the abandoned cinnabar roasting oven complex. Lidar concentration data were compared with data recorded with a portable mercury point-monitor, operated from a vehicle equipped with a GPS localization system. Concentrations and fluxes were comparatively low due to low temperature and rainfall.

**Key Words:** Lidar, Atmospheric mercury flux, Mercury mine

### INTRODUCTION

The Idrija mercury mine is the second largest mercury mine in the world, second only to the Almadén mine in Spain. Mercury was found here in 1490 and the mine was in operation for 500 years. With mining operations now stopped the surroundings are still mercury and cinnabar contaminated.

The objectives for the one-week late October lidar (light detection and ranging) measurement campaign were to map the emission sources from the mine and to estimate the total flux of mercury from the site.

The Lund group has developed differential absorption lidar techniques for three-dimensional mapping of atmospheric atomic mercury<sup>[1, 2]</sup>. Lidar measurements of the concentrations of mercury utilize the Hg absorption

peak at 254 nm and a close-by reference wavelength for differential measurements in the backscattered light. By vertical scanning of the measurement direction, a cross-section of the mercury plume can be found. The total flux can then be obtained by taking the wind speed into account.

The lidar system has previously been used in measurements at the two other main mercury mining areas, Abbadia San Salvatore (Italy)<sup>[3]</sup> and Almadén (Spain)<sup>[4]</sup>. High concentrations, up to 5 µg/m<sup>3</sup> were found and at Almadén a total flux of 600-1200 g/h could be determined in a September measurement campaign. At the Italian site, particularly high concentrations were found around the mercury distillation plant<sup>[3, 5]</sup>. The present measurements at Idrija were concentrated to the area around the abandoned distillation plant, where high concentrations were ex-

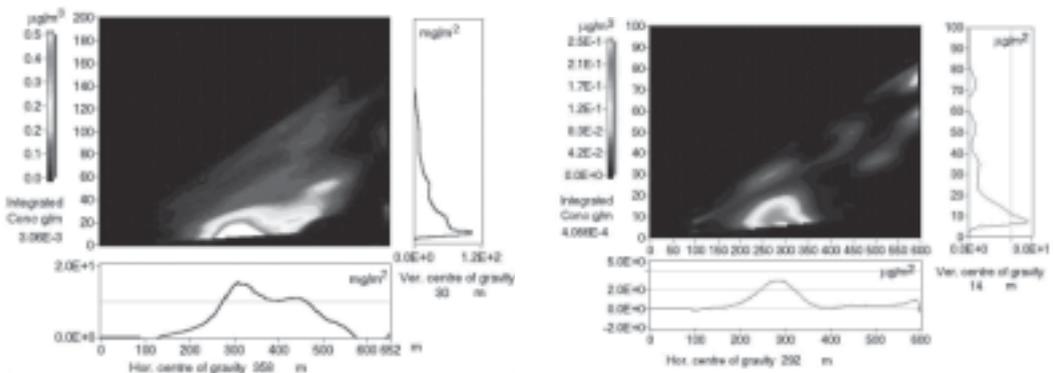
pected from previous point-monitoring measurements.

## RESULTS AND DISCUSSION

The Idrija measurements were performed during the time October 30 – November 4, 2003. The terrain in Idrija with a rather narrow valley along the Idrijca river is somewhat complicated in view of positioning lidar scans for flux measurements. Wind conditions were not very favourable for flux measurements: frequently the wind speeds were very low. Heavy rainfall and associated low temperatures during most of the campaign decreased the mercury emission from the ground. Lidar measurements were performed from two locations. The first one was located inside the city of Idrija at an elevation of about 30 meter above the Idrijca river, and close to the present visitors entrance to the mine. From here mostly horizontal scans over the city was made in directions where the beam was not obstructed by vegetation or other structures and all results showed fairly low concentrations. The second location was close to the Idrijca river, about 250 meters downstream of the distil-

lation plant and about 10 meter above the river surface. From here vertical scans downwind from the distillery were made, and also horizontal scans over the valley in the direction towards the city of Idrija.

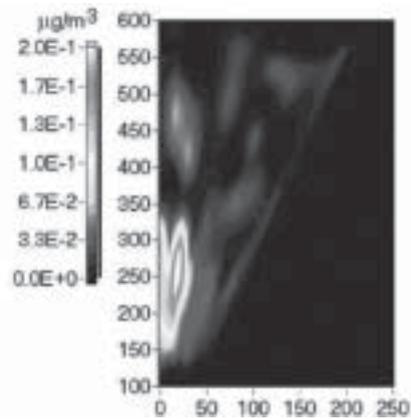
The results of vertical scans downwind from the distillation plant as recorded from the second lidar site are shown in Figures 1 and 2. Strongly elevated concentrations of the order of a few hundred  $\text{ng}/\text{m}^3$  at a length integration interval of 7.5 m are observed associated with the plant. The wind was blowing down the valley with a quite small and non-optimal angle between the wind and scan directions. This lowers the accuracy in a flow determination. Further, because of buildings blocking the lowest directions of interest some mercury flow escapes under the scan. However, from the two diagrams measured flux values of 2.4 g/h and 5.6 g/h can be evaluated. Horizontal scans starting at the distillery which is quite close to the quickly rising valley side, and extending out over the Idrijca river in a 20 degree sector are shown in Figure 3. Again, it can be seen that the concentrations rapidly fall off away from the plant.



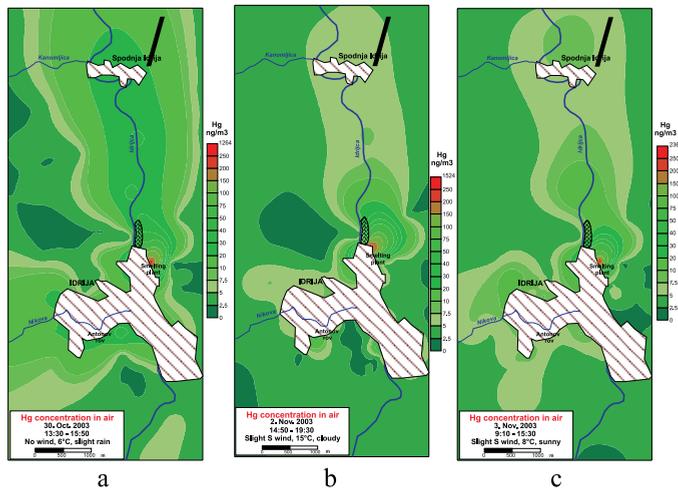
**Figures 1. and 2.** Vertical scans downwind from the distillation plant corresponding to elemental mercury fluxes of 2.4 g/h and 5.6 g/h, respectively.

As mentioned above, mercury mapping over the area were also performed using the portable absorption spectrometer installed in a car traversing the roads of the area with the geometry given by GPS recordings. Results from October 30, November 2 and 3, 2003 are given in Figures 4 a, b and c. The concentration values recorded in individual points are here smoothed into a map using a computer routine. The data sampling time varies between about 2 and 7 hours. As can be seen, the distillery completely dominates the emission situation with values reaching above  $2 \mu\text{g}/\text{m}^3$  being observed. It could be noted that such values corresponds to sampling 1 meter above the road surface in direct vicinity to the plant. Average temperatures were 6, 15

and 8 degrees centigrade during the recordings of Fig. 4a, b and c, respectively.



**Figure 3.** Horizontal scan over the distillation plant and the river valley.



**Figure 4.** Concentration maps obtained using a portable mercury point-monitor

## CONCLUSIONS

Lidar and point-monitoring data were found to be complementary in mapping the mercury distribution. Lidar provides a fast mapping and the potential for total flux measurements for favourable wind conditions. The mobile point monitor provided powerful

large area mapping, but recording times are rather long which may influence mapping accuracy during changing wind and temperature conditions. Generally, comparatively low concentrations and fluxes were observed at Idrinja due to reduced ambient temperatures and rainfall during the measurement campaign.

## ACKNOWLEDGEMENTS

This work was supported by the Swedish Research Council, the Knut and Alice Wallenberg Foundation and the Jožef Stefan Institute.

## REFERENCES

- [1] ALDÉN, M., EDNER, H., SVANBERG, S. (1982): Remote Measurement of Atmospheric Mercury Using Differential Absorption Lidar; *Optics Letters* 7, pp. 221-223.
- [2] EDNER, H., FARIS, G. W., SUNESSON, A., SVANBERG, S. (1989): Atmospheric Atomic Mercury Monitoring using Differential Absorption Lidar Techniques; *Applied Optics* 28, pp. 921-929.
- [3] EDNER, H., RAGNARSSON, P., SVANBERG, S., WALLINDER, E., FERRARA, R., MASERTI, B.E., BARGAGLI, R. (1993): Atmospheric Mercury Mapping in a Cinnabar Mining Area; *The Science of the Total Environment* 133, pp. 1-15.
- [4] FERRARA, R., MASERTI, B. E., ANDERSSON, M., EDNER, H., RAGNARSSON, P., SVANBERG, S., HERNANDEZ, A. (1998): Atmospheric Mercury Concentrations and Fluxes in the Almadén District (Spain); *Atmospheric Environment* 32, pp. 3897-3904.
- [5] FERRARA, R., MASERTI, B. E., MAZZOLAI, B., DI FRANCESCO, F., EDNER, H., SVANBERG, S., WALLINDER, E. (1999): Atmospheric Mercury in Abandoned Mine Structures and Restored Mine Buildings at Mt. Amiata, Italy; In *Environmental Science Mercury Contaminated Sites* (Ed., R. EBINGHAUS ET AL.) Springer-Verlag, Berlin Heidelberg 1999.

## Mercury Emissions from Chlor-Alkali Plants Measured by Lidar Techniques

RASMUS GRÖNLUND, MIKAEL SJÖHOLM, PETTER WEIBRING, HANS EDNER, SUNE SVANBERG

Atomic Physics Division, Lund Institute of Technology, P.O. Box 118, 221 00 Lund, Sweden,  
e-mail: rasmus.gronlund@fysik.lth.se

**Abstract:** The EC-supported EMECAP (European Mercury Emissions from Chlor-Alkali Plants) project aims at risk assessment of the mercury emission from European chlor-alkali plants. Three pilot sites are selected, one in Sweden, one in Italy and one in Poland. The objective of the Lund group has been to perform lidar (light detection and ranging) measurements of the mercury flux from the plants, and to map the distribution of elemental mercury around the plants. This has been performed at each of the sites, in Sweden and Italy both in summer and winter, whereas in Poland only a summer campaign has been performed.

**Key Words:** Lidar, atmospheric mercury flux, chlor-alkali plant

### INTRODUCTION

The objectives of the EMECAP project are risk assessment of the mercury emissions from European chlor-alkali plants. The project includes atmospheric concentration and flux measurements, human health influence, vegetable, fish and soil concentration measurements, data handling as well as development of new technology for mercury monitoring, all to provide decision makers with an improved tool to evaluate the risk for human health and for the environment around MCCA (Mercury Cell Chlor-Alkali) plants<sup>[1]</sup>.

Three test sites has been selected, one in Sweden, one in Italy and one in Poland. A total of 6 measurement campaigns has been performed. In 2001 an intercalibration campaign was performed in Sweden to test the lidar concentration measurements compared

to conventional mercury point-monitors<sup>[2]</sup>. Moreover, in Sweden and Italy both winter and summer campaigns has been performed, in Poland only a summer campaign.

The Lund group was responsible for measurements of elemental mercury flux from the different test sites. The DIAL (Differential Absorption Lidar) technique<sup>[3]</sup> was used, employing the mercury absorption line at 254 nm to measure the concentration of elemental mercury along the laser beam. By vertical scanning of the laser beam, a cross-section of the mercury plume can be found. Each such sweep takes about 4 minutes to perform. The area integrated concentration multiplied by the perpendicular wind direction yields the mercury flux.

The measurements were performed using the mobile lidar system of the Lund Institute of Technology. The system, built inside a Volvo

F610 truck, utilises an OPO (Optical Parametric Oscillator), pumped by a 20 Hz tripled Nd:YAG laser at 355 nm, to generate the radiation at the desired wavelength. The OPO is modified to be able to switch wavelength on a shot-to-shot basis. The line width of the system is typically  $<0.2 \text{ cm}^{-1}$ . The laser radiation is transmitted to the atmosphere through the dome, which can be rotated 360° and a mirror can be tilted to direct the radiation from -10° to 55° vertically. An overview of the system is found in Fig. 1<sup>[4]</sup>.

Each measurement campaign was carried out over 10 days during which time many scans could be performed, that were later averaged to give a final value for the elemental mercury flux from the plant over the entire period. During the measurements, the wind was monitored all the time, using wind vanes and anemometers.

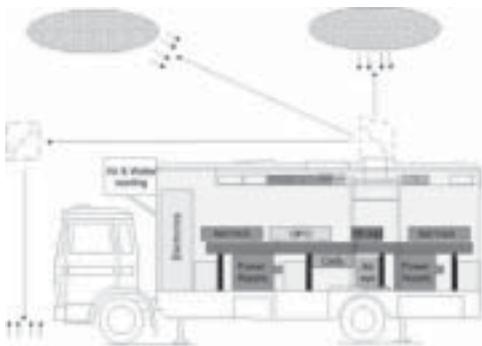


Figure 1. An overview of the Swedish mobile lidar system.

## RESULTS AND DISCUSSION

Each vertical scan yields a vertical cross-section of the mercury plume, an example is given in Fig. 2. This particular scan is from the summer campaign in Italy and with a wind speed of 2.9 m/s the flux was calculated to 35 g/h. Multiplying each scan with

the perpendicular wind speed gives a value for the mercury flux. The wind measurements gave uncertain results when wind speeds were low; these values have been excluded, as well as values where the wind direction gave a too large sinus correction. The final results can be seen in Fig. 3.

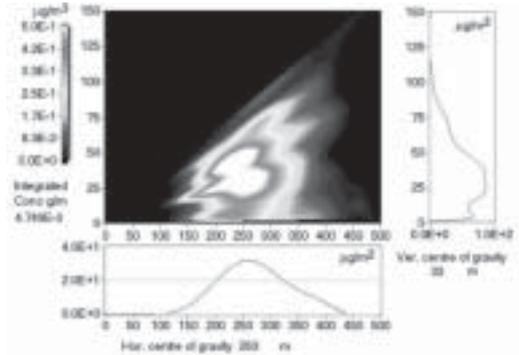


Figure 2. A cross-section of the mercury plume from the Italy summer campaign.

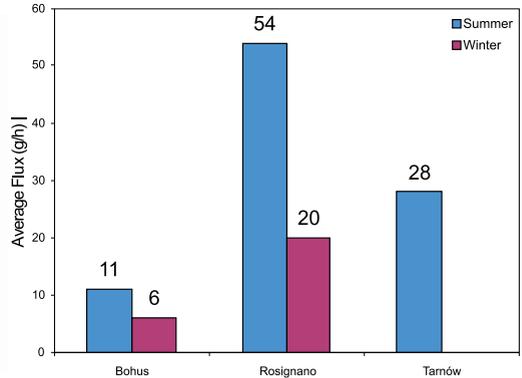
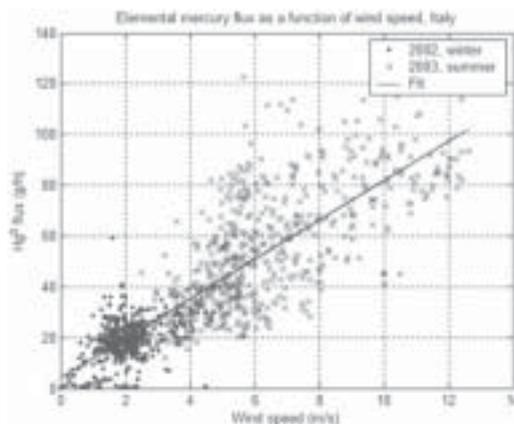


Figure 3. Total average results from the different campaigns.

As can be seen, the summer campaigns gave higher emission values, indicating that gassing from spills may be important, increasing with higher ambient temperatures. To make comparisons between the different plants, the results should be normalised with respect to chlorine production, which differs significantly between the sites<sup>[5]</sup>.



**Figure 4.** Mercury flux as a function of wind speed at the Italian campaigns.

During the summer campaign in Italy, it was found that there was a correspondence between the wind speed and the flux. It can be understood that this effect should be particularly large in Italy since the cell house has an open structure and a higher wind speed would allow greater gassing because the vapour pressure will be kept low. The flux from every different sweep has been plotted in Fig. 4 as a function of wind speed from the two Italian campaigns.

## REFERENCES

- [1] <http://www.emecap.com>
- [2] WÄNGBERG, I., EDNER, H., FERRARA, R., LANZILLOTTA, E., MUNTHE, J., SOMMAR, J., SJÖHOLM, M., SVANBERG, S., WEIBRING, P. (2003): Atmospheric mercury near a chlor-alkali plant in Sweden. *The Science of the total environment* 304, pp. 29-41.
- [3] SVANBERG, S. (1994): Differential Absorption Lidar (DIAL), in *Air Monitoring by Spectroscopic Techniques*. M. Sigrist (ed). Wiley, New York 1994.
- [4] WEIBRING, P., EDNER, H., SVANBERG, S. (2003): Versatile mobile lidar system for environmental monitoring. *Applied Optics* 42, pp. 3583-3594.
- [5] GRÖNLUND, R., SJÖHOLM, M., WEIBRING, P., EDNER, H. AND SVANBERG, S. (2004): Differential absorption lidar measurements of the atomic mercury flux from chlor-alkali plants, to appear.

The measurement of the wind has been good; however, it is only a point monitoring. The wind speed may be quite different over the cross-section area of the plume. Since the wind-profile is not known, the cross-section concentration is just multiplied by the measured wind. There may also be parts of the plume being trapped behind a building, and thus not adding to the flux at all, although the concentrations may be high. In measurements where this has been found to be the case, the lowest direction has been excluded.

## CONCLUSIONS

The Lidar technique could be successfully used to measure the total flux from individual chlor-alkali plants. These unique data are important in assessing environmental impact and as input for models of mercury dispersion.

## Acknowledgements

The EMECAP project is supported financially by the European Commission DG XII. We also acknowledge the Knut and Alice Wallenberg Foundation for generous support.

## Assessment of the significance of mercury release from coal fly ash

MAE GUSTIN<sup>1</sup>, KEN LADWIG<sup>2</sup>, MEI XIN<sup>1</sup> & RICHARD ZEHNER<sup>1</sup>

<sup>1</sup>University of Nevada, Reno Department of Natural Resources and Environmental Science. Mail Stop 370 Reno, NV 89557, USA; E-mail: msg@unr.nevada.edu

<sup>2</sup>EPRI, 3412 Hillview Ave., Palo Alto, CA 94303 USA

**Abstract:** The potential for mercury release from coal fly ash to the atmosphere and water was investigated using laboratory studies. The former was also investigated in the field at two coal fly ash landfills. All fly ash samples used in the laboratory with the exception of that derived from lignite-based coals acted as a sink for atmospheric mercury. Deposition rates were higher for ash collected from carbon injection demonstration projects used for mercury removal from the flue gas stream than from ash collected prior to injection. Deposition was the dominant mercury flux at one landfill while emission rates similar to that reported for soils with background concentrations of mercury occurred at the other. Mercury concentrations of SPLP leach extracts were < 14 ng/L. Data developed demonstrated that fly ash will not release significant amounts of mercury to the environment.

**Key words:** Coal fly ash, SPLP leaching procedure, air surface exchange, mercury flux

### INTRODUCTION

Mercury (Hg) occurs naturally in all types of coal<sup>[1]</sup>. During combustion for production of electricity, the Hg in the coal is emitted to the atmosphere or captured with the combustion by-products (CCB), such as fly ash and flue gas desulfurization solids. An estimated 75 tons of Hg are contained in the fuel burned annually at coal-fired power plants in the United States, with ~60 percent released to the atmosphere, and the remaining 40 percent removed by particulate and sulfur dioxide control devices and managed with the coal combustion by-products<sup>[2]</sup>. Previous work has indicated that Hg in the by-products is present in relatively low concentrations (<500 ng/g) and is relatively stable, with little evidence of leaching or volatiliza-

tion<sup>[3,4,5]</sup>. The amount of Hg in CCBs is expected to increase over the next 5 to 10 years due to enhanced Hg control technologies that are being required by US EPA.

This study examined the potential for Hg release from CCB samples using more sensitive laboratory techniques than most previous studies<sup>[6]</sup>. The primary focus was investigation of air-ash Hg exchange. Total and leachable Hg concentrations in the ash were also determined. The samples included fly ash derived from bituminous, subbituminous, and lignite coals collected from plants using a variety of combustion and particulate control technologies. Samples were also collected from demonstration projects using activated carbon injection (ACI) for enhanced Hg control. Two fly ash landfills were visited to de-

termine if laboratory derived Hg fluxes were similar to that measured in the field.

## RESULTS AND DISCUSSION

Ash samples for the laboratory study were collected dry from ash collection hoppers into clean amber glass bottles and shipped to the University of Nevada-Reno. Recoverable Hg concentrations (aqua regia digestion and cold vapor hydride generation and AA spectrometry) were < 600 ng/g and total Hg concentrations (aqua regia + hydrofluoric acid digestion) <2,300 ng/g. Total Hg and recoverable Hg concentrations were well correlated ( $r^2=0.94$   $p<0.05$ ), however recoverable concentrations were usually 30 to 60 % lower than total concentrations. Fly ash collected during activated carbon injection exhibited higher Hg concentrations than fly ash collected prior to injection. Mercury concentrations in the extracts derived using the Synthetic Precipitation Leaching Procedure (SPLP, EPA Method 1312), which is a weak acid (pH= 4.5 to 5) leach, were always less than 15 ng/L and in most cases less than 10 ng/L.

A single-pass gas exchange system was utilized for controlled laboratory measurement of atmospheric Hg flux (emission and deposition) associated with individual ash samples. Mercury fluxes measured from substrate with this system have been demonstrated to be similar to those measured in situ from soil using field flux chambers and micrometeorological methods<sup>[7]</sup>. All of the bituminous and subbituminous ash samples used in the laboratory study exhibited negative flux, or deposition of atmospheric Hg for the three experimental conditions (dark

25 °C, light 25 °C and dark 45 °C). All lignite derived ash samples, with the exception of one, consistently exhibited emissions. Deposition of atmospheric Hg to ash in the dark at 25°C was statistically significantly ( $p<0.05$ ) greater than that occurring during light and dark exposures at 45°C. For those samples for which a positive flux was measured at 25 °C in the dark, greater emission occurred at 25 °C in the light and at 45 °C in the dark than at the lower temperature. This is due to the fact that both light and temperature enhance Hg emissions<sup>[8, 9, 10]</sup>. There was net deposition of Hg from the ambient air to the fly ash for all samples collected from the ACI demonstration projects. Deposition was higher for ash collected during the ACI than that collected prior to carbon injection. It is possible that the higher carbon in the ash facilitated atmospheric Hg uptake. Air Hg concentrations were also found to significantly influence flux; that is as air concentrations increased, Hg emissions declined or deposition increased.

In situ Hg fluxes were measured a dynamic field flux chamber linked to a Tekran 2537A total Hg analyzer<sup>[11]</sup>. Simultaneously with Hg flux measurements, micrometeorological parameters were measured including air and soil temperature, relative humidity and incident light<sup>[6]</sup>. At a bituminous ash landfill, with relatively high Hg concentrations, Hg flux was measured from topsoil covered and vegetated ash (80 to 110 ng Hg/g), barren fly ash and vegetated ash (870 to 1500 ng/g). Even though the Hg concentrations of the fly ash were higher than concentrations considered representative of natural background substrate (<100 ng/g<sup>[12]</sup>) deposition of atmospheric Hg to the ash was the dominant flux and all emission fluxes mea-

sured were within the range for that reported for background soils<sup>[13]</sup>. At the second site, which had bituminous-subituminous derived and substrate Hg concentrations ranging from 21 to 230 ng/g, mean barren ash flux was 0.93 ng/m<sup>2</sup>h, and covered and vegetated ash was -0.7 ng/m<sup>2</sup>h. Average flux from the soils surrounding the deposit was 0.51 ng/m<sup>2</sup>h. Geographic Information System technology was applied to scaling up Hg flux for these landfills and based on the field data ~ 6 g of Hg would be deposited to the bituminous site over a year. If emissions were scaled up for a naturally enriched site, with similar Hg concentrations in the substrate, the total annual flux would be on the order of 20 g per year (based on data in<sup>[14]</sup>). Approximately 0.2 g would be emitted per year from the bituminous-subituminous ash landfill, which is roughly the same as that would be emitted from a similar area of the surrounding soil.

## CONCLUSIONS

Most samples of fly ash, with the exception of that which is lignite-based, were sinks for atmospheric Hg. Air Hg concentrations, light and temperature significantly influenced deposition and emission rates. Fly ash from carbon injection projects had higher rates of

atmospheric Hg deposition than did ash collected prior to carbon injection. The addition of carbon could have enhanced deposition for Hg has a strong affinity for carbon. Similar Hg fluxes, and factors influencing these fluxes, were measured in the field and laboratory indicating that the laboratory chamber serves as a good surrogate for field measurements as was indicated in earlier work (cf. 7). Mercury released from fly ash directly to water, investigated using SPLP leaching procedures, was very low. Fly ash samples used in this study released little Hg to the air and water, indicating that releases will be insignificant. Even if the worse case scenario for emissions from a lignite-based ash of 50 ng/m<sup>2</sup>hr were applied to a landfill of 100,000 m<sup>2</sup> approximately 43 g would be emitted per year. This is small in comparison to that estimated to be emitted or from naturally enriched areas, ~10 to 100's of kg/yr<sup>[15]</sup>.

## Acknowledgements

This work was funded by EPRI. Thanks to all the facilities that provided fly ash samples for this project and special thanks for the cooperation with personnel at the landfill sampling site. Thanks to Tony Gigliani, Melissa Markee, David Nacht, Justin Piper and Richard Zehner for help with data collection and analyses.

## REFERENCES

- [1] QUICK, J., BRILL, T., TABEL, D. E. (2003): Mercury in US Coal: Observations Using the COALQUAL and ICR Data; *Environmental Geology* 43, pp. 247-259.
- [2] EPRI (2002): *An Assessment of Mercury Emissions from U. S. Coal-Fired Power Plants*; Technical Report 1000608, Palo Alto, CA: EPRI 2002.
- [3] EPRI (1999): *The Stability of Mercury Captured on Sorbent Surface*; Technology Review TE-113926, Palo Alto, CA: EPRI 1999.
- [4] CHU, R., CHANG, R. (1999): *Mercury Stability in Power Plant Fly Ash and Scrubber Sludge: An Overview of Recent Studies by EPRI and others*; White Paper WP-114687, Palo Alto, CA: EPRI 1999.
- [5] EPRI (2001): *Occurrence and Fate of Mercury in Coal Ash and Flue Gas Desulfurization Sludge*; Technical Report 1005212, Palo Alto, CA: EPRI 2001.
- [6] GUSTIN, M., LADWIG, K. (2004): An Assessment of the Significance of Mercury Release from Coal Fly Ash; *Journal of Air and Waste Management Association* 54, pp. 320-330.
- [7] GUSTIN, M., RASMUSSEN, P., EDWARDS, G., SCHROEDER, W. (1999): Use of a Laboratory Gas Exchange Chamber to Predict in Situ Mercury Emissions; *Journal of Geophysical Research-Atmospheres* 104 D17:21, pp. 873-78.
- [8] GUSTIN, M., BIESTER, H., KIM, C. (2002): Investigation of Light Enhanced Emission of Mercury from Naturally Enriched Substrate; *Atmospheric Environment* 36, pp. 3241-3254.
- [9] GUSTIN, M., TAYLOR, G., MAXEY, R. (1997): Effect of Temperature, Wind Velocity and Concentration on the Flux of Elemental Mercury From Mill Tailings to the Atmosphere; *Journal of Geophysical Research* 102, pp. 3891-3898.
- [10] LINDBERG, S., JACKSON, D., HUCKABEE, J., JANZEN, S., LEVIN, M., LUND, J. (1979): Atmospheric Emission Plant Uptake of Mercury from Agricultural Soils Near the Almaden Mercury Mine; *Journal of Environmental Quality* 8, pp. 572-578.
- [11] ENGLE, M., GUSTIN, M., ZHANG, H. (2001): Quantifying Natural Source Mercury Emissions From the Ivanhoe Mining District, North-Central Nevada, USA; *Atmospheric Environment* 35, pp. 3987-3997.
- [12] GUSTIN, M., LINDBERG, S., AUSTIN, K., COOLBAUGH, M., VETTE, A., ZHANG, H. (2000): Assessing the Contribution of Natural Sources to Regional Atmospheric Mercury Budgets; *The Science of the Total Environment* 259, pp. 61-72.
- [13] ZHANG, H. LINDBERG, S., MARSIK, F., KEELER, G. (2001): Mercury Air/Surface Exchange Kinetics of Background Soils of the Tahquamenon River Watershed in the Michigan Upper Peninsula; *Water Air Soil Pollution* 126, pp. 151-169.
- [14] ZEHNER, R., GUSTIN M. (2002): Estimation of mercury vapor flux from natural substrate in Nevada; *Environmental Science and Technology* 36, pp. 4039-4045.
- [15] GUSTIN, M. (2003): Are Mercury Emissions from Geologic Sources Significant? A Status Report; *Science of the Total Environment* 304, pp. 153-167.

# Experimental examination of the influence of precipitation and moisture content on mercury emissions from soils

MAE GUSTIN\*, RICHARD ZEHNER, JELENA STAMENKOVIC

<sup>1</sup>University of Nevada, Reno Department of Natural Resources and Environmental Science.  
Mail Stop 370 Reno, NV 89557, USA; \*E-mail: msg@unr.nevada.edu

**Abstract:** Several studies have demonstrated that the addition of water causes a significant and immediate release of Hg from substrate. The effect of water addition and soil moisture on Hg fluxes, from soils enriched in Hg and with low Hg concentrations, was investigated using large mesocosms and small dynamic field flux chambers. The addition of water resulted in a significant release of Hg from both types of soils, however if soil pores were initially saturated with water, an increase in emissions was not observed until the next day. As the soils dried out over time, Hg flux also declined. Increasing soil moisture content for an extended period of time resulted in elevated daytime and nighttime Hg emissions relative to that occurring from dry soils. Addition of water during the day did not elicit the same response as nighttime addition due to competition with other factors controlling Hg flux. Data suggests that precipitation is an important process facilitating Hg emission and re-emission, of deposited atmospheric Hg, from soils.

**Key words:** soil moisture, air surface exchange, mercury flux

## INTRODUCTION

In order to estimate Hg emissions from soils, those processes controlling emissions and the forcing potential of those processes must be understood. It has been demonstrated that temperature<sup>[1, 2]</sup>, light<sup>[3, 4]</sup>, precipitation<sup>[5, 6]</sup>, air Hg concentration<sup>[6]</sup> and chemistry<sup>[7]</sup>, and soil Hg concentration<sup>[8]</sup> are important parameters controlling emissions. For several of these factors, algorithms have been developed that allow us to apply light intensity, temperature and substrate Hg concentration for estimating Hg emission from soils<sup>[6, 9, 10]</sup>. Several studies have demonstrated that the addition of water significantly enhances Hg release from soil<sup>[5, 6]</sup>. FRESCHOLTZ ET AL.<sup>[12]</sup> demonstrated that for one substrate type the magnitude of the release was correlated with Hg concentration. This release of Hg has

been hypothesized to be due to displacement of Hg by the more polar water molecules<sup>[6]</sup>. FRESCHOLTZ ET AL.<sup>[12]</sup> found no simultaneous increase in CO<sub>2</sub> flux in controlled laboratory experiments and suggested that this indicated that soil microbes were not responsible. Similar observations have been made for a variety of types of pesticides with emissions facilitated by soil wetting by rain, dew or irrigation<sup>[13, 14]</sup>. A marked increase in the diurnal emission of pesticide was also observed when the soil was moist<sup>[15]</sup>. Similar to the hypothesis regarding Hg emissions, these responses were attributed to the adsorption of the pesticide being reduced under moist conditions.

This study focused on characterizing the effect of irrigation and soil moisture on the release of Hg from background and enriched

soils through controlled experiments using large mesocosms and small dynamic field chambers. Three experimental designs were applied. Two utilized the Ecologically Controlled Enclosed Lysimeter Laboratories (EcoCELLs) at Desert Research Institute, Reno, NV. These mesocosms (7.3 x 5.5 x 4.5 m (l x w x d)) are totally enclosed and naturally lit plant growth chambers<sup>[16]</sup>. Whole mesocosm Hg flux response to watering was measured along direct soil surface flux using dynamic flux chambers (cf. 6). The first experiment (EXP 1) used Hg-enriched soils and two EcoCELLs. The substrate was sandy loam topsoil amended with Hg containing mill tailings ( $12000 \pm 1400$  ng Hg g<sup>-1</sup>). Water was added directly to the soil surface by a drip irrigation system daily. During the first year, approximately 100 one-year-old bare-rooted dormant whips of *Populus tremuloides* (quaking aspen) were planted in each of the EcoCELLs. During 2001 only one EcoCELL was planted.

The second experiment (EXP 2), that is ongoing, uses four EcoCELLs containing intact monoliths of tall grass prairie vegetation and soil (~ 10 ng/g Hg) obtained from Oklahoma, USA (cf. 17). In this experiment water is added from an overhead sprinkling system to maintain soil moisture and precipitation volume typical of annual averages in Oklahoma. The third experimental design (EXP 3) used tubs (39 x 28 x 16 cm) of approximately 4.7 L of soil housed in a temperature-controlled greenhouse. Mercury flux from the soil surface was measured using the dynamic flux chamber. Low Hg concentration topsoil obtained from the Oklahoma field site and naturally Hg-enriched soils (~ 4500 ng/g) were used. Experiments were configured to investigate the influence

of soil moisture and wetting and drying on Hg flux.

## RESULTS AND DISCUSSION

During the mesocosm EXP 1, watering occurred daily typically in the evening. With every watering event over a ~1.5 year period a pulse of Hg was released. During nighttime watering, Hg release was immediate and it took > 3 hours for the flux to decline to previous values. When water was added during the day the peak was short-lived and not as apparent suggesting that other factors were more significant in driving emissions. When watering occurred close to daybreak, the increase in flux with increasing light was not as dramatic. Nighttime peaks in Hg flux due to watering were greater than midday fluxes. The magnitude of the Hg release with watering was influenced by the presence or absence of plants, with a greater response in the unplanted cell.

In EXP 2 distinguishing whole system response to watering is difficult using the daytime data due to the low flux and other factors influencing flux. We are currently adjusting watering times to the night to see if a flux response occurs.

In EXP 3 for both enriched and background soils after initial watering to 25 % moisture content, there was no immediate increase in Hg flux. However, the day after watering daytime fluxes were significantly elevated above that occurring from dry soils; ~5-fold for unenriched soils and 3-fold for enriched soils. After watering daytime flux from Hg-enriched soils remained exacerbated above dry soil flux and declined gradually over time

similarly to the decline in soil moisture. Flux from low Hg soils returned to the original dry flux within two days after watering although soil moisture remained elevated suggesting that the available pool of Hg will influence the longevity of the effect. Watering of enriched soils to 13 % elicited an immediate flux response indicating the amount of water added will affect the initial response. For tubs whose soil moisture was elevated and maintained at 13 % and 20 % nighttime and midday Hg fluxes were in general significantly greater than for dry soils.

## CONCLUSIONS

With the addition of water to substrate Hg flux is enhanced; however, environmental

conditions, the amount of water added, the available soil Hg pool and the presence of vegetation will influence the magnitude of the response. This study demonstrated that precipitation events will play an important role in the re-emission and recycling of atmospherically deposited Hg, as well as enhance the release of Hg from naturally enriched soils. It is thought that similar to pesticides, water addition and increased soil moisture reduce the adsorption of Hg to soils and therefore facilitate its release.

## Acknowledgements

This work was funded an EPA EPSCoR grant, an EPA STAR grant- R82980001, an Atmospheric Sciences NSF grant and by EPRI.

## REFERENCES

- [1] LINDBERG, S., JACKSON, D., HUCKABEE, J., JANZEN, S., LEVIN, M., LUND, J. R. (1979): Atmospheric Emissions and Plant Uptake of Mercury From Agricultural Soils Near the Almaden Mercury Mine; *Journal of Environmental Quality* 8, pp. 572-578.
- [2] GUSTIN, M., TAYLOR, G., MAXEY, R. (1997): Effect of Temperature, Wind Velocity and Concentration on the Flux of Elemental Mercury From Mill Tailings to the Atmosphere; *Journal of Geophysical Research* 102, pp. 3891-3898.
- [3] ZHANG, H., LINDBERG, S., MARSIK, F., KEELER, G. (2001): Mercury Air/Surface Exchange Kinetics of Background Soils of the Tahquamenon River Watershed in the Michigan Upper Peninsula; *Water, Air and Soil Pollution* 126, pp. 151-169.
- [4] GUSTIN, M., BIESTER, H., KIM, C. (2002): Investigation of Light Enhanced Emission of Mercury From Naturally Enriched Substrate; *Atmospheric Environment* 36, pp. 3241-3254.
- [5] LINDBERG, S., ZHANG, H., GUSTIN, M., CASIMIR, A., EBINGHAUS, R., EDWARDS, G., FITZGERALD, C., KEMP, J., KOCK, H., LEONARD, T., MAJEWSKI, M., MARSIK, F., OWENS, J., POISSANT, L., RASMUSSEN, P., SCHAEGLICH, F., SCHNEEBERGER, D., SOMMAR, J., TURNER, R., VETTE, A., WALLSCHLAEGER, D., XIAO, Z. (1999): The Role of Rainfall and Soil Moisture on Mercury Emissions from Mercuriferous Desert Soils; *Journal of Geophysical Research- Atmospheres* 104 D17, pp. 21,879-21,888.
- [6] ENGLE, M., GUSTIN, M., ZHANG, H. (2001): Quantifying Natural Source Mercury Emissions From the Ivanhoe Mining District, North-Central Nevada, USA; *Atmospheric Environment* 35, pp. 3987-3997.
- [7] ENGLE, M., GUSTIN, M., LINDBERG, S., GERTLER, A. (2004): Investigation of the Effect of Tropospheric Oxidants on Mercury Emission From Substrates; *RMZ-Materials & Geoenvironment*, (in press, this issue).

- [8] GUSTIN, M. (2003): Are Mercury Emissions From Geologic Sources Significant?: A Status Report; *Science of the Total Environment* 304, pp. 153-167.
- [9] COOLBAUGH, M., GUSTIN, S., RYTUBA, J. (2002): Annual Emissions of Mercury to the Atmosphere From Three Natural Source Areas in Nevada and California; *Environmental Geology* 42, pp. 338-349.
- [10] ZEHNER, R., GUSTIN, M. (2002): Estimation of Mercury Vapor Flux from Natural Substrate in Nevada; *Environmental Science and Technology* 36, pp. 4039-4035.
- [11] NACHT, D., GUSTIN, M. (2004): Mercury Emissions From Background and Altered Geologic Units Throughout Nevada; *Water, Air and Soil Pollution* 151, pp. 179-193.
- [12] FRESCHOLTZ, T., GUSTIN, M. (2004): Soil and Foliar Mercury Emission as a Function of Soil Concentration; *Water, Air and Soil Pollution* (in press).
- [13] GROVER, R., SHEWCHUK, S., CESSNA, A., SMITH, A., HUNTER, J. (1985) Fate of 2,4-D Iso-octyl Ester After Application to a Wheat Field; *Journal of Environmental Quality* 14, pp. 203-210.
- [14] HARPER, L., WHITE, A., BRUCE, R., THOMAS, A., LEONARD, R. (1976): Soil and Microclimate Effects on Trifluralin Volatilization; *Journal of Environmental Quality* 5, pp. 236-242.
- [15] PARMELE, L., LEMON, E., TAYLOR, A. (1972): Micrometeorological Measurement of Pesticide Vapor Flux From Bare Soil and Coren Under Field Conditions; *Water, Air and Soil Pollution* 1, pp. 433-351.
- [16] GRIFFIN, K., ROSS, P., SIMS, D., LUO, Y., SEEMANN, J., FOX, C., BALL, J. (1996): EcoCELLS: Tools for Mesocosm Scale Measurements of Gas Exchange. *Plant, Cell and Environment* 19, pp. 1212-1221.
- [17] OBRIST, D., GUSTIN, M., ARNONE, J., JOHNSON, D., SCHORRAN, D., VERBURG, P. (2004): Large Annual Mercury Emissions to the Atmosphere Measured Over Tallgrass Prairie Ecosystems; *RMZ-Materials & Geoenvironment* (in press, this issue).

## Regional Differences in Methylmercury Concentrations in Wet Deposition to Northern Areas of Wisconsin, Michigan, and Ontario

B HALL, G.J. KEELER, J.P. HURLEY, H. MANOLOPOULOS, J. GRAYDON & V.L. ST. LOUIS

**Abstract:** Methylmercury (MeHg) and total mercury (THg) concentrations were measured in precipitation samples collected using automated precipitation collectors situated in Wisconsin, Michigan, and northwestern Ontario. Precipitation samples were taken between May 1997 and October 1999 at two sites of the southern shore of Lake Superior (Brule River, WI and Tahquamenon River, MI) and at the Isle Royale National Park (MI). Precipitation collection from Eagle Harbor (MI) and Devil's Lake (WI) occurred between May 1997 and December 2003 and between October 2002 and December 2003, respectively. MeHg and THg concentrations were compared to a longer dataset (1992-2003) of MeHg and THg in precipitation collected at the Experimental Lakes Area (ELA) in northwestern Ontario.

Detectable MeHg levels ( $>0.01 \text{ ng L}^{-1}$ ) were found in the majority of rain and snow samples collected from all sites. In general, the highest MeHg levels in precipitation were observed in samples collected from Brule River and Eagle Harbor, where concentrations often exceeded  $0.2 \text{ ng L}^{-1}$  and were as high as  $0.8 \text{ ng L}^{-1}$ . The lowest MeHg concentrations were observed in samples taken at the ELA, where concentrations never exceeded  $0.2 \text{ ng L}^{-1}$ . THg concentrations in precipitation were between 10 and  $60 \text{ ng L}^{-1}$ , with THg concentrations exceeding  $80 \text{ ng L}^{-1}$  in precipitation collected from the Brule River, Isle Royale, and DevilsLake sites. The proportion of THg that was MeHg (% MeHg) was under 7 % MeHg for samples taken from all sites, with the exception of 7 events sampled at the Tahquamenon River that between 7 % and 18 % MeHg. Although the highest MeHg concentrations were found in low volume precipitation events, there was no correlation between MeHg concentrations and event volume ( $r^2 = 0.044$ ). Differences in MeHg and THg concentrations and % MeHg will be explored using storm trajectory data which will help determine the sources of MeHg and THg to remote ecosystems.

## Mercury emission to atmosphere from natural sources in Chongqing, China

LEI HE<sup>1</sup> & DINGYONG WANG<sup>1</sup>

<sup>1</sup>College of Resources and Environment, Southwest Agricultural University, Chongqing 400716, P. R. China, e-mail: wangdy@swau.cq.cn

**Abstract:** This report is to estimate the mercury emissions to the atmosphere from the natural sources in Chongqing, China, and to present an assessment of the contribution to the local mercury budget from selected natural sources. Air/surface exchange of mercury was investigated over five soil sites of three different areas (mercury polluted area, farmland and woodland) and above tow surfaces of watershed (Jialing river and Beibei reservoir in north Chongqing) from August to November in 2003. Measurements of mercury fluxes were performed by dynamic flux chamber (DFC). The results indicated that mean mercury emission fluxes were  $8.4 \pm 2.1 \text{ ng m}^{-2} \text{ hr}^{-1}$  for five soil sites and  $21.6 \pm 5.9 \text{ ng m}^{-2} \text{ hr}^{-1}$  for tow watersheds. Mercury dry deposition fluxes was observed over tow soil sites at overcast days (mean= $6.4 \pm 1.5 \text{ ng m}^{-2} \text{ hr}^{-1}$ ). The mercury release fluxes measured at those soil sites are similar to those found other soil sites in Guizhou province, China. A diurnal cycle was observed for mercury emission from a campus site, with day-time volatilization rates significantly higher than night-time rates (mercury release to the atmosphere from land surface during day, deposition to earth surface from atmosphere during night). Rapid response of mercury emission to solar radiation was observed, whereas soil or surface water temperature was found to less influential to mercury air/surface exchange over those sites. Based on local weather situation and results of field measurement, the emission factors of soil and water were  $16 \text{ g Hg km}^{-2} \text{ yr}^{-1}$  and  $59 \text{ g Hg km}^{-2} \text{ yr}^{-1}$ , respectively, were used to estimate natural release of mercury. The annual emission to atmosphere from natural sources is about 1.36 t of mercury in Chongqing, China.

**Key words:** Atmosphere, dynamic flux chamber, natural mercury emission

# Modelling RGM Concentrations from Hg<sup>0</sup> Measurements in the Pacific Ocean and Mediterranean Sea: Comparison with Measured Values

IAN M. HEDGECOCK<sup>1</sup>, GIUSEPPE A. TRUNFIO<sup>1</sup>, FRANCESCA SPROVIERI<sup>1</sup>, NICOLA PIRRONE<sup>1</sup>,  
FABIEN LAURIER<sup>2</sup> AND ROBERT P. MASON<sup>2</sup>

<sup>1</sup>CNR - Istituto sull'Inquinamento Atmosferico, c/o UNICAL (Polifunzionale),  
Rende, 87036, Italy; E-mail: i.hedgecock@cs.iiia.cnr.it

<sup>2</sup>Chesapeake Biological Laboratory, Center for Environmental Science, University of Maryland,  
P.O. Box 38, Solomons, MD 20688-0038, U.S.A.; E-mail: laurier@cbl.umces.edu

**Abstract:** Measured Hg<sup>0</sup><sub>(g)</sub> and ancillary chemical and meteorological data have been used to constrain the multiphase photochemical box model AMCOTS (Atmospheric Mercury Chemistry Over The Sea), and the predicted Hg<sup>II</sup><sub>(g)</sub> (HgCl<sub>2</sub>, HgBr<sub>2</sub> and HgO) concentration compared to the Reactive Gaseous Mercury (RGM) results obtained during two oceanographic cruises. The two oceanographic Hg measurement campaigns - the R.V. Melville campaign from Japan to Honolulu, and the R.V. Urania campaign around the Mediterranean - used the same techniques to determine the atmospheric concentrations of Hg<sup>0</sup><sub>(g)</sub> and Hg<sup>II</sup><sub>(g)</sub>. The model reproduces both the magnitude and temporal variation of RGM for both data sets, using all the measured meteorological and chemical species concentration data and just one fitting parameter. The different atmospheric and chemical conditions encountered on the two cruises are reflected in the relative importance of the OH and halogen oxidation reactions. The halogen oxidation reactions account for by far the greater part of RGM in the Pacific simulations, whilst in the summertime Mediterranean simulations OH played an important role as the halogen oxidation reactions.

**Key words:** mercury, modelling, measurements, marine boundary layer

## INTRODUCTION

The measurement of significant, consistent and diurnally varying concentrations of RGM in the MBL has led to the hypothesis that the same halogen chemistry which is believed to be responsible for polar spring-time Mercury Depletion Events (MDEs) also occurs to a lesser extent, but on a daily basis in the MBL. Photochemical box modelling studies have shown that the cycling of oxidised Hg compounds (such as HgO<sub>(g)</sub>) via the sea salt aerosol could result in the out-

gassing of the more stable and more volatile HgCl<sub>2</sub> resulting in a non-anthropogenic contribution to measured RGM in the MBL (HEDGECOCK AND PIRRONE, 2001). These first modelling studies could not however account for the levels of RGM actually measured. Inclusion in the photochemical model of the recently measured reactions between Hg<sup>0</sup><sub>(g)</sub> and halogen compounds (ARIYA ET AL., 2002), particularly the Br radical, showed that as a result of the release of active halogen compounds from deliquescent sea salt aerosol, Hg<sup>0</sup><sub>(g)</sub> oxidation could occur at an appreciable

rate, producing RGM levels compatible with experimentally determined concentrations in the MBL, (HEDGECOCK ET AL., 2003; HEDGECOCK AND PIRRONE, 2004). The modelling and experimental results above were primarily concerned with the Mediterranean, which is not however representative of the 'typical' MBL, being almost landlocked, influenced by anthropogenic emissions, and warm both in terms of sea and air temperature. Therefore, in order to test the model more comprehensively it has been used to simulate  $\text{Hg}^{\text{II}}_{(\text{g})}$  concentrations using measured  $\text{Hg}^0_{(\text{g})}$  concentrations, and has been further constrained by the use of measured  $\text{O}_3$ , and meteorological data and other available ancillary data pertinent to the model. The details of the measurements performed and the precise routes of the two oceanographic cruises can be found in the literature; LAURIER ET AL. (2003) describe the R.V. Melville campaign, lasting from May 1st to June 5th 2002, which started from Osaka, Japan and finished in Honolulu, Hawaii, and SPROVIERI ET AL. (2003) describe the R.V. Urania campaign between July 14th and August 5th 2000, in both the Eastern and Western Basins of the Mediterranean. During both cruises  $\text{Hg}^0_{(\text{g})}$  and RGM were measured using the same analytical techniques and the same type of instrument: the Tekran 1130 speciation unit coupled with to the Tekran 2537A analyser (Tekran, Inc., Toronto, Canada). The AMCOTS model is described in HEDGECOCK AND PIRRONE (2004). It is based on the MOCCA model chemical reaction database (SANDER, 1999), but uses a different photolysis rate calculation routine, (FAST-J, WILD ET AL., 2000), and a different integration routine, ROS2 a second order Rosenbrock method for stiff ordinary differential equations, (SANDU ET AL., 1997,

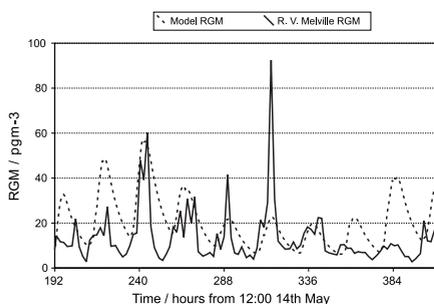
DAMIAN-IORDACHE ET AL., 2002). The Hg chemistry includes gas and aqueous phase reactions and aqueous phase equilibria, as well as phase transfer processes. Deposition is modelled using a constant deposition velocity which means that loss via deposition is directly dependent only on MBL height,  $-d(\text{Hg}^{\text{II}}_{(\text{g})})/dt = v_{\text{dep}}/z_{\text{MBL}}$  where  $v_{\text{dep}}$  is the deposition velocity and  $z_{\text{MBL}}$  is the height of the MBL expressed using the same length units as  $v_{\text{dep}}$ . It proved to be necessary to vary  $z_{\text{MBL}}$  during the simulations to ensure a reasonable fit between the simulated concentrations of  $\text{Hg}^{\text{II}}_{(\text{g})}$  and measured RGM values.

## RESULTS AND DISCUSSION

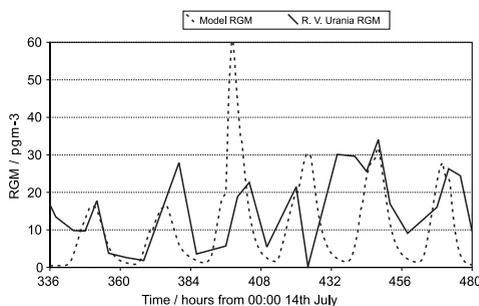
A reasonable fit of the maxima and also daily variation of the simulated  $\text{Hg}^{\text{II}}_{(\text{g})}$  concentration with measured RGM values was obtained using just three  $z_{\text{MBL}}$  values to fit the data over the entire campaign period, for both the Pacific and Mediterranean measurements. The timing and the magnitude of the changes in  $z_{\text{MBL}}$  were chosen solely to obtain a reasonable fit with the measured data. However it comes as no surprise that the timing of the  $z_{\text{MBL}}$  changes in the simulations correspond to changing meteorological conditions as measured during the campaigns. Temperature, pressure and relative humidity as measured on board the research vessels have been included with the  $\text{Hg}^0_{(\text{g})}$  and  $\text{O}_3$  concentrations in the model input; the meteorological parameter not included specifically is wind speed, which has an effect on sea salt aerosol production, which affects directly affects atmospheric liquid water content, and in time the multiphase chemistry of the MBL, (VON GLASOW ET AL., 2002). Introducing a parameterisation of sea salt aerosol produc-

tion would have added another possible source of error to the model, and as the aim was to assess the validity of the chemistry model, the use of just  $z_{\text{MBL}}$  to fit the data was preferred. Bearing in mind the ‘typical’ MBL heights for the Pacific and Mediterranean, 1000 m and 400 m respectively, the values used in the simulations were as follows: for the Pacific: day 1 to day 8, 100 m; day 8 to day 17, 700 m, and after day 17, 200 m; for

the Mediterranean: day 1 to day 14, 50 m, day 14 to day 20, 200 m, and after day 20, 100 m. The first two figures below (Figs. 1a and b), show the periods in which  $z_{\text{MBL}}$  is at its highest value. The fit is not perfect but it can be seen that the general trend is reproduced, although some of the highest measurements are noticeably greater than the simulated concentrations.



**Figure 1a**



**Figure 1b**

**Figure 1.** The modelled and measured RGM concentrations during the periods in which  $z_{\text{MBL}}$  was closest to its typical value, for the Pacific (a)  $z_{\text{MBL}} = 700$  m, for the Mediterranean (b)  $z_{\text{MBL}} = 200$  m.

One of the more interesting results from the simulations arises from the comparison of the relative importance of the  $\text{Hg}^0_{(\text{g})} + \text{Br} \rightarrow \text{Hg}^{\text{II}}_{(\text{g})}$  and  $\text{Hg}^0_{(\text{g})} + \text{OH}_{(\text{g})} \rightarrow \text{Hg}^{\text{II}}_{(\text{g})}$  reactions. Figures 2a and b show the production rates in molecules  $\text{cm}^{-3} \text{s}^{-1}$ , for the periods when the fitting parameter  $z_{\text{MBL}}$  was at its highest in the Pacific and Mediterranean cases respectively. It is clear that in the Mediterranean oxidation by the OH radical is of much greater importance than in the remote MBL.

This is due both to the geographical location and the specific meteorological conditions encountered in the Mediterranean during the

summer. The high air temperatures and insolation in the Mediterranean favour the production of  $\text{O}_3$ , as does the general southerly air flow from the more industrial and urbanised areas of Europe toward the Mediterranean Basin, bringing with it  $\text{O}_3$  precursor pollutants. In fact large areas of the Mediterranean regularly exceed the European 8 hour exposure limit for  $\text{O}_3$ . This difference in average  $\text{O}_3$  concentration between the Pacific and the Mediterranean can be seen from the results obtained during the R.V. Melville and Urania cruises: less than 40 ppb for the Pacific (less than 20 ppb in the latter stages of the campaign) and over 50 ppb for the Mediterranean.

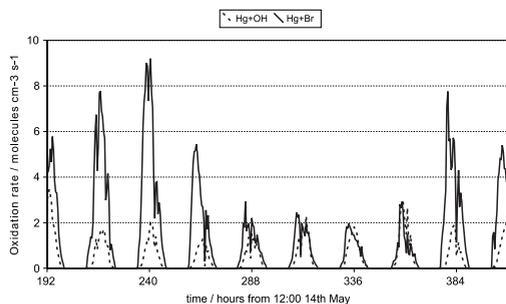


Figure 2a

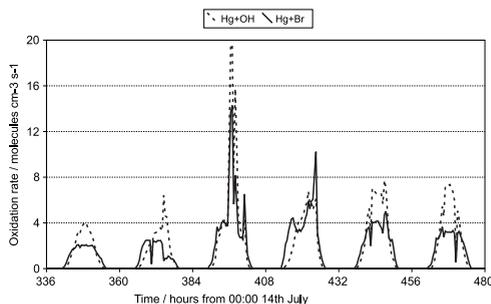


Figure 2b

**Figure 2.** The modelled rate of  $\text{Hg}^0_{(g)}$  oxidation by the Br and the OH radicals for the same periods as Figure 1. Figure 2a is the Pacific simulation and Figure 2b the Mediterranean. The higher overall rate and generally higher contribution from OH for the Mediterranean simulation can be seen clearly.

## CONCLUSIONS

The AMCOTS model has been used to study results obtained from the Pacific and the Mediterranean with reasonable success. This study has highlighted the differences between the chemistry that occurs in the re-

spective MBLs. However, AMCOTS, being a box model, has limitations in terms of being able to predict  $\text{Hg}^{\text{II}}_{(g)}$  concentrations, as discussed above, but it is generally applicable in the sense that it may be used to investigate the relative importance of the chemical reactions and physical processes which occur in the MBL.

## REFERENCES

- DAMIAN-IORDACHE, V., SANDU, A., DAMIAN-IORDACHE, M., CARMICHAEL, G. R., POTRA, F. A. (2002): The kinetic preprocessor KPP a software environment for solving chemical kinetics; *Comput. Chem. Eng.*, Vol. 26, pp.1567-1579.
- HEDGECKO, I. M., TRUNFIO, G. A., SPROVIERI, F., PIRRONI, N., LAURIER F. J. G., MASON, R. P. (2004): Modelled Reactive Gaseous Mercury Concentrations in the Marine Boundary Layer: A Comparison with Measurements from the Pacific and the Mediterranean; Submitted to *Env. Sci. Technol.*
- HEDGECKO, I. M., PIRRONI, N. (2001): Mercury photochemistry in the marine boundary layer modelling studies suggest the in situ production of reactive gas phase mercury; *Atmos. Environ.*, Vol. 35, pp. 3055-3062.
- HEDGECKO, I. M., PIRRONI, N. (2004): Chasing Quick-silver: Modelling the atmospheric lifetime of in the marine boundary layer; *Env. Sci. Technol.*, Vol. 38, pp. 69-76.
- HEDGECKO, I. M., PIRRONI, N., SPROVIERI, F., PESENTI E. (2003): Reactive gaseous mercury in the marine boundary layer: Modelling and experimental evidence of its formation in the Mediterranean region; *Atmos. Environ.*, Vol. 37, pp. 41-49.
- LAURIER, F. J. G., MASON, R. P., WHALIN, L., KATO, S. (2003): Reactive gaseous mercury formation in the North Pacific Ocean's marine boundary layer: A potential role of halogen chemistry; *J. Geophys. Res.*, Vol. 108(D17), p. 4529. doi:10.1029/2003JD003625.
- MASON, R. P., SHEU, G.-R. (2002): The role of the ocean in the global mercury cycle; *Global Biogeochemical Cycles* 16(4), p1093. doi:10.1029/2001GB001440.

- SANDER, R. (2001): *MOCCA and Mocalce user manual for version 66*; <http://www.mcph-mainz.mpg.de/sander/mocca>.
- SANDU, A., VERWER, J. G., BLOM, J. G., SPEE, E.J., CARMICHAEL, G. R., POTRA, F. A. (1997): Benchmarking stiff ode solvers for atmospheric chemistry problems II: Rosenbrock solvers; *Atmos. Environ.*, Vol. 31, pp. 3459-3472.
- SPROVIERI, F., PIRRONE, N., GLRDFELDT K., SOMMAR, J. (2003): Mercury speciation in the marine boundary layer along a 6000 km cruise path around the Mediterranean Sea; *Atmos. Environ.*, Vol. 37, pp. 63-71.
- VON GLASOW, R., SANDER, R., BOTT, A., CRUTZEN, P. J. (2002): Modeling halogen chemistry in the marine boundary layer I. Cloud free MBL; *J. Geophys. Res.*, Vol. 107, p. 4341. doi: 10.1029/2001JD000942.

## On the Atmospheric Lifetime of Elemental Mercury

IAN M. HEDGECKOCK, GIUSEPPE A. TRUNFIO AND NICOLA PIRRONI

CNR - Istituto sull'Inquinamento Atmosferico, Rende, 87036, Italy;

E-mail: i.hedgecock@cs.iiia.cnr.it

**Abstract:** The lifetime of elemental mercury in the Marine Boundary Layer (MBL) has been studied as a function of time of year, latitude, temperature, liquid water content and cloud optical depth using the AMCOTS (Atmospheric Chemistry of Mercury Over the Sea) box model. The model includes gas and aqueous phase chemistry, and includes heterogeneous reactions as well as mass transfer processes. The sea salt and sulphate components of the ambient aerosol are treated separately. Photolysis rate constants are calculated as a function of latitude, time of year and cloud optical depth. Simulation of Hg<sup>0</sup>(g) depletion and Hg<sup>II</sup>(g) production show that under clear sky conditions significant reduction (up to 90 %) of Hg<sup>0</sup>(g) concentrations could occur within a week, in the absence of emissions, and that over the same period Hg<sup>II</sup>(g) concentrations could reach more than 100 pg m<sup>-3</sup>.

**Key words:** mercury, modeling, lifetime, MBL

### INTRODUCTION

The AMCOTS (Atmospheric Mercury Chemistry Over The Sea) model is a 0-dimensional combination of gas and atmospheric aqueous phase MBL chemistry, gas and aqueous phase Hg chemistry, (the aqueous phase being either sea salt or sulphate aerosols), mass transfer between phases and gas and aqueous phase photolysis. The chemical reaction database used to simulate the chemistry of the MBL is based on that used in the MOCCA model (SANDER, 2001), the rate constants have been updated where appropriate with reference to VON GLASOW ET AL. (2002); the Hg chemistry included is described in HEDGECKOCK ET AL. (2003) and HEDGECKOCK AND PIRRONI (2004).

Simulations were performed starting with an initial Hg<sup>0</sup>(g) concentration of  $4.5 \times 10^6$  molecules cm<sup>-3</sup> (1.5 ng m<sup>-3</sup> at 1 atmosphere,

298K). The other initial gas phase concentrations used were from SANDER AND CRUTZEN (1997) and VON GLASOW ET AL. (2002). The aerosol number density and radii used, were those from MOCCA and the respective LWC values were  $1.07 \times 10^{-12}$  and  $3 \times 10^{-11}$  vol/vol for the sulphate and sea-salt particles respectively. Aerosol deposition is simulated using an atmospheric lifetime of 2 and 7 days for sea-salt and sulphate particles respectively. Dry deposition is modelled as a constant deposition velocity, for HgO, HgCl<sub>2</sub>, and HgBr<sub>2</sub>, 2 cms<sup>-1</sup> was used, the same as that used in MOCCA for the inorganic acid gases HNO<sub>3</sub>, HCl and H<sub>2</sub>SO<sub>4</sub>. The air temperature was taken from the monthly averages for the Atlantic ocean (ISCCP, 2002). In all simulations a boundary layer height was assumed to be 1000 m and clouds assumed to be above this if present. Cloud optical depths used were 10, 20, 40 and 60.

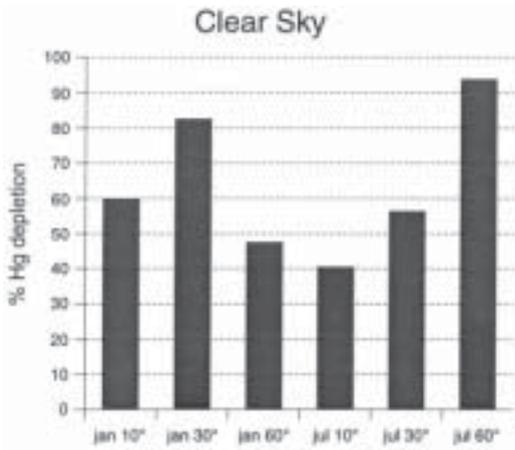


Figure 1.

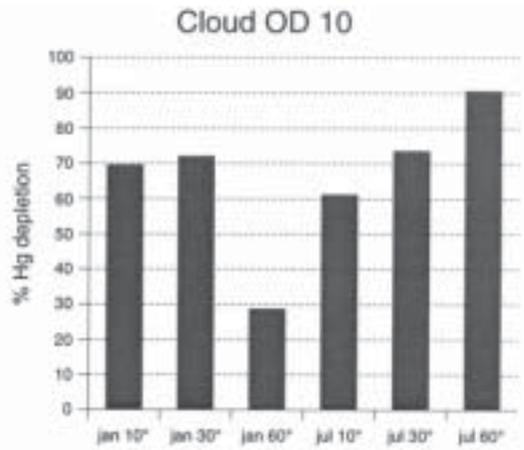


Figure 2.

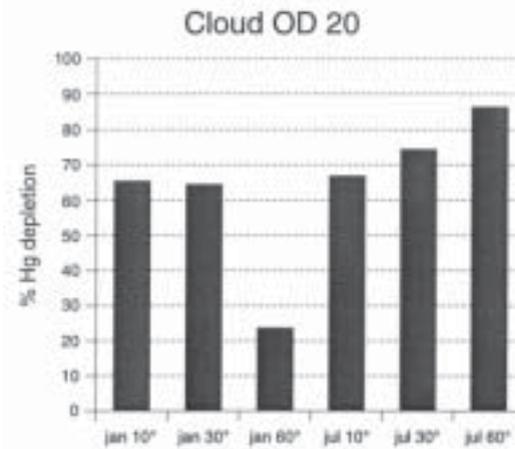


Figure 3.

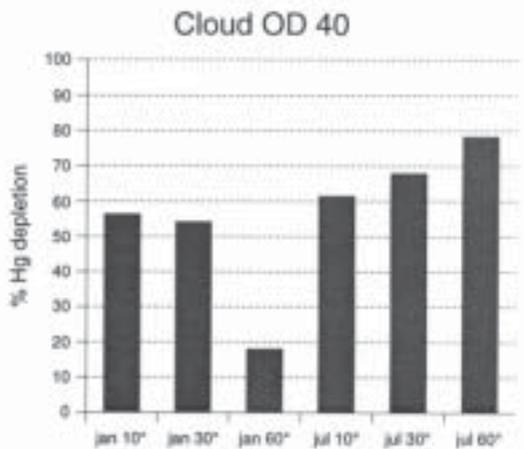


Figure 4.

Cloud OD 60

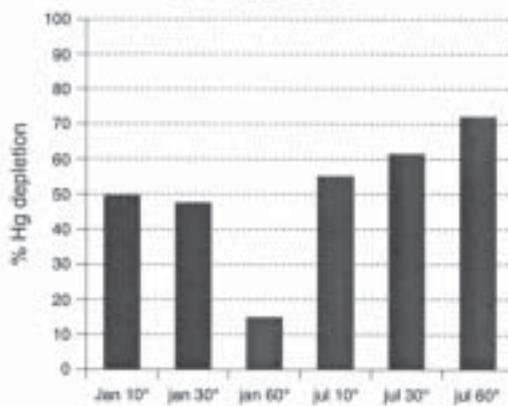


Figure 5.

## RESULTS AND DISCUSSION

The reduction of the  $\text{Hg}^0_{(g)}$  concentration expressed as a percentage of the starting concentration is shown in Figures 1-5 for different latitudes ( $^{\circ}\text{N}$ ) in January and July for the five cloud optical depth scenarios simulated.

The influence of sunlight on  $\text{Hg}^0_{(g)}$  depletion is evident from both the generally lower depletion seen at  $60^{\circ}\text{N}$  in January, shorter days and the generally decreasing depletion seen with increasing cloud optical depth. There are some results in the simulations which at first sight seem a little odd. For example  $\text{Hg}^0_{(g)}$  depletion at  $10^{\circ}\text{N}$  in July has a maximum with a cloud optical depth of 20. The  $\text{Hg}^0_{(g)}$  depletion at  $30^{\circ}\text{N}$  in January is higher than that at  $10^{\circ}\text{N}$  in the same month even though at  $30^{\circ}\text{N}$  the days are shorter. The reasons behind these apparent anomalies lie in the influence of air temperature, and the wavelength dependent attenuation of incoming solar radiation by clouds on the processes which lead to the production of reactive halogen species in the MBL, (HEDGECK AND PIRRONE, 2004). Cooler air temperatures increase the solubility of acidic gases in the sea salt aerosol increasing the rate of acidification and enhancing the rate

of reactive halogen precursor species outgassing from the aerosol. Hence the greater depletion at  $30^{\circ}\text{N}$  where the air temperature is lower than at  $10^{\circ}\text{N}$  where it is warmer. One of the major sinks BrO (formed from  $\text{O}_3 + \text{Br}$ , and rapidly photolysed to  $\text{Br} + \text{O}$ , and therefore in dynamic equilibrium with Br, recently identified as an important  $\text{Hg}^0_{(g)}$  oxidant (ARIYA ET AL., 2002), is  $\text{HO}_2$ , which depends for its production on the OH radical which is therefore strongly influenced by the rate of  $\text{O}_3$  photolysis. The attenuation of incoming solar radiation by clouds is greater at the shorter wavelengths which photolyse  $\text{O}_3$  than at the longer wavelengths which photolyse  $\text{Br}_2$  and  $\text{BrCl}$ , the two principal precursors for Br. Therefore, up to a certain point increasing cloud cover reduces  $\text{HO}_2$  production, limiting the BrO sink, whilst at the same time having a lesser effect on the photolysis of Br precursors. Thus under slightly cloudy conditions the Br concentration can be higher than under clear sky conditions enhancing  $\text{Hg}^0_{(g)}$  depletion. Using average cloud optical depth and surface air temperatures the lifetime of  $\text{Hg}^0_{(g)}$  can be calculated. The lifetime is the sum of the inverse of the oxidation reaction rates (rate constant multiplied by concentration):

$$\tau = \{ k(\text{Hg}^0 + \text{O}_3) \cdot [\text{O}_3] + k(\text{Hg}^0 + \text{OH}) \cdot [\text{OH}] + k(\text{Hg}^0 + \text{Br}) \cdot [\text{Br}] \}^{-1},$$

$$\tau^{-1} \approx 2 \times 10^{-8} + 8.7 \times 10^{-8} + 1 \times 10^{-6} \text{ thus, } \tau \approx 10.5 \text{ days,}$$

alternatively the lifetime with respect to the individual reactions under the model conditions are:  $t(\text{Hg}^0 + \text{O}_3) = 578$  days,  $t(\text{Hg}^0 + \text{OH}) = 133$  days and  $t(\text{Hg}^0 + \text{Br}) = 11.5$  days (HEDGECK AND PIRRONE, 2004). The atmospheric lifetime of  $\text{Hg}^0_{(g)}$  therefore would appear to depend on which part of the atmosphere is being considered; in the free tro-

posphere and in continental boundary layers the answer is probably around a year as is generally thought, although it should be borne in mind that the  $\text{O}_3$  concentration used in these studies (21 ppb) for the remote MBL is low compared to the concentrations found for example in the Mediterranean and also in some continental air masses. Higher  $\text{O}_3$

itself would not lead to a much lower lifetime, but the higher OH concentrations resulting from increased  $O(^1D)$  would decrease the  $Hg^0_{(g)}$  lifetime with respect to OH oxidation. If the daily average concentration increased to say  $5 \times 10^6$  molecules  $cm^{-3}$  the lifetime with respect to OH oxidation would decrease to a little less than 1 month. However global scale modelling studies have found that such a rapid rate of oxidation is difficult to reconcile with the stable hemispheric background concentrations, whilst noting that the reaction of  $Hg^0_{(g)}$  with  $O_{3(g)}$  is too slow to account for all the  $Hg^0_{(g)}$  removal, (Bergan and Rodhe, 2001). In the MBL, depending on time of year and atmospheric conditions, the atmospheric lifetime of  $Hg^0_{(g)}$  may well be as short as two weeks, and this would apply also to continental air masses moving over the sea. Bearing in mind that halogen activation is more rapid under polluted (high  $NO_x$ ) conditions (SANDER AND CRUTZEN, 1996)  $Hg^0_{(g)}$  from continental air masses could be deposited relatively close to the coast. This would particularly be the case in areas such as the Mediterranean.

## CONCLUSION

Using a detailed multiphase photochemical box model of the MBL, it has been shown that it is probable that  $Hg^0$  in the remote MBL can have an atmospheric lifetimes as short as 10 days, depending on time of year, cloud cover (optical depth) and latitude. The factors influencing the rate of  $Hg^0$  oxidation are the relative rates of  $O_3$  and  $Br_2/BrCl$  photolysis, the air temperature and the length of the day. The role of  $Hg^0$  emission from the world oceans in global Hg budget estimations needs to be reassessed. This already been addressed to some extent by MASON AND SHEU (2002), who have revised downwards their estimate of the contribution of the  $Hg^0$  evasion flux to the overall global budget, due to the more rapid cycling and re-deposition of Hg in the MBL when compared to the continental boundary layer. However it should now be possible to constrain these estimates even more closely, with knowledge of average cloud optical depth, surface air temperatures and perhaps parametrizing aerosol production rates

## Acknowledgements

This work is part of the MERCYMS (<http://www.cs.iaa.cnr.it/MERCYMS/project.htm/>) funded by the European Commission (Contr. No. EVK3-2002-00070).

## REFERENCES

- ARIYA, P. A., KHALIZOV, A., GIDAS, A. (2002): Reaction of gaseous mercury with atomic and molecular halogens: kinetics, products studies, and atmospheric implications; *J. Phys. Chem. A*, Vol. 106, pp. 7310-7320.
- BERGAN, T., RODHE, H. (2001): Oxidation of elemental mercury in the atmosphere: Constraints imposed by global scale modelling; *J. Atmos. Chem.*, Vol. 40, pp. 191-212.
- HEDGECOCK, I. M., PIRRONE, N. (2004): Chasing Quick-silver: Modelling the atmospheric lifetime in the marine boundary layer; *Env. Sci. Technol.*, Vol. 38, pp. 69-76.
- HEDGECOCK, I. M., PIRRONE, N., SPROVIERI, F., PESENTI E. (2003): Reactive gaseous mercury in the marine boundary layer: Modelling and experimental evidence of its formation in the Mediterranean region; *Atmos. Environ.*, Vol. 37, pp. 41-49.
- ISCCP (2002): *International Satellite Cloud Climatology Project, Cloud analysis Part 3 Seasonal variations of cloud and surface properties*; <http://isccp.giss.nasa.gov/climanal3.html>.
- MASON, R. P., SHEU, G.-R. (2002): The role of the ocean in the global mercury cycle; *Global Biogeochemical Cycles* 16(4), p. 1093, doi:10.1029/2001GB001440.
- SANDER, R. (2001): MOCCA and MokkaIce user manual for version 66, <http://www.mcp-mainz.mpg.de/sander/mocca>.
- SANDER, R., CRUTZEN, P. J. (1996): Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea; *J. Geophys. Res.*, Vol. 101, pp. 9121- 9138.
- VON GLASOW, R., SANDER, R., BOTT, A., CRUTZEN, P. J. (2002): Modeling halogen chemistry in the marine boundary layer I. Cloud free MBL; *J. Geophys. Res.*, Vol. 107, 4341.

## Biomonitoring of mercury in air by transplanted lichens

MILENA HORVAT<sup>1</sup>, JOŽE KOTNIK<sup>1</sup>, ZDRAVKO SPIRIC Z<sup>2</sup>, VESNA FAJON<sup>1</sup>,  
ZVONKA JERAN<sup>1</sup>, RADOJKO JACIMOVIĆ<sup>1</sup>

<sup>1</sup>Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia;

E-mail: milena.horvat@ijs.si

<sup>2</sup>INA-Naftaplin, Šubiceva 29, Zagreb, Croatia; E-mail: zdravko.spiric@ina.hr

**Abstract:** Mercury biomonitoring in air using transplanted lichens specie *Hypogymnia physodes* was used at natural gas treatment facilities, reference stations and former mercury mining areas. The results indicated excellent agreement between predicted Hg concentrations in air and Hg concentrations in transplanted lichens.

**Keywords:** mercury, air, biomonitoring, lichens, gas and oil industry, mercury mining

### INTRODUCTION

It is well known that lichens continuously accumulate Hg and other elements from the atmosphere, and therefore concentrations depend on ambient levels of these elements, the age of the lichens and their physiological conditions (HORVAT ET AL., 2000; LOPPI, 2001; CONTI AND CECCHETTI, 2001). Concentrations of mercury in lichens represent the average long-term Hg status in air, while Hg measurements in air represent only the average value during the sampling period (e.g. from several minutes to the maximum daily average concentrations). Natural gas contains various forms of inorganic and organic Hg species which have to be removed from the gas due to technological and environmental reasons. Legislation requires regular monitoring of mercury emissions into the atmosphere where various techniques could be used. Biomonitoring investigated in this study represents cost-effective means to assess the level of contamination of ambient mercury around hot spots of mercury pollution.

### Sampling, transplantation of lichens and sample preparation

In the present study various geographical areas were studied: (a) the INA Naftaplin Gas Treatment Plants in Croatia, where the efficiency of an industrial facility for removal of Hg from natural gas was investigated, and (b) Zutica and Etan, (c) the mercury mining area, Idrija, Slovenia, and (d) Reactor center which represents clean area close to Ljubljana. Experimental sites are presented in Figure 1.

As the first step, the lichen species *H. physodes* was collected from orchard trees at a pristine area in Slovenia approximately one week before transplantation. In the laboratory, lichens were carefully cleaned from the branches and collected within polyethylene nets. Three nets were fastened to branches or on an artificial rod about 1.5-2 m above the ground at each location in Croatia, as well as at three reference locations, one in Ljubljana at the Reactor Center (no mercury source) and two in Idrija (known elevated mercury concentrations in the air

due to previous mining activity). Some lichen material was kept in the laboratory for determination of the initial concentration of Hg and other trace elements. Samples were then further prepared according to the procedure described elsewhere (HORVAT ET AL., 2000). At the same time, as lichens were

transplanted, soil samples were collected at same locations. For determination of elements in soil we collected approximately 2 kg of composite soil sample to polyethylene bags. One soil sample was composed from at least four sub-samples collected in the radius of 10 to 20 m.



**Figure 1.** Dates of transplantation and sampling of lichens and locations in Croatia and Slovenia

## ANALYTICAL METHODS

Determination of total mercury was performed by CV AAS (Cold Vapor Atomic Absorption Analysis) (HORVAT ET AL., 1986; HORVAT ET AL., 1991). The accuracy of the results was checked by the use of the certified reference material: IAEA-336, Trace and Minor Elements in Lichens. Scandium and other elements (not discussed in this presentation) were determined by instrumental neutron activation analysis (INAA) (JAČIMOVIĆ ET AL., 2003).

The data was treated to account for geological background the results for lichens and soil samples were normalized to the concentration of scandium (Sc) and enrichment factors were calculated (Equation 1).

$$EF = \frac{\frac{concEl_x}{concSc} LICHEN}{\frac{concEl_x}{concSc} SOIL} \quad (1)$$

Where:  $EF$  = enrichment factor,  $concEl_x$  = concentration of element (in  $mg\ kg^{-1}$ ),  $concSc$  = concentration of scandium (in  $mg\ kg^{-1}$ )

## RESULTS AND DISCUSSION

Mercury concentration in lichens before transplantation was relatively low (about 0.12 mg/kg). After 3 and 6 months of exposure Hg increased significantly at MOLVE stations CPS-1 and CPS-2, as well as at one station in Idrija. (Figure 2, left) Very step increase was observed at station CPS-2 from 6 to 12 months of exposure. Due to the well known volatility of elemental Hg these concentrations are probably directly correlated with the average elevated concentrations at two CPS stations. After 12 months of exposure slight increase of Hg was also observed at stations MOL-11 and MOL-12, while at Đurđevac and Etan-2 the increase was less

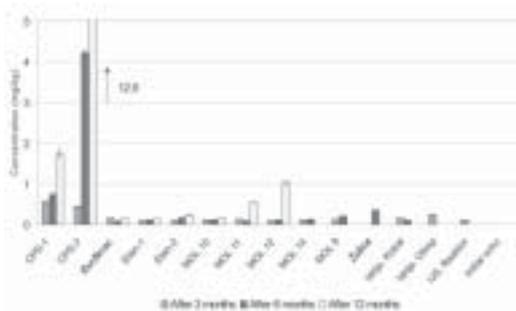


Figure 2. Mercury concentration in transplanted lichens

Based on the previous work conducted at similar locations a relationship with average Hg concentration in air and in lichens was established (HORVAT ET. AL., 2000). The relationship is shown in Figure 3. Therefore after 6 months of exposure of lichens, it can be estimated that the average concentrations of Hg in air at CPS-1 ion the first 6 months of exposure was in the range between 10 to 100 ng/m<sup>3</sup>, and at CPS-2 in the range between 2000 to 3000 ng/m<sup>3</sup> and at Idrija Olimp of up to about 70 ng/m<sup>3</sup>. Concentrations of

than 20%. The same applies for the second experiment, where mercury was elevated only Idrija, which means that at other gas and oil treatment facilities mercury is not emitted into the atmosphere.

Highest Hg concentrations were found at the station CPS 1 and CPS-2 after 12 months of exposure (up to 12,9 mg.kg<sup>-1</sup> dry weight). This is related to the emission of Hg from the technological facility for natural gas treatment including elimination of Hg from the original gas. These results are in agreement with the results of a similar experiment performed in 1997 and 1999 (HORVAT ET. AL., 1997, 1998, 2000).

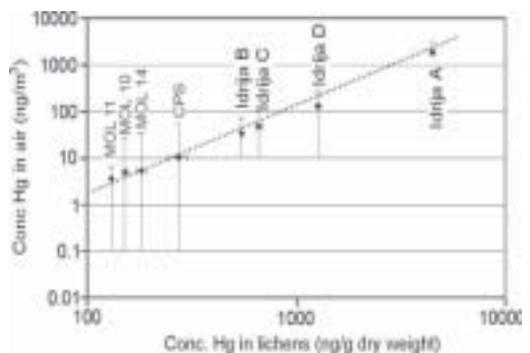
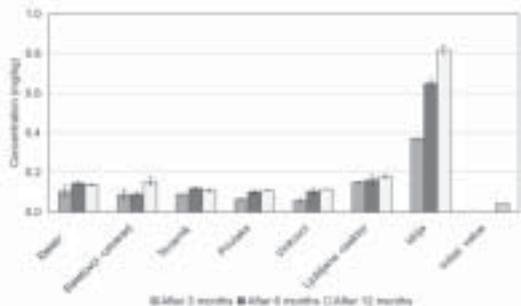


Figure 3. Correlation between mercury concentrations in air and in transplanted lichens (*H. physodes*) after 6 month of exposure

Hg in air in Idrija at Olimp was continuously measured and it was in the range between 30 to 90 ng/m<sup>3</sup> with an average of 65 ng/m<sup>3</sup>, which is in excellent agreement with predicted value from Figure 3 and serve as the validation of the relationship previously established. As the concentrations of Hg in lichens significantly increased at CPS-2 during the last 6 months of exposure (from 5 to 12 months) the average concentration of Hg during this period must have been much higher, exceeding 10 000 ng/m<sup>3</sup>.

Geochemical normalization with Sc and calculation of enrichment factors is presented in Figure 4, which confirms the increased Hg concentration affected by anthropogenic sources at MOLVE and Idrija..

## CONCLUSIONS

In conclusion, the results show that mercury concentrations at the gas treatment and pumping stations have been elevated only at MOLVE while at other stations it has not been increased significantly. At the Reactor center in Ljubljana, mercury concentrations in lichens remained the

same throughout the year in response to the stable and low concentrations of Hg in the air (average concentration in the air is between 2-3 ng. m<sup>-3</sup>). In Idrija, where mercury concentrations are significantly elevated in the air due to mercury mining, mercury levels in lichens significantly increased. The results of this study again confirmed the suitability of epiphytic lichens as biomonitors of air pollution with Hg.

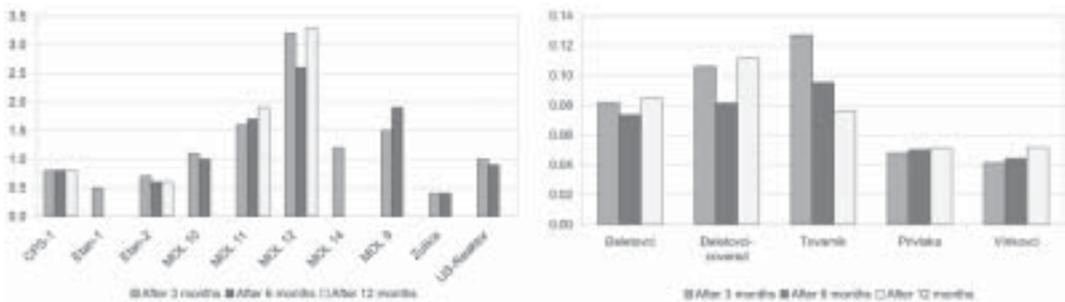


Figure 4. Enrichment factors

## Acknowledgements

This work was done in the frame of the project funded by Ina Naftapljin. Ms. Janja Smrke is acknowledged for the preparation of lichens and Ms. Vesna Jereb for her assistance during transplantation phase. INA Naftapljin is acknowledged for financial support.

**REFERENCES**

- CONTI, M. E. AND CECCHETTI, G. (2001): Biological monitoring: lichens as bioindicators of air pollution assessment – a review; *Environ. Poll.*, vol. 114, pp. 471-492.
- HORVAT, M., JERAN, Z., SPIRIČ, Z., JAČIMOVIĆ, R., MIKLAUČIČ, V. (2000): Mercury and other elements in lichens near the INA Naftaplin gas treatment plant, Molve, Croatia; *J. Environ. Monit.*, Vol. 2, pp. 139-144.
- HORVAT, M., LUPŠINA, V., PIHLAR, B. (1991): Determination of total mercury in coal fly ash by gold amalgamation and vapour atomic absorption spectrometry; *Anal. Chim. Acta*, Vol. 243, pp. 71 – 79.
- JACIMOVIC, R., SMODIŠ, B., BUČAR, T., STEGNAR, P. (2003):  $k_0$ -NAA quality assessment by analysis of different certified Reference materials using the KAYZERO/SOLCOI software; *J. Radioanal. Nucl. Chem.* 257(3), pp. 659-663.
- LOPPI, STEFANO (2001): Environmental distribution of mercury and other trace elements in the geothermal area of Bagnore (Mt. Amiata, Italy); *Chemosphere* 45(6-7), pp.991-995.

## A preliminary study on total gaseous mercury exchange rate between air and soil in Guiyang, China

HOU YA-MIN<sup>1,2</sup>, FENG XIN-BIN<sup>1,\*</sup>, QIU GUANG-LE<sup>1,2</sup>, WANG SHAO-FENG<sup>1,2</sup>

<sup>1</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry Chinese Academy of Sciences, Guiyang 550002, PR China.

<sup>2</sup>Graduate School of the Chinese Academy Sciences, Beijing 100039, P R China

\*Corresponding author; E-mail: xinbin.feng@mail.gyig.ac.cn

**Abstract:** The mercury exchange flux between air and soil surfaces was measured using dynamic flux chamber method in Guiyang and its suburbs. At the same time, meteorological parameters such as air temperature, soil temperature, humidity, solar radiation, wind direction and wind speed were recorded using a multi-function mini-weather station. The results illustrate that both solar radiation and soil temperature significantly correlate with Hg flux.

**Key words:** Guiyang; suburb; soil; air; mercury; exchange flux

### INTRODUCTION

Mercury (Hg) is a specially highly toxic non-essential heavy metal. It has been considered as a global pollutant due to its ability to undergo long distance transportation in the atmosphere. Thus, great attention has been paid to the study of mercury behaviors in the environment internationally since the 1980s. Mercury is emitted into the atmosphere by both anthropogenic and natural sources. Evaporation of mercury from soil is a large atmospheric source<sup>[1]</sup>. But there are only a few published flux data on air/soil exchange of mercury in China<sup>[2, 3]</sup>.

The province of Guizhou in Southwestern China is currently one of the world's most important mercury production areas. Guiyang city (E106°27', 107°03', N26°11', 26°55') is situated in the central of Guizhou province with the total area of 2406 km<sup>2</sup>.

Study showed that total gaseous mercury (TGM) concentration in the ambient air of Guiyang is elevated compared to the global background values<sup>[4]</sup>, but the atmospheric emission sources are not well identified though it is speculated that coal combustion emissions are the primary source. In order to evaluate the contribution of atmospheric mercury from soil emission, we conducted an intensive field study on air/soil exchange of mercury in Guiyang city.

From May 21 to June 5, 2003, we measured the Hg exchange flux between air and soil surface using the method of Dynamic Flux Chamber at four sampling site in Guiyang city and its suburb as shown in Fig. 1. At the same time, we recorded data of air temperature, relative humidity, intensity of solar radiation, wind direction and wind speed using a multi-function mini- weather station. Soil samples in study area were also collected.

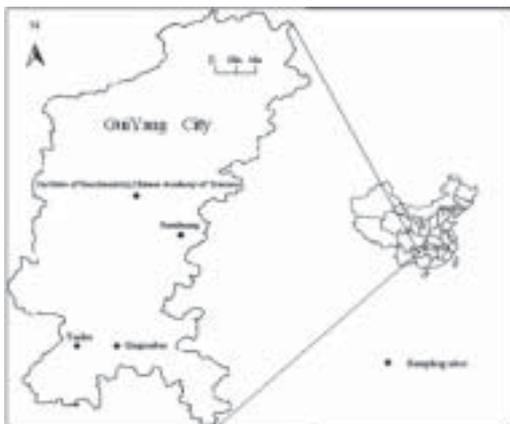


Figure 1. The locations of the sampling sites.

## RESULTS AND DISCUSSION

The mercury concentration in soils at four sampling sites are  $0.146 \text{ mg kg}^{-1}$ ,  $0.215 \text{ mg kg}^{-1}$ ,  $0.254 \text{ mg kg}^{-1}$  and  $0.627 \text{ mg kg}^{-1}$ , respectively. It is obvious therefore that soils in this area are contaminated with mercury in some extent because the background mercury concentration in soil is usually less than  $0.1 \text{ mg kg}^{-1}$ . Total gaseous mercury (TGM)

concentrations in the ambient air is relatively high compared to the global TGM background value ( $1.5\text{--}2.0 \text{ ng m}^{-3}$ ).

The mercury exchange rates at Institute of Geochemistry and Yanlou site are higher than that of Hongfeng Reservoir region in summer ( $27.4 \text{ ng m}^{-2}\text{h}^{-1}$ )<sup>[3]</sup>. The mercury exchange rates at Qingyanbao and Ganzhuang are however lower than that of Hongfeng Reservoir in summer. At four sampling sites, day deposition of mercury from air to soil surface occurred frequently. Mercury flux between soil and air varied with time and the flux reached peak at noon and then decreased to the minimum before the sunrise.

It is widely accepted that mercury emitted from soil is mainly  $\text{Hg}(0)$  and at most a small portion of dimethyl mercury. Factors controlled  $\text{Hg}(0)$  evaporates from soil is various. Physical parameters, such as temperature, radiation or moisture, can promote the production of volatile Hg species since they induce or stimulate these chemical forma-

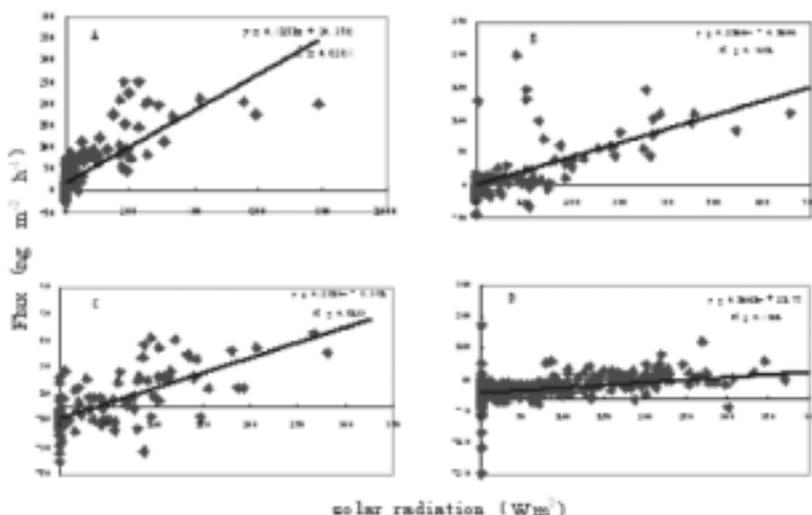
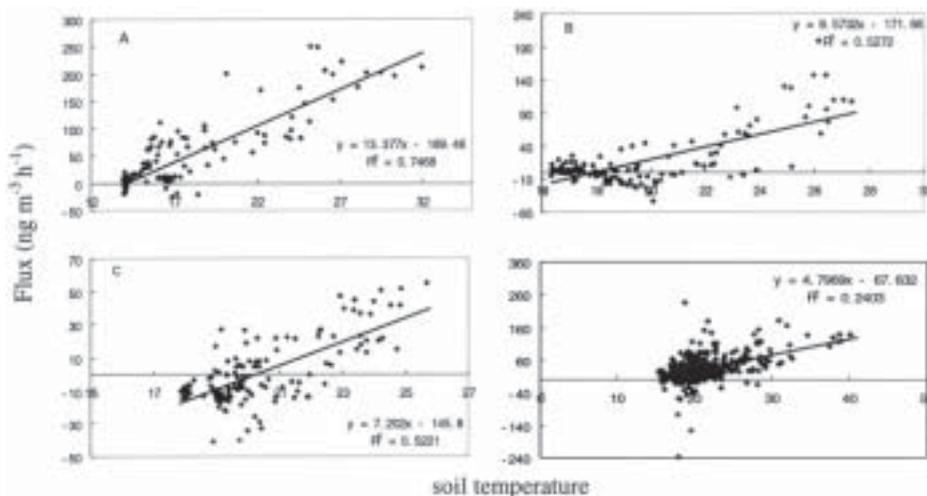


Figure 2. Relationship between mercury flux and solar radiation: A Yanlou, B Qingyanbao, C Ganzhuang, D Institute of Geochemistry, Chinese Academy of Sciences.



**Figure 3.** Relationship between mercury flux and soil temperature: **A** Yanlou, **B** Qingyanbao, **C** Ganzhuang, **D** Institute of Geochemistry, Chinese Academy of Sciences.

tions. Thus, the correlations between mercury flux and meteorological parameters are very important.

Our data showed a good correlation between mercury flux and solar radiation, soil temperature as shown in Fig. 2 and Fig.3.

## CONCLUSIONS

Mercury emissions from soil generally increase during the day, peak around noon, and

decline at night. There are significant correlation between mercury flux and meteorological parameters. Solar radiation is most important in controlling Hg flux at the 4 sampling locations.

## Acknowledgements

This work was financially supported by Chinese Academy of Sciences through “Hundred Talent Plan”, and also by Chinese National Natural Science Foundation (No. 40173037).

## REFERENCES

- [1] SCHROEDER, W. H., MUNTHE, J. (1998): Atmospheric mercury – an overview; *Atmospheric Environment* 32, 809-822.
- [2] FENG, X. B., CHEN, Y. C., ZHU, W. G. (1996): The fluxes of volatile mercury over soil surface in Guizhou Province; *Environ. Sci.* 17(2), 20-25.
- [3] WANG SHAOFENG, FENG XINBIN, QIU GUANGLE ET AL.(2004): Comparison of Air/Soil Mercury Exchange Between Warm and Cold Season in Hongfeng Reservoir Region; *Environmental Science* 25(1), 123-127.
- [4] FENG, X., TANG, S., SHANG, L., ET AL. (2003): Total gaseous mercury in the air of Guiyang, PR China; *The Science of the Total Environment* 304, 61-72.

# Laser Induced Fluorescence Studies of Atmospheric Mercury Cycling: Ultra-Sensitive Detection and Laboratory Kinetics

ANTHONY J. HYNES, DEANNA DONOHOUE, DIETER BAUER

Division of Marine and Atmospheric Chemistry  
Rosenstiel School of Marine and Atmospheric Science  
University of Miami  
4600 Rickenbacker Causeway, Miami, FL 33149, USA

**Abstract:** We have studied the reactions of Hg(0) with Cl and Br using photolysis of Cl<sub>2</sub> and Br<sub>2</sub> monitoring the decay of Cl and Br in an excess of Hg(0). Our results suggest that the rate coefficients for reactions (1) and (2) are slower than  $5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 200 Torr in N<sub>2</sub>. We have photolyzed HgCl<sub>2</sub> at 266 nm and directly monitored HgCl on the <sup>2</sup>A<sub>3/2</sub>-<sup>2</sup>G transition. This is the first observation of this molecule using the laser induced fluorescence technique. We have obtained LIF spectra of the (0-0) and (1-0) bands. In addition we have obtained dispersed fluorescence spectra, pumping the (0-0) and (1-0) bandheads. This demonstrates that we can use photofragment LIF to unambiguously monitor HgCl<sub>2</sub>. We have examined the use of sequential two photon laser induced fluorescence (LIF) detection techniques for detection of gas phase Hg(0) and Reactive Gaseous Mercury (RGM) using preconcentration in gold tubes and KCl denuders.

**Key words:** mercury chemistry, chemical kinetics, photochemistry, spectroscopy

## INTRODUCTION

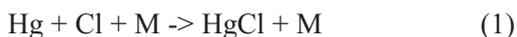
A detailed understanding of the role of mercury in the environment is a critical issue from a human health perspective. Knowledge of the rates and mechanisms of emission, deposition and chemical transformation of elemental mercury is essential in understanding the cycling of mercury in aquatic and terrestrial ecosystems. Until recently Hg(0) was thought to be unreactive in the gas phase under atmospheric conditions. Estimates of its atmospheric lifetime were approximately one year<sup>[1,2]</sup> although it was noted that this was highly uncertain. New measurements of the rapid depletion of atmospheric mercury in the arctic have demonstrated that, at least

under some circumstances, mercury can undergo fast atmospheric cycling<sup>[3,4]</sup>. These depletion events correlate well with the depletion of atmospheric ozone that appears to be triggered by the photolysis of labile halogen species released from the snow pack after the arctic sunrise. The implications of this for atmospheric mercury chemistry on a global scale are unclear because the precise mechanism of the arctic depletion events is not known and very little data is available for rate coefficients of Hg(0) with halogens. The overall goals of our research program are a series of measurements and technique developments that will allow the chemical reactivity, the atmospheric concentrations, and the rates of emission and deposition of

both elemental and reactive gaseous mercury, to be better defined. In contrast to recent reports of mercury kinetics which have used relative rate techniques our laboratory studies are attempting the direct measurement of the rate coefficients for the reactions of Hg(0) with the hydroxyl radical, halogen atoms, X, and halogen monoxides, XO, where X= Cl, Br, I. We are attempting to study the kinetics under conditions which will allow the pressure and temperature dependence of the rate coefficients to be determined. In addition, when feasible, the reaction products and their yields will be identified. In addition we are investigating the use of laser based excitation schemes for the rapid, ultrasensitive detection of gas phase elemental mercury and reactive gaseous mercury. We have examined the sensitivity of single and sequential two photon laser induced fluorescence (LIF) detection techniques for gas phase Hg(0) under atmospheric conditions. These techniques combine extremely high detection sensitivity, selectivity and very fast time response. Each approach involves an initial laser excitation of the  $6^3P_1$ - $6^1S_0$  transition at 253.7 nm. In the sequential two photon LIF technique this is followed by excitation with a second laser to either the  $7^1S_0$  or  $7^3S_1$  levels. Either blue or red shifted laser induced fluorescence is then monitored with a photomultiplier tube (PMT). In previous work we have compared excitation schemes and described the analytical application of the most sensitive approach [5,6]. In this work we examine the use of this technique using a compact laser system with presampling on gold tubes and KCl denuders.

## RESULTS AND DISCUSSION

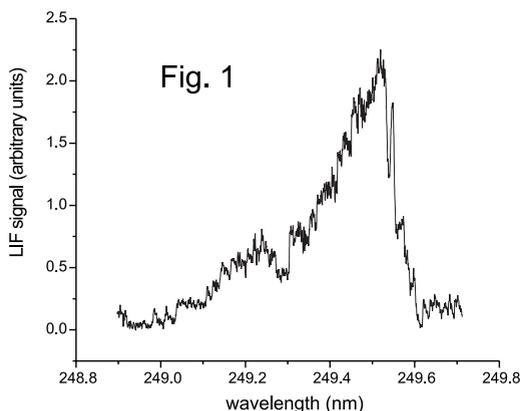
*Kinetics:* Our kinetics studies are currently focused on the reactions of Br, Cl with Hg(0). Our technique uses laser photolysis to produce the radical of interest followed by detection with a second laser using laser induced fluorescence and its use to study the reaction of OH with Hg(0) has been published recently [6]. We have studied the reactions of Hg(0) with Cl and Br using photolysis of Cl<sub>2</sub> and Br<sub>2</sub> monitoring the decay of Cl and Br in an excess of Hg(0).



Despite the slow published rates for the reaction of Hg(0) with Cl<sub>2</sub> and Br<sub>2</sub> we observed an apparent rapid loss of Hg(0) in the presence of both halogens. We monitored the absolute concentration of Hg(0) by photometry measuring the attenuation of the 253.7 nm output of a low pressure mercury lamp. To ensure that our absolute concentration measurements were accurate we calibrated the absorption measurements by simultaneously monitoring the Hg(0) concentration with a Tekran 2537A after known dilution. We measured an effective absorption cross section of  $\Phi = 1.26 \times 10^{-14} \text{ cm}^2 \text{ molecule}^{-1}$ . To perform kinetics measurements with Hg(0) in excess requires that we maximize the Hg(0) concentration. Because of the complications from the reaction of Hg(0) with halogens we used very low halogen concentrations and short mixing times. We monitored Hg(0) before and after our reaction cell and under these conditions loss of Hg(0) never exceeded 15 %. We estimate that loss between the initial absorption cell and the

reaction zone is less than 5 %. We performed measurements at 100 and 200 Torr in  $N_2$ . We saw no evidence for any reaction within the precision of our measurements. To ensure that our experimental approach was reasonable we monitored the decay of Cl atoms in a known concentration of  $C_2H_6$  and obtained good agreement with the literature value for this reaction. Our results suggest that the rate coefficients for reactions (1) and (2) are slower than  $5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 200 Torr. We are currently monitoring the decay of Hg(0) in an excess of Cl and Br atoms monitoring both species by LIF.

*Reaction Product Detection:* In addition we have photolyzed  $HgCl_2$  and directly monitored HgCl on the  ${}^2A_{3/2} - {}^2\Gamma$  transition. This is the first observation of this molecule using the laser induced fluorescence technique. In these experiments we pass helium over solid  $HgCl_2$  at room temperature. The gas mixture is photolyzed at 266 nm and, after a short delay the probe laser interrogates the photolysis volume. The photolysis laser is scanned and the total undispersed fluorescence signal is monitored. Fig. 1 shows the LIF spectrum of the  ${}^2A_{3/2} - {}^2\Gamma$  (1-0) band obtained by scanning the probe laser between 248.8 and 249.8. It can be seen that we ob-



tain a scan of the vibrational band which shows two, reproducible features but that resolution of individual rotational features is not possible.

We obtained a similar LIF spectrum of the (0-0) band at 251.7 nm. To confirm our assignments we then monitored spectrally resolved fluorescence. In this experiment we again generate the HgCl by photolysis however we now fix our probe laser wavelength and monitor the dispersed fluorescence. Fluorescence is dispersed using a 0.5 M spectrometer and monitored using 1024 element intensified diode array. The dispersed fluorescence signal, obtained by pumping the band heads of the (1-0) and (0-0) bands, shows vibrational progressions are seen in each case corresponding to transitions from the initially pumped  ${}^2A_{3/2}$  (1 or 0) level to a series of vibrational levels in the  ${}^2\Gamma$  ground state. These results unambiguously demonstrate the first observation of HgCl using LIF. They show that it should be possible to both monitor its production in kinetics experiments and to perform additional kinetics studies to determine its fate. In addition this shows we can use photofragment LIF to unambiguously monitor  $HgCl_2$ .

### Ambient Detection of Hg(0) and Reactive Gaseous Mercury (RGM)

We have attempted to quantify the factors limiting detection sensitivity of Hg(0) and RGM using a compact laser system in conjunction with preconcentration on gold tubes (Hg(0)) and KCl denuders (RGM). In this work we sample Hg(0) onto a gold tube and then thermally desorb the Hg(0) in argon carrier gas. For RGM detection we sample onto a KCl denuder and can thermally de-

compose/desorb Hg(0) in argon carrier gas. We can sample the Hg(0) directly or go through the amalgamation step onto a gold tube followed by a second desorption step. We detect the Hg(0) by an initial laser excitation of the of the  $6^3P_1$ - $6^1S_0$  transition at 253.7 nm, followed by excitation of the  $7^1S_0$ - $6^3P_1$  transition at 407.8 nm. Fluorescence is observed on the  $6^1P_1$ - $6^1S_0$  transition at 184.9 nm using a solar blind photomultiplier tube. Our initial results give a detection sensitivity in excess of 0.5 pg Hg(0). However our detection sensitivity is limited by our background Hg(0) blank, rather than the LIF signal to noise ratio. We can directly detect the Hg(0) desorbed from a KCl de-

nuder after ambient sampling of RGM. We see rapid decomposition/ desorption of Hg(0) on a timescale of a few minutes suggesting that a amalgamation step is not necessary. Work to calibrate the KCl denuder signals is progress.

### Acknowledgements

This research has been supported by a grant from the U.S. Environmental Protection Agency's Science to Achieve Results (STAR) program. We would like to thank Matt Landis, Bob Stevens and Tom Atkeson for the loan of the Tekran 253A and the gold tubes and KCl denuders and for invaluable advice on their use.

### REFERENCES

- [1] LIN, C. J. AND PEHKONEN, S. O. (1999): The chemistry of atmospheric mercury: a review. *Atmos. Environ.* 33, 2067- 2079
- [2] BERGAN, T. AND RODHE, H. (2001): Oxidation of elemental mercury in the atmosphere; Constraints imposed by global scale modeling. *J. Atmos. Chem.* 40, 191-212.
- [3] SCHROEDER, W. H., ANLAUF, K. G., BARRIE, L. A., LU, J. Y., STEFFEN, A., SCHNEEBERGER, D. R. AND BERG, T. (1998) Arctic springtime depletion of mercury. *Nature*, 394, 331-332.
- [4] LINDBERG, S. E., BROOKS, S., LIN, C.J., SCOTT, K. J., LANDIS, M. S., STEVENS, R. K., GOODSITE, M. AND RICHTER, A. (2002) Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environ. Sci. Technol.* 36, 1245-1256.
- [5] BAUER, D., CAMPUZANO-JOST, P., HYNES A.J. (2002): Rapid, ultra-sensitive detection of gas phase elemental mercury under atmospheric conditions using sequential two-photon laser induced fluorescence. *J. Environ. Monitor.* 4, 339-343
- [6] BAUER, D., D'OTTONE, L., CAMPUZANO-JOST, P., HYNES, A.J. (2003): Gas phase elemental mercury: a comparison of LIF detection techniques and study of the kinetics of reaction with the hydroxyl radical. *J Photoch. Photobio. A* 157, 247-256.

# Modelling of mercury transboundary pollution in Europe and its long-term trends

ILIA ILYIN

Meteorological Synthesizing Centre - East of EMEP

**Abstract:** According to UN-ECE Protocol, EMEP Programme has to provide European countries with information on depositions, concentrations and transboundary transport of heavy metals, and, in particular, of mercury. To fulfill this task three-dimensional Eulerian-type regional-scale model was developed. The aim of this work is to present main results of the model, with particular emphasis on evaluation of long-term (1990 - 2001) trends of mercury atmospheric pollution in Europe. For the considered period depositions of mercury in Europe decreased about 1.5 times, but the rate of the reduction differs from country to country. Rate of deposition decrease is less than rate of emission reduction mainly because of inter-continental transport of mercury and the influence of natural emissions and re-emission. Comparison of modelled results against measurements showed that air concentrations were well reproduced by the model, and concentrations in precipitation were somewhat overestimated. The comparison also demonstrates that long-term trends of pollution levels were captured by the model.

**Key words:** Modelling, long-range transport, trends, Europe.

## INTRODUCTION

UN-ECE Protocol, aimed at control of heavy metal atmospheric emissions, came into effect in 2003. According to the Protocol, one of priority metals is mercury. Meteorological Synthesizing Centre East (MSC-E) is authorized by EMEP Programme to develop a regional-scale model of atmospheric transport, transformations and deposition of mercury in order to estimate transboundary pollution and its long-term trends in Europe. The aim of this work is to present results of the regional-scale numerical modelling of mercury pollution. Main attention was paid to evaluation of long-term trends of mercury atmospheric pollution in Europe for 1990 – 2001, and verification of modelling results by comparison with measurement data.

## MODEL DESCRIPTION

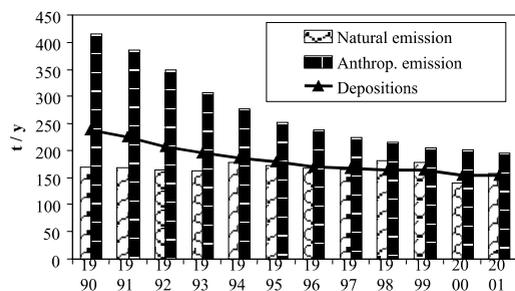
The 3D Eulerian-type regional scale model (MSCE-HM) is intended to simulate transboundary transport, transformations and deposition of heavy metals, and in particular, of mercury. It accounts for advection, turbulent diffusion, chemical transformation of mercury, wet and dry depositions, and inflow of a pollutant into the model through the domain boundaries. Three mercury forms are considered in the model: gaseous elemental mercury (GEM), total particulate mercury (TPM) and reactive gaseous mercury (RGM). The model domain is so called EMEP region, including Europe, north of Africa and north-western part of the Atlantic. Calculations are carried out on stereographic projection with spatial resolution

50 km at 60° latitude. Vertical structure of the model consists of 5 non-uniform layers. The model top is at height of about 4 km. All details of the parameterisations can be found in ILYIN ET AL. (2002).

Meteorological information for 1990–2001 is based on the data of NCEP/NCAR Re-analysis project. Emission database consists of emissions, officially submitted by European countries, and expert estimates. For each country individual speciation between RGM, TPM and GEM is used. For the entire Europe, emission of GEM makes up 55 %, TPM -15 % and RGM – 30 %. The model includes also emission from natural sources and re-emission (ILYIN ET AL., 2002). Total re-emission from Europe is about 50 t/y, and natural emission – about 170 t/y.

## RESULTS AND DISCUSSION

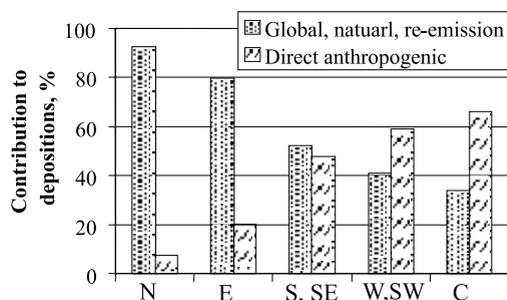
Trends of mercury depositions and concentrations in Europe were evaluated for the period from 1990 to 2001 (Fig. 1). For the entire Europe, anthropogenic emissions, used



**Figure 1.** Emission and deposition changes in Europe for 1990 – 2001.

in model, decreased from 420 to 195 t. Total depositions decreased from 240 to 150 t (~1.5 times). The difference in rates of emission and deposition reduction is explained by the influence of sources located outside Europe and by natural emission and re-emission.

In different parts of Europe rate of mercury deposition decrease varied significantly. The highest (3.5 – 1.5 times) reduction took place in central and western parts of Europe – in Germany, United Kingdom, Czech Republic, and in some countries of southern or south-eastern Europe, e.g., Bulgaria, Macedonia. This is mainly connected with the reduction of anthropogenic emissions in these countries. Relatively low changes took place in southern part of Europe, e.g. Spain, Portugal, Greece, and in the Nordic countries. In the southern part little deposition decrease is mainly connected with relatively low rate of emission reduction (1 – 1.5 times). In the northern part of Europe emissions of mercury decreased significantly, but reduction of depositions was not as high as that of emissions because of predominating role of global atmospheric transport of mercury.



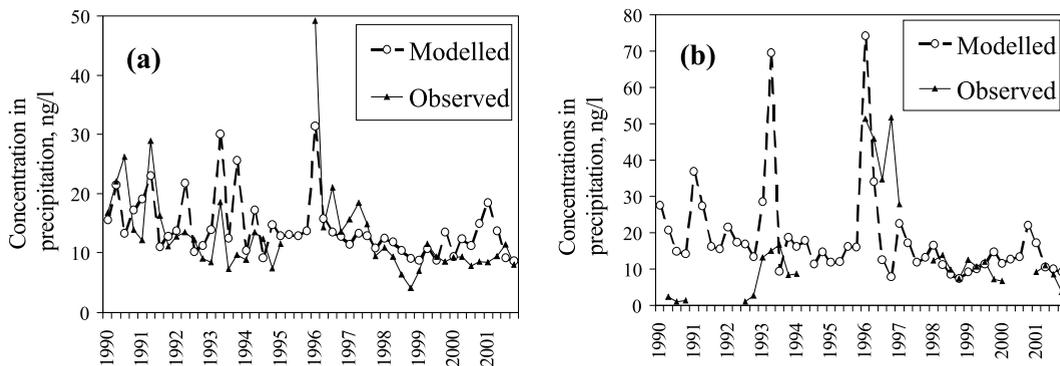
**Figure 2.** Contributions of global, natural, re-emission and direct anthropogenic sources to deposition in various regions of Europe: N – northern, E – eastern, S – southern, SE – south-eastern, W – western, SW – south-western, C – central.

The role of global, natural emission and re-emission is the highest for the northern part of Europe (Fig. 2). Contribution to depositions of mercury, emitted by European anthropogenic sources does not exceed 10 %. The highest contribution was obtained for central Europe, followed by western/south-western and eastern/south-eastern regions. This connected with relatively high anthropogenic emissions in these regions. Significant role of global sources in regional-scale pollution implies that mercury atmospheric transport should be evaluated not only on regional, but also on hemispherical/global scales.

Verification of the model included comparison of modelling results with measurement data. Currently information on mercury concentrations in air or/and in precipitation is available from 15 monitoring stations.

The model tends to overestimate measured concentrations in precipitation approximately 1.5 times on average. Possible reasons for this can be uncertainties of the model parameterisations, or too high fraction of TMP and RGM in the emissions. Comparison for total gaseous mercury (TGM) concentrations does not show large scatter of the results. Measured TGM concentrations ranged from 1.1 to 2.0 ng/m<sup>3</sup> for period 1990 – 2001, and modelled concentrations at the same stations – from 1.5 to 1.9 ng/m<sup>3</sup>. For most stations, discrepancy between model and measurements is within 30 %.

Two stations measuring mercury in precipitation and one - in air have long time series long enough for trend analysis. In figure 3 seasonal mean modelled concentrations in precipitation are compared with measured



**Figure 3.** Modelled versus observed seasonal-mean concentrations of Hg in precipitation at station Rörvik, Sweden (a) and Westerland, Germany (b).

**Table 1.** Statistical parameters for comparison of modelled concentrations in precipitation with measurements at stations Rörvik and Westerland

Station	Correlation	Factor 2	Slope of linear trend (obs)	Slope of linear trend (mod)
Rörvik	0.63	90 %	-0.19	-0.14
Westerland*	0.43	70 %	-0.43	-0.28

\* Observed values for 1990 and 1992 were ignored

values at station Rörvik (Sweden, 57°25'N, 11°56'E) and Westerland (Germany, 54°55'N, 8°18'E). Statistical parameters of the comparison are summarised in table 1. Long-term modelled concentrations in precipitation agree relatively well with those observed at Rörvik (Fig. 3a). About 90 % of modelled/measured values do not differ more than twice. Correlation is 0.63. High discrepancies between model and measurements for station Westerland are indicated for 1990 and 1992 (Fig 3b). However, measured values for these years seem to be very low compared to data for other years. As these data are most probably erroneous, they were ignored when analysing trends. About 70 % of values fall within factor of 2 and the correlation is 0.62. Slopes of linear trend approximation indicate, that both model and measurements demonstrate long-term decline of mercury concentrations in precipitation.

Comparison of modelled long-term TGM concentrations against measured values was performed only for station Zeppelinfjell (Norway, 78°54'N, 11°53'E). Relative bias

for each year does not exceed 20 %, with only exception for 1997. Correlation coefficient is about 0.5, when annual mean values are compared.

## CONCLUSIONS

Long-term trends of mercury levels of atmospheric pollution were evaluated. For the period 1990 – 2001 emissions of mercury decreased about twice, and depositions – about 1.5 times. The rate of deposition reduction in different regions of Europe varies significantly. The role of global mercury transport and natural emissions is very important for pollution of Europe, and can exceed 90 % in some regions of Europe. For more correct evaluation of this role global or hemispherical models are needed. Model shows good agreement with measurements for TGM, and some overestimation of measured concentrations in precipitation. Long-term trends of TGM and concentrations in precipitation were well captured by the model.

## REFERENCES

- ILYIN, I., RYABOSHAPKO, A., AFINIGENOVA, O., BERG, T., HJELLBREKKE, A. G., LEE, D. S. (2002): *Lead, cadmium and mercury transboundary pollution in 2000*; MSC-E/CCC Technical Report 5/2002.
- RYABOSHAPKO, A., BULLOCK, R., EBINGHAUS, R., ILYIN, I., LOHMAN, K., MUNTHE, J., PETERSEN, G., SEIGNEUR, C., AND WANGBERG, I. (2002): Comparison of mercury chemistry models; *Atmospheric Environment* 36, pp. 3881-3898.

## Transport and chemical processing of mercury during long-range transport in the Pacific

DAN JAFFE, ERIC PRESTBO, PETER WEISS & PHIL SWARTZENDRUBER

**Abstract:** Budget studies in the northwestern U.S. have identified global mercury sources as a significant contributor to regional mercury burdens. This is consistent with our previous observations, which show that ozone, CO and aerosols are frequently transported to the U.S. from sources on the Eurasian continent via the prevailing westerly winds. For this reason we initiated a project to examine the inflow of mercury to the western U.S. Key factors associated with this flux are the large mercury emissions associated with coal use in East Asia and the substantial modulating effects of the Pacific Ocean.

We have now made more than one year of observations of Hg(0), RGM and PHg at the Cheeka Peak Observatory, a surface site on the western tip of Washington state. These observations have led to some rather surprising findings on the rapid cycling of Hg in both marine and continentally influenced air. In air with signatures of recent urban pollution, we generally find Hg(0) concentrations that are lower than the background, presumably due to rapid loss with some component of urban air, possibly ozone or aerosols. In marine air, we find a significant diurnal cycle for Hg(0) during summer, consistent with a photochemically driven removal process over the oceans.

Regarding the possible influence from Asian emissions on mercury at the Cheeka Peak Observatory, based on Asian emissions we would expect an Hg(0) enhancement of about  $0.1 \text{ ng/m}^3$  for a 20 ppbv enhancement in CO. Since we started our Hg observations we have observed 3 long-range transport events at Cheeka Peak. In these 3 events Hg(0) concentrations are  $-0.09, 0.03 +0.08 \text{ ng/m}^3$  above, or in one case below, the marine background. This leads us to believe that the ocean is playing a significant modulating effect on the Hg(0) concentrations we observe.

In addition to the surface observations at Cheeka Peak, we are now coupling these with vertical profiles of Hg(0) and related species. This is based on our understanding of other pollutants (e.g. CO, aerosols), where the flux to North America from long-range transport is greatest in the free troposphere. Finally, during the spring of 2004 we are planning a campaign on the Japanese Island of Okinawa, which will allow us to quantify the outflow flux of Hg from, presumably, large sources in East Asia.

In addition to the observations, we are using the GEOS-CHEM global transport model to help integrate and understand these observations. We have previously used the GEOS-CHEM model to understand the budgets and cycling of ozone and related species in the North Pacific atmosphere. Mercury emissions, chemistry and deposition have been integrated into the model and we are now using it to interpret the observations and to identify key gaps in our understanding. In this presentation we will give an overview of these results and attempt to tie them together into a unified picture of the atmospheric fate and transport of Hg in the North Pacific with an emphasis on what we know and what we don't.

**Key words:** Pacific, long-range transport, Asia

# Exchange of Mercury between the Atmosphere and Snowpack in Western Hudson Bay: Cycles of Oxidation and Reduction

JANE L. KIRK & VINCENT L. ST. LOUIS

University of Alberta, Edmonton, Alberta, Canada;  
E-mails: jkirk@ualberta.ca; vince.stlouis@ualberta.ca

**Abstract:** Wildlife in the western Hudson Bay ecoregion are showing signs of mercury (Hg) contamination. In the spring of 2003 we conducted snow surveys over western Hudson Bay to: 1) determine if atmospheric Hg depletion events are occurring in this sub Arctic region, and 2) determine the fate of deposited Hg(II) in snowpacks. We found that although extremely large quantities of Hg(II) were repeatedly deposited into snowpacks, this Hg(II) was quickly reduced to gaseous elemental Hg(0) and reemitted back to the atmosphere. Therefore, despite numerous springtime atmospheric Hg depletion events occurring in the region, only a very small fraction of the Hg(II) deposited from the atmosphere enters western Hudson Bay in snowmelt.

**Key words:** Sub Arctic, Hudson Bay, atmospheric Hg depletion events, snow/snowmelt, Hg(II), gaseous Hg(0)

## INTRODUCTION

High levels of methyl mercury (the neurotoxin that bioaccumulates through foodwebs) have been found in marine mammals and fishes of many regions of the high and sub Arctic<sup>[1]</sup>. In the western Hudson Bay ecoregion, concentrations of Hg in the livers of beluga whales and ring seals are some of the highest in the Canadian north, and have increased up to tenfold over the past 15-20 years<sup>[1]</sup>. In the high Arctic, atmospheric Hg depletion events have been implicated as the source of elevated Hg(II) concentrations (sometimes exceeding 100 ng/L) found in the surface of snowpacks, and a potential gross loading of 50 T of Hg(II) to the Canadian archipelago each year<sup>[2,3]</sup>. It has been hypothesized that the Hg deposited to snowpacks during atmospheric Hg depletion events en-

ters marine ecosystems as a large pulse of bioavailable Hg(II) at snowmelt<sup>[3]</sup>. However, others have shown that Hg(II) in snowpacks can be reduced by photo-initiated reactions to gaseous elemental Hg(0) and lost back to the atmosphere<sup>[4,5]</sup>. This “re-emission” of Hg to the atmosphere influences the residence time of Hg in snowpacks, and therefore *net* Hg deposition to the biosphere.

We conducted snow surveys over western Hudson Bay in the spring of 2003 to: 1) determine if atmospheric Hg depletion events are occurring along the western coast of Hudson Bay, and 2) determine the short and long-term fate of deposited Hg(II) in snowpacks. We sampled concentrations of total Hg (THg, all forms of Hg) in surface snow, as well as gaseous elemental Hg(0) concentrations in the interstitial airspaces of the

snowpack, every day between 15 April – 15 May 2003 at sites 1 km over the sea ice in the region of Churchill, Manitoba.

## RESULTS AND DISCUSSION

During our field campaign, we observed approximately four periods when concentrations of THg in surface snow were elevated well above background concentrations of ~5 ng/L. In each case, concentrations of THg in surface snow reached at least 100 ng/L, and in one case, THg concentrations peaked at over 650 ng/L. These concentrations were much higher than those previously found in snow following atmospheric Hg depletion events in the high Arctic at Alert, Nunavut (e.g., 20-50 ng/L) or along the east coast of Hudson Bay in Kuujjuarapik, Quebec (80 ng/L) where atmospheric Hg depletion events have also been detected.

A few days following each period when concentrations of THg spiked in surface snow, however, the majority of the deposited THg disappeared from the snowpack. During Hg “deposition” events, concentrations of gaseous elemental Hg(0) in air in the surface layers of snowpacks began to increase above atmospheric levels of ~1.7 ng/m<sup>3</sup>. As concentrations of THg in the surface snow then decreased, concentrations of gaseous elemental Hg(0) in the interstitial airspaces of the upper layers of the snowpack increased

sharply to between 60 and 160 ng/m<sup>3</sup> before returning to background concentrations of ~1.7 ng/m<sup>3</sup> within a day or two. These observations suggest that there was a rapid reduction of the deposited Hg(II) to Hg(0), which then diffused out of the snowpack. At snow melt, concentrations of THg in melt water ponds were around 3.5 ng/L indicating that only a small fraction of the Hg deposited from the atmosphere enters western Hudson Bay in snowmelt despite numerous springtime atmospheric Hg depletion events.

## CONCLUSIONS

This study shows that although a large quantity of Hg(II) does repeatedly get deposited into snowpacks over the western Hudson Bay region during atmospheric Hg depletion events, almost all of the Hg(II) is subsequently reduced to Hg(0) and lost back to the atmosphere. Our results show that even in coastal sub Arctic ecoregions, Hg is involved in complex cycles of oxidation and reduction, with the end result of little Hg(II) actually entering marine ecosystems at snowmelt.

## Acknowledgements

We wish to thank the generous financial support of Manitoba Hydro, the Churchill Northern Studies Centre and NSERC Canada.

## REFERENCES

- [1] Canadian Arctic Contaminants Assessment Report II; Highlights (2003): *Indian and Northern Affairs Canada*.
- [2] SCHROEDER, W.H., ANLAUF, K.G., BARRIE, L.A., LU, J.Y., STEFFEN, A., SCHNEEBERGER, D.R., BERG, T. (1998): Arctic springtime depletion of mercury. *Nature* 394, pp. 331-332.
- [3] LINDBERG, S.E., BROOKS, S., LIN, C.-J., SCOTT, K.J., LANDIS, M.S., STEVENS, R.K., GOODSITE, M., RICHTER, A. (2002): Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environmental Science and Technology* 36, pp. 1245-1256.
- [4] LALONDE, J.D., POULAIN, A.J., AMYOT, M. (2002): The role of mercury redox reactions in snow on snow-to-air mercury transfer. *Environmental Science and Technology* 36, pp. 174-178.
- [5] DOMMERGUE, A., FERRARI, C.P., POISSANT, L., GAUCHARD, P.-A., BOUTON, C.F. (2003): Diurnal cycles of gaseous mercury within the snowpack at Kkuujjuarapik/ Whapmagoostui, Quebec, Canada. *Environmental Science and Technology* 37, pp. 3289-3297.

# Long-term trends and seasonal variations of atmospheric mercury concentrations at Mace Head, Ireland and Zingst, Germany

KOCK H. H.<sup>1</sup>, BIEBER E.<sup>2</sup>, EBINGHAUS R.<sup>1</sup>, SPAIN T. G.<sup>3</sup> AND THEES B.<sup>2</sup>

<sup>1</sup>GKSS Research Centre Geesthacht, Institute for Coastal Research, 21502 Geesthacht, Germany

<sup>2</sup>Federal Environmental Agency (UBA), Paul-Ehrlich-Str.29, 63225 Langen, Germany

<sup>3</sup>National University of Ireland, Department of Experimental Physics, Galway, Ireland

**Abstract:** Monitoring of total gaseous mercury (TGM) concentrations has been carried out at Mace Head on the west coast of Ireland and at Zingst on the southern shore-line of the Baltic Sea. Between 1998 and 2003 average TGM-concentrations measured at Mace Head and Zingst remained fairly stable. At both stations we measured higher TGM levels during winter months and lower concentrations during summer months. We observed an unexpected west to east gradient seen between Mace Head and Zingst and found that the averaged Mace Head TGM-concentrations are higher than those of Zingst.

**Key words:** mercury in ambient air, long-term trends, spatial distribution, seasonal variations.

## INTRODUCTION

In the past ten years automated high time-resolution measurements of mercury species in ambient air have promoted remarkable progress in the understanding of the behavior of this priority pollutant in the lower troposphere. We used the continuous measurements to assess the long-term trends and the seasonal variations of TGM concentrations from the monitoring stations at Mace Head and Zingst during the same time period.

Mace Head is the most westerly atmospheric research station in Europe and is operated by the Atmospheric Science Research Group at the National University of Ireland, Galway. The climate at Mace Head may be classified as maritime. There is no industrial or agricultural activity, which would influence measurements at the station. The shoreline of the

Atlantic is only 50 m apart. The German sampling site Zingst is a monitoring station of the German Environmental Protection Agency (UBA). The Facility is located east of the seaside resort Zingst at a distance of about 500 m from the southern shore-line of the Baltic Sea and is surrounded by agricultural land.

The continuous measurements of total gaseous mercury concentrations were carried out with Tekran 2537A mercury vapor analyzers. For quality assurance, the analyzer at Mace Head was calibrated every 25 h with the internal automatic permeation source injection. At Zingst automated standard additions had been carried out every 12 h to correct the Tekran readings. The accuracy of the measurements was verified by manual injections of saturated air with a gas tight syringe at defined temperatures. At the Zingst site,

the air sample inlet was installed on the roof of the monitoring station and thus the air intake was at a height of approximately 4 m above ground (grass- and pine-covered field), while at the Mace Head station the air intake was located on a sampling tower at about 5 m above ground (covered with grass and rocks).

## RESULTS AND DISCUSSION

Between 1998 and 2003 average TGM-concentrations measured at Mace Head ( $1.73 \text{ ng m}^{-3}$ ) and Zingst ( $1.65 \text{ ng m}^{-3}$ ) remained fairly stable and clearly reflect northern hemispheric background values. As can be seen from Fig.1, no significant trends in the concentration levels have been detected during the measurement period. Compared with the Mace Head site the TGM pattern at Zingst shows an increased variability. Probably, the TGM peaks observed in Zingst are caused by plumes of regional point sources. The comparison of the frequency distributions supports the assumption of local diffuse emissions at Zingst during wintertime. A comparatively broad shape with a clearly evident positive skewness characterizes the

wintertime distribution. The frequency distribution of the summertime measurements shows a more normal Gaussian shape.

Monthly averages for the individual months have been used to evaluate seasonal variations in the TGM levels. Every year in the summertime we see a decrease in the TGM levels. At Zingst the autumn and winter months show higher TGM concentrations ( $1.75 \text{ ng m}^{-3}$ ) compared with the spring and summer months ( $1.55 \text{ ng m}^{-3}$ ). At Mace Head we measured higher TGM levels during winter and spring months ( $1.8 \text{ ng m}^{-3}$ ) and lower concentrations during summer and autumn months ( $1.6 - 1.7 \text{ ng m}^{-3}$ ). The seasonal variation with summer minimum is characteristic of the majority of trace gases, which are removed from the atmosphere by oxidation processes (SLEMR AND SCHEEL, 1998). The major oxidation species in the troposphere is the OH radical which has a pronounced seasonal cycle at middle and higher latitudes. Higher OH concentrations in summer lead to faster removal by oxidation to more soluble species and to a summer minimum in pollutant concentrations. The seasonal variability of the averaged TGM monthly means at Zingst and Mace Head is shown in Fig.2.

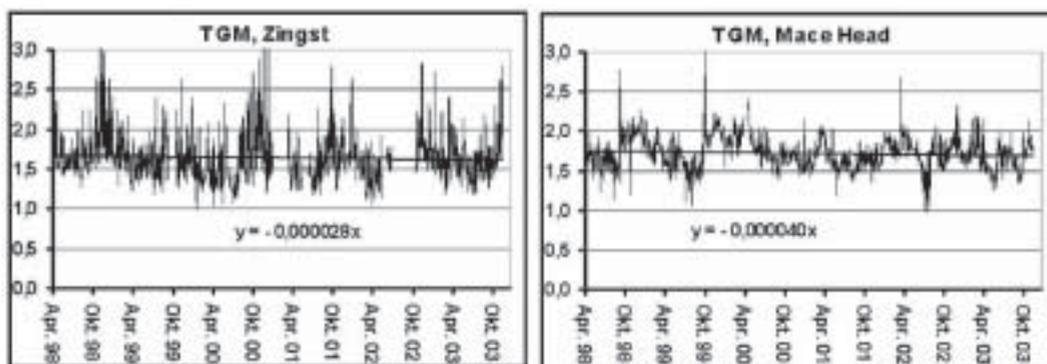


Figure 1. TGM-concentrations measured at Zingst and Mace Head (1998 – 2003)

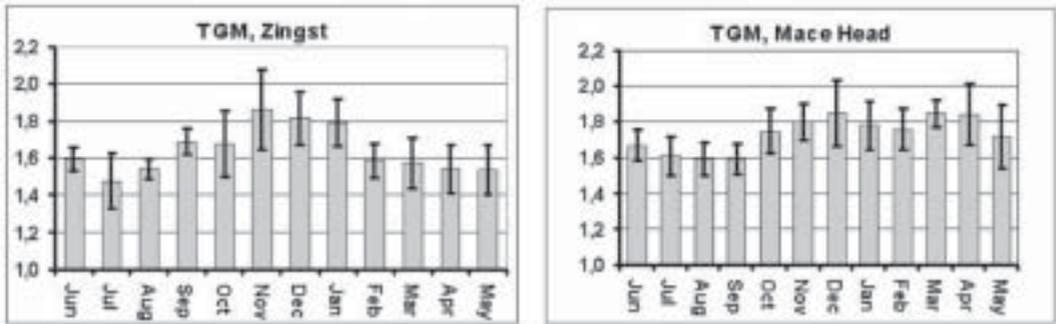


Figure 2. Seasonal variability of the averaged TGM monthly means

We observed an unexpected west to east gradient seen between Mace Head and Zingst and found that the monthly averaged Mace Head data are about  $0.08 \text{ ng m}^{-3}$  higher than those of Zingst. From February to May the Mace Head TGM results are significantly elevated compared to the Zingst values. The reason for the observed west-to east decreasing TGM gradient from Mace Head to Zingst is not yet clear, but may partly be explained by increased mercury emissions to the atmosphere in the marine boundary layer at the west coast of Ireland during springtime. Natural processes with volatilization of mer-

cury and gas exchange between the surface water and the atmosphere is considered the major mechanisms driving mercury from marine aquatic environments to the air.

Dissolved gaseous mercury (DGM) measurements were performed in coastal Atlantic seawater (GARDFELDT ET AL., 2003) during September 1999 at the Mace Head Atmospheric Research Station. The predicted average mercury evasion from the coastal Atlantic water was  $2.7 \text{ ng m}^{-2} \text{ h}^{-1}$  implying that the concentration of TGM in the Atlantic air is enhanced by mercury evasion from the sea.

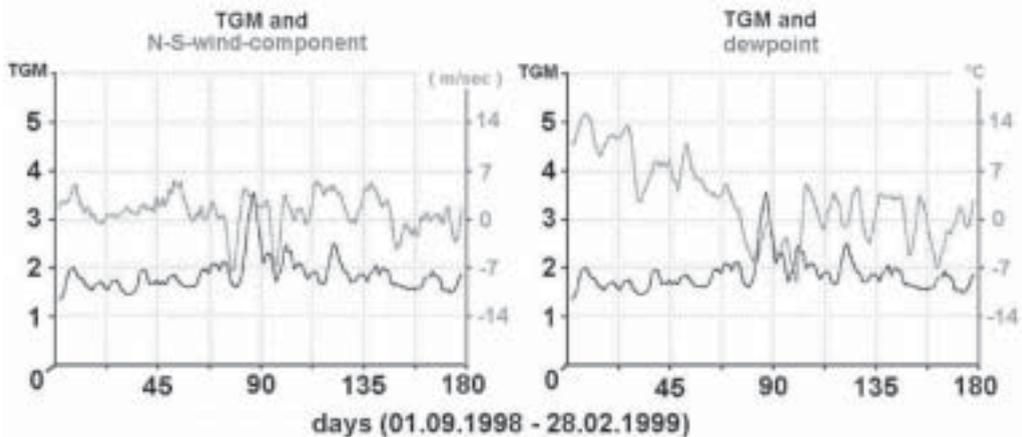


Figure 3. Comparisons of TGM concentrations with N-S-wind-component and dewpoint measured at Zingst

A statistical evaluation, using the time series analysis shows a clear difference in time periodicity of the Zingst and Mace Head TGM data. Examination of the Mace Head data shows that the remote site in Ireland indicates a significant periodicity of 1 day during spring and summertime. The remarkable diurnal periodicity of the TGM concentration supports the assumption of local diffuse emissions of TGM. Mercury containing air masses originating from medium or long-range transport should not show such a stable 24 h frequency as the observed peak events. Since no local anthropogenic sources exist near the Mace Head station, enhanced emission from the sea appears to provide the most probable explanation for the observed differences. The diurnal trend in mercury evasions from the Atlantic water surface therefore seems very reasonable. In this examples of about 6 winter and summer month, periods of 6 days and 18 days were detected at Zingst. It is thought that the 6- and 18-day periods can be addressed to a weather cycle. Comparisons of the variations in atmospheric mercury concentrations measured at Zingst were made with several meteorological parameters (wind direction, wind speed and dewpoint) (Fig.3). The short-term variations in the TGM-concentration series refers to the periodicity at which weather systems pass through a given area. Over Northern Europe this occurs at roughly 6- and 18-days increments.

## REFERENCES

- SLEMR, F. AND SCHEEL, H. E. (1998): Trends in atmospheric mercury concentrations at the summit of the Wank mountain, southern Germany; *Atmos. Environ.*, Vol. 32, pp. 845-853.
- GARDFELDT, K. ET. AL. (2003): Evasion of mercury from coastal and open waters of the Atlantic Ocean and the Mediterranean Sea; *Atmos. Environ.*, Vol. 37, pp. 73-84.

## CONCLUSIONS

Between 1998 and 2003 average TGM-concentrations measured at Mace Head and Zingst remained fairly stable and clearly reflect northern hemispheric background values. No significant trends in the concentration levels have been detected during the measurement period.

At Mace Head and Zingst we measured higher TGM levels during winter months and lower concentrations during summer months.

We observed an unexpected west to east gradient seen between Mace Head and Zingst and found that the averaged Mace Head TGM-concentrations are higher than those of Zingst. Since no local anthropogenic sources exist near the Mace Head station, enhanced emission from the sea appears to provide the most probable explanation for the observed differences.

Comparisons of the variations in atmospheric mercury concentrations measured at Zingst were made with several meteorological parameters. The short-term variations in the TGM-concentration series refers to the periodicity at which weather systems pass through this area.

# Estimation of Mercury Emissions Due to Combustion of Fossil Fuels in Slovenia

JOŽE KOTNIK, MILENA HORVAT

Jozef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia; E-mail: joze.kotnik@ijs.si

**Abstract:** Combustion of fossil fuels is most important anthropogenic source of Hg to in the global atmosphere. Most important industrial Hg sources in republic of Slovenia are fossil fuels burning thermal power plants (TPP Šoštanj, TPP Ljubljana, TPP Trbovlje). Mass balance calculations for TPP Šoštanj showed that between 300 to 400 kg of Hg is released to the atmosphere yearly. Total Hg emissions from Slovenian power plants are estimated to be around 450 kg yearly. Small industry and private houses contribute only 7 % of that amount. Hg emissions due to oil and gasoline consumption are much lower, estimated to be only 2.7 kg yearly.

**Key words:** power plants, Hg emissions, fossil fuel combustion

## INTRODUCTION

Fossil fuels combustion is the greatest source of anthropogenic emissions of mercury into the environment. Present-day worldwide fossil fuel combustion was estimated to produce emissions of Hg of about  $0.7\text{-}3.8 \times 10^3$  ton/yr (NRIAGU AND PACYNA, 1988; PACYNA, 1996). Most important source are thermal power plants that combust coal, liquid or gaseous fossil fuels. ). Due to high combustion temperatures mercury become volatile and it is emitted into the atmosphere via flue gases. Mercury that is released from power plants can be in different oxidation states (i.e., elemental ( $\text{Hg}^0$ ) or oxidized ( $\text{Hg}^{2+}$ )). The proportion between them depends upon coal type and composition, combustion and flue gas conditions, and flue gas cleaning technologies. This has significance for several reasons. The chemical form of the Hg may affect the degree of its removal, as well as its atmospheric fate, health effects and risk assessment.

In the atmosphere Hg undergoes various physical and chemical transformations, and finally is removed from the air by wet or dry deposition. After it is deposited into aquatic environment Hg undergoes transformations such as: methylation, demethylation, reduction, oxidation, diffusion, settling and burial, evaporation, etc.

In Slovenia there are four important thermal power plants Power Plant Šoštanj (775 MW), Power Plant Trbovlje (125 MW), Power Plant Ljubljana (175 MW) and Power Plant Brestanica (228 MW). First three power plants use lignite or brown coal for electricity or heat production. PP Brestanica use natural gas or oil as a fuel.

Fossil fuel combustion in individual heating systems and in small industry contribute smaller part of total Hg emissions.

## RESULTS AND DISCUSSION

According to data from International Energetic Agency (1996), the majority of coal in Slovenia is burned in power plants, mostly lignite from Velenje coal mine (4,340,000 t/y) following by brown coal (1,540,000). After closure of Zasavje coal mines most brown coal is imported. Only 17,000 t of black coal is burned yearly in Slovenia, mostly by industry.

Šoštanj power plant is the biggest energetic system in Slovenia, which produce more than one third of Slovenian electricity. It uses lignite from near mine in Velenje. Average Hg content in burnt lignite is 82 – 99 ng/g (dry weight) (KOTNIK ET AL., 2000). Mass balance calculations showed that it emitted into environment about 356 kg Hg yearly. From that amount 42 kg Hg are deposited on fly ash landfill. About 314 kg of Hg is emitted into the atmosphere by flue gases. Most emitted

Hg is in elemental form (80 %), and the remaining is divalent mercury.

Power Plants Trbovlje and Ljubljana use brown coal from different coal mines in the world. Average Hg content in brown coal is 53 ng/g (BAKER, 1994). Both power plants burn up about 1,540,000 tones of coal. Taking into account, that more than 90 % of Hg is emitted into the atmosphere, yearly Hg emission to atmosphere would be 73 kg. From that amount Trbovlje Power Plant contributes 30.4 kg Hg yearly and Ljubljana Power Plant about 42.6 kg Hg per year. The data about natural gas consumption in Brestanica Power Plant were not available, but from data given by CHU AND PORCELLA (1995) we assumed that yearly emission is less than 10 kg of Hg per year. Locations and yearly emissions from Slovenian power plants are presented on Figure 1. Due to coal combustion Hg emissions in Slovenia are around 416 kg. Slovenian emissions due to coal combustion are shown in Table 1.

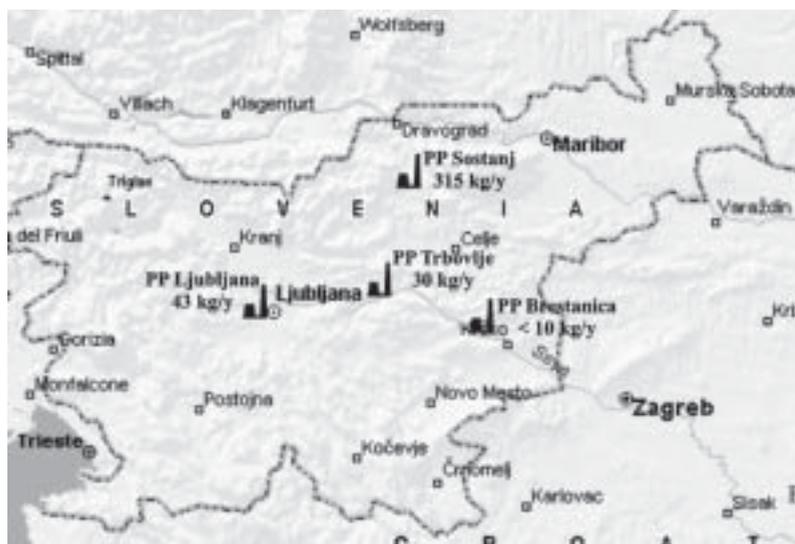


Figure 1. Slovenian thermal power plants and yearly emissions of Hg.

**Table 1.** Yearly Hg emissions due to coal combustion in Slovenia (in kg/year).

	Lignite		Brown coal		Black coal		Total
	Consumption (×1000 ton)	Emission (kg Hg/y)	Consumption (×1000 ton)	Emission (kgHg/y)	Consumption (×1000 ton)	Emission (kg Hg/y)	Emission (kg Hg/y)
<b>Thermal power plants</b>	4095	332	1129	53.9	0	0	386
<b>Industry</b>	66	5.3	57	2.7	17	1,3	9.3
<b>Households</b>	179	14.5	142	6.8	0	0	21.3
<b>Total</b>	4340	351.5	1328	63.3	17	1,3	<b>416</b>

Similar calculations as for coal have been also done for oil and its products. In calculations data from CHU AND PORCELLA (1995) and LIAN ET AL. (1996) have been applied. For oil they obtained average Hg content between 2 and 8 ng/g and for natural gas 20 ng Hg/m<sup>3</sup> or 0,56 ng Hg/MJ. LIAN ET AL. (1996) reports average Hg content in gasoline bought in Slovenia to be 1,2 ng/g. We assumed that 100 % of Hg is emitted to atmosphere.

Most Hg emissions from oil derivatives have been found to be due to combustion of petroleum spirit in small Power plants. The yearly Hg emissions do not exceed 1,2 kg Hg. Transportation contribute another 1,4 kg of Hg mostly combusted in gasoline engines (64 %). Total Slovenian emissions from oil and its derivatives consumption was estimated to be around 2,7 kg/Hg per year. Atmospheric Hg emissions due to oil and its derivatives combustion in Slovenia are shown in table 2.

**Table 2.** Hg emissions to atmosphere due to oil and its derivatives consumption in Slovenia (in kg Hg/year).

	Oil		Petroleum spirit		Gasoline		Total
	Consumption (×1000 ton)	Emission (kg Hg/y)	Consumption (×1000 ton)	Emission (kg Hg/y)	Consumption (×1000 ton)	Emission (kg Hg/y)	Emission (kg Hg/y)
<b>Small thermal power plants</b>	N/A		155	0.2			0.2
<b>Industry</b>	N/A		184	0.3			0.3
<b>Transport</b>	353	0.5	N/A		765	0.9	1.4
<b>Households</b>	56	0.1	446	0.7			0.8
<b>Total</b>	409	0.6	785	1.2	765	0.9	<b>2.7</b>

## CONCLUSIONS

Slovenian contribution of mercury to the global atmosphere due to fossil fuel combustion is less than 0.02 % (approximately 420 kg) (of which 99 % of Hg originates from

coal. Most Hg is released by three thermal power plants (386 kg of Hg) that use lignite or brown coal as a source of thermal energy. Households and other industries represent minor source of Hg to the total Slovenian Hg emissions. References

## Acknowledgement

We acknowledge the financial support of Ministry of the Environment and Physical Planning.

## REFERENCES

- International Energetic agency - IEA (1996): *Energetic Policy of republic of Slovenia*; Overview 1996, OECD-IEA, Paris, France, 122 p.
- KOTNIK, J., HORVAT, M., FAJON, V., LOGAR, M. (2002): Mercury in small freshwater lakes: a case study; Lake Velenje, Slovenia; *Water, Air and Soil Pollut.* 134, pp. 319-339.
- KOTNIK, J., HORVAT, M., MANDIČ, V., LOGAR, M. (2000): Influence of the Šoštanj coal-fired thermal power plant on mercury and methyl mercury concentrations in Lake Velenje, Slovenia; *Sci. Total. Environ.* 259, pp. 85-95.
- LIANG, L., HORVAT, M., DANILCHIK, P. (1996): A novel analytical method for determination of picogram levels of total mercury in gasoline and other petroleum based products; *The Science of the Total Environment* 187, pp. 57-64.
- NRIAGU, J. O., AND PACYNA, J. M. (1988): Quantitative assessment of worldwide contamination of air, water and soils by trace metals; *Nature* 333, pp. 134-139.
- PACYNA, J. M. (1996): Emission inventories of atmospheric mercury from anthropogenic sources; In *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances* (W. BEAYENS ET AL., Eds.), Kluwer Academic Publishers, Netherlands, pp. 161-177.

# Study of Atmospheric Gaseous Mercury in Taiwan

TIEN-HO KUO<sup>1</sup>, MAY-YIN HWA<sup>1</sup>, ANDRIUS URBA<sup>2</sup> & KESTUTIS KVIETKUS<sup>2</sup>

<sup>1</sup>Tung-Nan Institute of Technology, No.152 Sec. 3 PeiSheng Rd., ShenKeng, Taipei 222, Taiwan;  
E-mail: thkuo@mail.tnit.edu.tw

<sup>2</sup>Atmospheric Pollution Research Lab., Institute of Physics, Savanoriu 231, Lithuania; E-mail:  
urba@ktl.mii.lt

**Abstract:** The first attempt to systematically investigate the atmospheric mercury over the territory of Taiwan has been undertaken. Six sampling sites were selected in localities, which can be characterized as suburban, industrial-rural and rural, within the Northern part of Taiwan. The sites were monitored for TGM alternately from September 2003 until April 2004, by using a portable automated mercury analyzer Model Gardis-3. The results have shown rather high atmospheric TGM levels (up to 30 ng/m<sup>3</sup> at rural sites and up to 80 ng/m<sup>3</sup> at the suburban site) which may indicate the presence of considerably strong point and area mercury sources which origin still has to be detected more precisely.

**Key words:** atmospheric, mercury, TGM, pollution, emission.

## INTRODUCTION

Taiwan is an island about 160 km southeast from mainland China. Contemporary Taiwan is a heavily industrialized country with still many agricultural activities. It can be expected that a huge amount of different toxic pollutants, including mercury, may be emitted into the environment from numerous in-

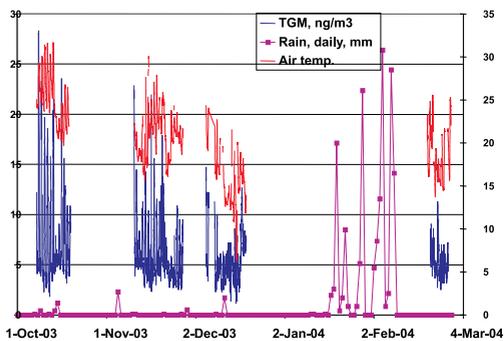
dustrial facilities. According to our knowledge, gaseous mercury was not yet systematically investigated in the atmosphere of Taiwan, therefore the intention of our pilot study was to fill in this gap.

## RESULTS AND DISCUSSION

Total six sampling locations in the Northern Taiwan were selected for the current study. One of them was selected in a suburban region of Taipei city, at the Tung-Nan Institute of Technology (TNIT, see Figure 1), and five others were located close to each other in a lowland mainly used for agriculture activities, which corresponded to the territory of local EPA branch of Taiwan, called Hsin-Chu EPB. The alternately monitored five EPB sites TGM results did not show significant differences among each other, therefore in this short paper we present the results from all of them altogether.



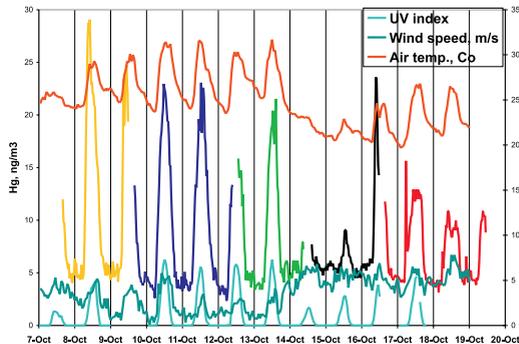
**Figure 1.** Northern part of Taiwan and the sampling sites.



**Figure 2.** Time series atmospheric TGM concentration, rain events and air temperature at EPB, October 2003 to March 2004.

It is important to note that relief of Taiwan is highly variable, considerable part of the territory being covered with mountains. Although the EPB region is only about 100 kilometers from the TNIT, due to different relief features the weather statistics is dramatically different. The examples are different wind roses (NE strongly dominated at EPB and E strongly dominated at TNIT) and different precipitation time series. While the rain events were distributed more or less evenly in time from October 2003 until April 2004 at TNIT, the EPB region experienced almost completely dry months from October to December, and heavy showers from mid January to mid February (see Figure 2).

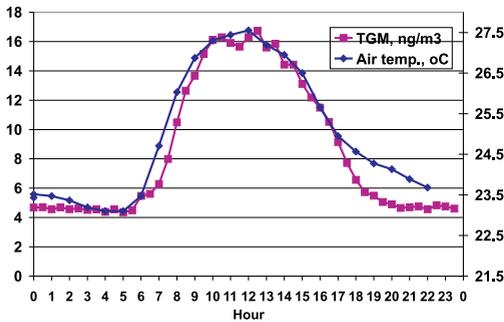
From the very beginning of the sampling campaign, October 2003, all the EPB sites showed surprisingly regular and strongly expressed atmospheric TGM diurnal variability patterns with the TGM maximum peaks around the midday (see Figure 3), whereas dependence on the wind direction was not as significant. The TGM peak values exceeded background values for more than 5 times, and approached as much as 25 ng/m<sup>3</sup> concentration.



**Figure 3.** Time series Atmospheric TGM concentration, UV index, wind speed and air temperature. Mercury sampled at different EPB sites is shown in appropriate colors.

Vice versa, at the TNIT, diurnal variability was not as clearly expressed as at EPB but the TGM obviously depended on the wind direction which could be readily attributed to the Mu- Cha incinerator located at about 2 km distance North-West direction (315 degrees) from the TNIT. Only very episodically, and only during good atmospheric mixing conditions (midday) wind was available from 315 degrees direction at the TNIT site, which still enabled to detect the peak TGM values of as high as 80 ng/m<sup>3</sup>. It can easily be assumed that, at the downwind direction from the incinerator, and during low atmospheric mixing conditions, the TGM concentrations could be found even much higher and probably exceeding the permissible levels (300 ng/m<sup>3</sup>). It is important to note that, downwind from the incinerator, the Taipei city itself is located.

The strongly expressed diurnal TGM variability and high midday TGM values (up to 30 ng/m<sup>3</sup> Hg at EPB) and peak values at TNIT were somewhat record-breaking if we compare them to similar studies carried out in neighboring countries such as China, Korea, and Japan: KIM AND KIM (2002), KIM AND

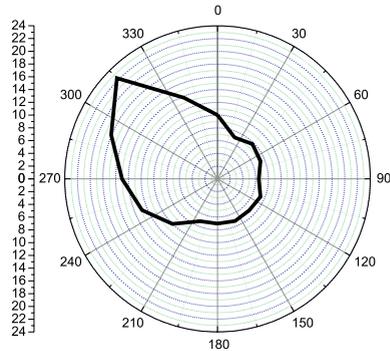


**Figure 4.** Diurnal variability of TGM concentration and air temperature at the EPB, October 2003.

KIM (2000), NAKAGAWA (1995), KIM ET AL. (2002). Only at the industrial Beijing central site the peak TGM values in the atmosphere were found comparable to Taiwan suburban TNIT: LIU ET AL. (2002); and only China Guiyang city (Guizhou province) sometimes showed the daily TGM peaks comparable to Taiwan mainly agricultural region EPB.

It should be noted however, that the China Guiyang city is known as one of the most polluted cities in China, whereas the province Guizhou is famous for accounting 70 % of China cinnabar deposits and mercury production for over 600 years. Whereas, our knowledge, the EPB region does not contain cinnabar deposits, and mercury was never produced there. Therefore, the reason for such high TGM concentration values in the air still has to be detected.

We hypothesize that the midday TGM peaks at the EPB were caused by the Hg re-emis-



**Figure 5.** Mean TGM concentration versus air direction at the TNIT, September 2003 – April 2004.

sion from the polluted background soil surfaces. Pretty good correlation with the diurnal variability of ambient air temperature (Figure 4) is likely to confirm that hypothesis. On a longer time scale, the midday TGM peaks seemed to be also directly dependant on temperature, decreasing following the mean daily air temperature decrease from October to December, 2003. Still, although the air temperature tended to come back to higher levels again in February, 2004, TGM concentration remained to be low. This can be explained by high humidity of soil after the January-February showers (see Figure 2) In accordance with the emission from the background soils modeling by SCHOLTZ ET AL. (2003), Hg emission from the background soil is negatively correlated with the soil humidity. In order to point out the Hg source at the EPB region precisely, and in order to evaluate the Hg exchange rate, micrometeorological study is required and therefore it is planned to do in the next future.

## CONCLUSIONS

Preliminary results show that a number of considerably strong, both point and surface Hg sources, representing both anthropogenic emission and re-emission from the background soil surfaces, may exist in Taiwan. Somewhat more extended study (to include more sampling sites and more prolonged

observation time, desirable simultaneous measurements at different sites), and some additional experiments (e.g. micrometeorological study) is required to characterize these Hg sources more precisely.

## Acknowledgements

The part of this work was supported by the Hsin-Chu Environment Protection Bureau.

## REFERENCES

- FENG, X., TANG, S., SHANG, L., YAN, H., SOMMAR, J., LINDQVIST, O. (2003): Total gaseous mercury in the atmosphere of Guiyang, PR China; *The Science of the Total Environment* 304, 61-72.
- KIM, K. H., KIM M. Y. (2002): A decadal shift in total gaseous mercury concentration levels in Seoul, Korea: changes between the late 1980s and the late 1990s; *Atmospheric Environment* 36, 663-675.
- KIM, K. H., KIM, M. Y. (2000): The effects of anthropogenic sources on temporal distribution characteristics of total gaseous mercury in Korea; *Atmospheric Environment* 34, 3337-3347.
- KIM, K. H., KIM, M. Y., KIM, J., LEE, G. (2002): The concentrations and fluxes of total gaseous mercury in a western coastal area of Korea during late March 2001; *Atmospheric Environment* 36, 3413-3427.
- LIU, S., NADIM, F., PERKINS, C., CARLEY, R. J., HOAG, G. E., LIN, Y., CHEN, L. (2002): Atmospheric mercury monitoring survey in Beijing, China; *Chemosphere* 48, 97-107.
- NAKAGAWA, R. (1995): Studies of the levels in atmospheric concentrations of mercury in Japan; *Chemosphere*, Vol. 31, No. 2, 2669-2676.
- SCHOLTZ, M. T., VAN HEYST, B. J., SCHROEDER, W. H. (2003): Modelling of mercury emissions from background soils; *The Science of the Total Environment* 304, 185-207.
- TAN, H., HE, J. L., LIANG, L., LAZOFF, S., SOMMAR, J., XIAO, Z. F., LINDQVIST, O. (2000): Atmospheric mercury deposition in Guizhou, China; *The Science of the Total Environment* 259, 223-230.

## Net accumulation of mercury in Arctic snow during springtime

NAZAFARIN LAHOUTIFARD, MELISSA SPARLING & DAVID LEAN

Department of Biology, Faculty of Science, University of Ottawa, 150 Louis Pasteur, MacDonald Hall, Ottawa, Ontario K1N 6N5 Canada; E-mail: dlean@science.uottawa.ca

**Abstract:** Total gaseous mercury was measured simultaneously at 150 and 10 cm above the snow to determine the concentration gradient and thus infer transport of mercury from the atmosphere to the snow or volatilization from snow to the atmosphere. Experiments were conducted from 7 May (day 127) to 12 June (day 163) 2003 near Resolute Bay, Cornwallis Island, Nunavut, Canada at 74° 42'N, 94° 58'W. Additional losses from the snow due to snow-melt in the springtime were found to be significant. Methyl mercury, the most toxic form of mercury and the only form that accumulates in Arctic food chains was less than 1 % of total mercury in the snow and declined quickly with snowmelt. The highest levels of methyl mercury observed here are similar to that found in stream run-off water. Consequently, methyl mercury found in snow is a significant source to the Arctic ecosystems (see also LOSETO ET AL., this conference) leading to indigenous people.

**Key words:** mercury, methylmercury, Arctic, ecosystem, pollution

### INTRODUCTION

At Alert (82.5°N) high in the Canadian Arctic, episodic depletions of gaseous elemental mercury (GEM) have been observed (SCHROEDER ET AL., 1998) over a 3-month period following polar sunrise in mid-March. Depletions of GEM can last from a few hours to several days. Concurrent with these events, ozone is also depleted in the lower atmosphere. Photochemically initiated autocatalytic reactions involving halogens such as Br and BrO derived from sea-salt aerosols are involved (BARRIE AND PLATT, 1997). The oxidation of atmospheric Hg(0) increases the wet and dry deposition flux of less volatile, but more water soluble, Hg(II) in snow (LU ET AL., 2001). The total amount of Hg(II) depos-

ited in the Arctic each year is 50 tonnes or 5.6 to 7.8  $\mu\text{g m}^{-2} \text{y}^{-1}$  over the 3-month period.

Fortunately, Hg(II) in the snow can also be converted to Hg(0) through photolytic reduction and is emitted to the atmosphere as Hg(0) (LALONDE ET AL., 2002). They found that Hg levels decreased by 54 % within 24h after deposition and concluded that Hg depletion in snow was caused by a rapid snow-to-air Hg transfer resulting from Hg(II) photo-induced reduction to volatile Hg(0).

Clearly, there is a complex interplay of photochemical oxidation in the atmosphere and photochemical reduction in the snow that requires quantification. It is important to know the fate of this mercury and the amount

as methyl mercury, since it is methyl mercury that is by far the most toxic and bioaccumulates in the Arctic food chains leading local indigenous populations. It is known that the subsistence lifestyle of many northern residents have resulted in high levels of Hg in the blood and hair of these populations (WHEATLEY AND WHEATLEY, 1998).

Here we measured concentrations of GEM at 10 and 150 cm above the snow using a gas-phase mercury vapor analyzer model 2537A from Tekran. Experiments were conducted near Resolute Bay, Cornwallis Island, Nunavut, Canada at the Upper Air Station of Environment Canada located at 74° 42'N, 94° 58'W from May 7 (day 127) to June 12 (day 163) 2003, in 24h daylight. The gradient between these two heights provided some information on transport to and from the snow during each day, which was related to solar radiation, wind speed, temperature, as well as the concentration of total and methyl mercury in the snow. This site is located 760 km south of Alert (SCHROEDER ET AL., 1998) and 4900 km north of Kuujjuarapik, Quebec, site for other mercury depletion studies (POISSANT, 2000) and 6500 km north of Toronto, ON, Canada.

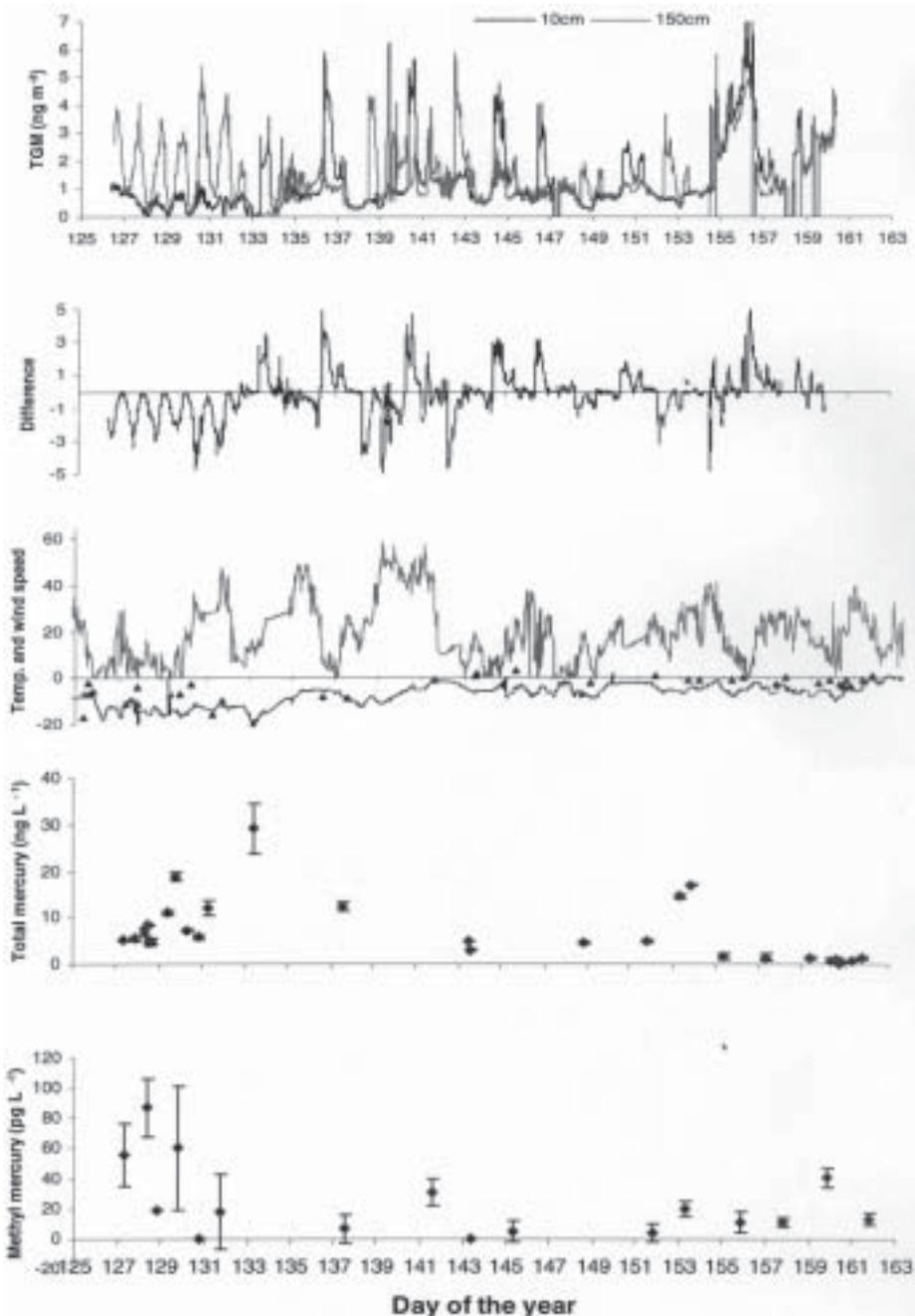
## RESULTS AND DISCUSSION

At the time of our experiments there was continuous daylight and long past polar sunrise (mid March). Nevertheless, there was still a noticeable daily pattern, which was shown to influence flux rates between the

atmosphere and the snow. Each day values of GEM increased from near zero to a maximum of 8 ng/m<sup>3</sup> before declining again to near zero as solar radiation reached the lowest point for the day.

In addition, measurements of total mercury (THg) and methyl mercury (MeHg) were monitored in the snow to determine the net accumulation. In other work (LOSETO ET AL., 2004 and this conference) showed that there were significant amounts of MeHg in stream runoff and that snow-melt was thought to be a source. Here we provide data for MeHg concentrations in snow that confirms this observation. Further work is however necessary to determine the exact contribution. At the present time there is little, if any, data for methyl mercury in the Arctic snow, rivers or lake waters.

Total mercury (THg) accumulation in the snow increased following 8 days of atmospheric mercury depletion in the air (Fig. 1) followed by intermittent reversals. Clearly there are many factors, which are involved. We did not see any direct influence of wind speed or temperature but as temperatures warmed there was a rapid loss of total and methyl mercury presumably through runoff. Solar radiation was an important factor (data not shown here). Methyl mercury in the snow decreased from peak levels near the start of the experiment to less than detection limit (10 pg/L) during snowmelt. The relative importance of photoreduction-volatilization and runoff after melting must be more carefully quantified.



**Figure 1.** Measurements of GEM at 10 cm (solid line) and 150 cm (dashed line) are provided from 7 May (day 127) to 12 June (day 163) 2003. Below is the difference between values. Positive values indicate transport from snow to air and negative values in the reverse direction. In the next panel below are continuous values for wind speed and air temperature as well as occasional values for temperature in the snow. In the panels at the bottom are values for total ( $\text{ng/L}$ ) and methyl mercury ( $\text{pg/L}$ ) in the snow.

## CONCLUSIONS

Clearly, these data provide a basis to design experiments that will provide more reliable budgets that can be used to determine the source and fate of mercury in the Arctic snow. Furthermore we must determine if the methyl mercury falls in the snow or is produced in the snow. We have confirmed that volatilization is a process that cannot be ignored. The accumulation of methyl mercury is significant in snow and this is a major source of methyl mercury to the freshwater and marine ecosystems of the Arctic. Although our experiments were extensive (38 days) we started too late and finished too early. Experiments lasting only a few days must be rejected, as they provide no new insights on the overall net transport of mercury.

## REFERENCES

- BARRIE, L. A. & PLATT, U. (1997): Arctic tropospheric chemistry: An overview; *Tellus*, Vol. 40B, pp. 450-454.
- LALONDE, J. D., POULAIN, A. J. & AMYOT, M. (2002): The role of mercury redox reactions in snow on snow to air mercury transfer; *Environ. Sci. Technol.* 36, pp. 174-178.
- LU, J. Y., SCHROEDER, W. H., BARRIE, L. A., STEFFEN, A., WELCH, H. E., MARTIN, K., LOCKHART, W. L., HUNT, R. V., BOILA, G., & RITCHER, A. (2001): Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry; *Geophys. Res. Lett.* 28, pp. 3219-3222.
- SCHROEDER, W. H., ANLAUF, K. G., BARRIE, L. A., LU, J. Y., STEFFEN, A., SCHNEEBERGER, D. R. & T. BERG (1998): Arctic springtime depletion of mercury; *Nature* 394, pp. 331-332.
- WHEATLEY, B. & WHEATLEY M. A. (1998): Methylmercury in the Canadian Arctic environment past and present-natural or industrial?; *Arctic Med. Res.* 47, pp. 163-167.
- POISSANT, L. (2000): Atmospheric mercury transport, oxidation and fallout in northern Québec (Nunavik): An important potential route of contamination, Northern Contaminants Program, Synopsis of Research 1999-2000, Indian and Northern Affairs Canada, ISBN 0-662-29320-7, pp 132-136.
- LOSETO, L., LEAN, D. R. S. & SICILIANO, S. (2004): Snow: A source of methyl mercury in the Arctic; *Environmental Science and Technology* (in press).

## Acknowledgements

The authors thank Environment Canada in Resolute for providing facilities, Polar Continental Shelf Project (PCSP) for logistical support, and Association for Canadian Universities for Northern Studies program Northern Scientific Training Program (NSTP) for a portion of the travel funding. We thank NRI (Nunavut Research Institute) for providing the license to work on their land. This work was supported by the National Sciences and Engineering (NSERC) Research Network called the Collaborative Mercury Research Network (COMERN) and an NSERC Strategic Grant to DL.

## Seasonal atmospheric mercury levels around the chlor-alkali plant of Rosignano Solvay (Italy)

ENRICA LANZILLOTTA<sup>1</sup>, CLAUDIA CECCARINI<sup>1</sup>, ROMANO FERRARA<sup>1</sup>, BARBARA MAZZOLAI<sup>2</sup>

<sup>1</sup>CNR-Istituto di Biofisica, Area della Ricerca, via Moruzzi 1, 56100 Pisa, Italy; E-mail: romano.ferrara@pi.ibf.cnr.it

<sup>2</sup>Scuola Superiore Sant'Anna, CRIM Laboratory, 56100 Pisa, Italy

**Abstract:** In the framework of the EMECAP (European Mercury Emission from Chlor-Alkali Plants) project four measurement campaigns (winter 2002 and 2003; summer 2002 and 2003) were performed at three representative MCCA (Mercury Cell Chlor-Alkali) plants located in Italy (Rosignano Solvay), in Sweden (Bohus) and in Poland (Tarnow) in order to determine the environmental mercury levels in air, soil and fish and the mercury emission from the plants. The results obtained on Total Gaseous Mercury, Reactive Gaseous Mercury and Total Particular Mercury concentration at the chlor-alkali plant in Italy are here reported. The impact of the plant on the nearby village resulted rather limited; concentration values were generally two-three times higher than those observed at the control station.

**Key words:** mercury, atmospheric mercury, mercury emission, chlor-alkali plant.

### INTRODUCTION

Mercury Cell Chlor-Alkali (MCCA) plants constitute one of the most important anthropogenic metallic mercury source (about 15 % of the global): this emphasizes the importance of investigating possible direct relationship between mercury emissions, environmental damages and onset of pathologies in human populations living in the neighbourhood of chlor-alkali plants.

The assessment of atmospheric mercury levels in the village near the plant, measured along the four campaigns constitutes an important requirement to investigate the effects on citizen's health.

### RESULTS AND DISCUSSION

The Solvay chlor-alkali plant, located in Rosignano Solvay (Central Italy) has been in operation since 1920. The capacity of the Solvay Chlor-alkali plant is around 120,000 tons/year of chlorine. The mercury emission into the atmosphere determined by the Lund Institute of Technology is in the range of 20-54 g/h (GRÖNLUND ET AL., 2004). It has been estimated that 12-14 tons/year of mercury flowed into the sea through a discharge ditch from the 1950s to 1973, and they were incorporated into the surrounding sediments. At present 400-500 kg of mercury are discharged into the sea per year (FERRARA ET AL., 2001).

Nine sampling stations were selected around the chlor-alkali plant in the village of Rosignano Solvay taking into account where citizens live. Four environmental campaigns were carried out in order to determine the atmospheric mercury levels. In particular the following parameters have been considered:

- Total Gaseous Mercury (TGM) concentration;
- Reactive Gaseous Mercury (RGM) concentration;
- Total Particulate Mercury (TPM) concentration.

A map of the village of Rosignano Solvay is reported in Fig.1, together with the position of the sampling stations. The village of Rosignano has 15,000 inhabitants.

The village of Donoratico, located 20 km south from Rosignano Solvay, was selected as a control station.

The deposition of mercury near the source has been evaluated on the base of mercury concentration in rain samples; the re-emission of mercury from soil to the atmosphere



**Figure 1.** Map of the village of Rosignano Solvay. Squares show the position of the sampling stations. Rectangles show the position of the cell-house (dark gray) and of the meteorological station (light gray).

was determined close to the plant. A detailed description of the analytical procedures used was reported by WÄNGBERG ET AL. (2003).

A summary of the results obtained during the four measurements campaigns is reported in Tab.1.

**Table 1.** Summary of the results obtained during the four measurement campaigns at the Rosignano Solvay village.

	<i>1° campaign winter 2002</i>	<i>2° campaign summer 2002</i>	<i>3° campaign winter 2003</i>	<i>4° campaign summer 2003</i>	<i>Average</i>
Rosignano TGM (ng/m <sup>3</sup> )	4.21	8.86	2.85	8.08	6.00
Control station TGM (ng/m <sup>3</sup> )	2.04	5.54	1.51	3.00	3.02
Rosignano RGM (ng/m <sup>3</sup> )	0.28	0.15	0.45	0.69	0.39
Control station RGM (ng/m <sup>3</sup> )	0.09	0.11	0.22	0.33	0.19
Rosignano TPM (ng/m <sup>3</sup> )	0.07	0.04	0.03	0.02	0.04
Control station TPM (ng/m <sup>3</sup> )	0.02	0.02	0.01	0.03	0.02

Total mercury concentration in rain samples at Rosignano Solvay: 6.0-15.0 ng/l

Total mercury concentration in rain samples at Donoratico: 4.6-5.5 ng/l

Mercury degassing rate from contaminated soil of Rosignano Solvay: 0.0-45.0 ng/m<sup>2</sup> h

Mercury degassing rate from soil of Donoratico: 0.0-2.5 ng/m<sup>2</sup> h

The TGM concentration values measured along the four sampling campaigns (each lasting 15 days) are in the range 8.0-8.7 ng/m<sup>3</sup> in summer (however peaks up to 100 ng/m<sup>3</sup> were observed in particular meteorological condi-

tions), while in winter the range is 2.8-4.2 ng/m<sup>3</sup>. The highest values obtained in summer are due to the elevated ambient temperatures with respect to those measured in winter. The values of TGM concentration determined at the control station of Donoratico are lower and range between 1.5 and 5.5 ng/m<sup>3</sup>.

Also the RGM concentration shows higher values in Rosignano (277-691 pg/m<sup>3</sup>) than in Donoratico (87-326 pg/m<sup>3</sup>). A similar trend was observed for the mercury associated with particulate matter ranging from 25 to 70 pg/m<sup>3</sup> at Rosignano, while at control station the range was 13-26 pg/m<sup>3</sup>.

## CONCLUSIONS

Results show that the impact of the chlor-alkali plant on the village of Rosignano Solvay (Italy) is rather limited and influences only the air very close to the cell house; it means that part of the mercury is deposited in a small area around the plant, while most of the mercury emitted increases the atmospheric pool, showing the characteristic of

this metal as a global pollutant.

Research performed in the framework of the EC EMECAP project (Contr. N° QLRT-2000-00489).

## REFERENCES

- agnostics and Monitoring*, p. 155, Bacoli.
- WÄNGBERG, I., EDNER, H., FERRARA, R., LANZILLOTTA, E., MUNTE, J., SOMMAR, J., SVANBERG, S., SJÖHOLM, M. and WEIBRING, P. (2003): Mercury emissions from a chlor-alkali plant in Sweden; *Sci. Total Environ.*, Vol. 304, pp. 29-41.
- FERRARA, R., LANZILLOTTA, E. AND CECCARINI, C. (2001): Dissolved gaseous mercury concentration and mercury evasion flux from seawater in front of a chlor-alkali plant; *Environ. Technol.*, Vol. 22, pp. 971-978.
- GRÖNLUND, R., SJÖHOLM, M., WEIBRING, P., EDNER, H. AND SVANBERG, S. (2004): Lidar monitoring of mercury fluxes from chlor-alkali industries; *Proc. International Conference on Optical Di-*

## Reactive Gaseous Mercury in the Marine Boundary Layer

FABIEN LAURIER

**Abstract:** To assess the role of human mercury (Hg) emissions, detailed knowledge on the various chemical transformations of Hg is required. Of particular significance for the cycling of Hg is its atmospheric processing followed by deposition in the boundary layer. The latter is the dominant source of Hg to many environments. Our recent studies have highlighted the importance of elemental mercury ( $\text{Hg}^0$ ) oxidation, and reactive (ionic) gaseous mercury (RGHg) formation, in the marine boundary layer (MBL) for Hg supply to the coastal and open ocean. Hg depletion in the Arctic boundary layer during polar sunrise with concurrent ozone ( $\text{O}_3$ ) depletion, first suggested that in-situ  $\text{Hg}_0$  oxidation could be linked to the halogen catalyzed reaction cycles that are responsible for the destruction of  $\text{O}_3$ . We will show that similar reactions could occur in other regions where elevated concentrations of reactive halogen species (RHS) are likely, such as the open ocean and marine coastal environments. We will also illustrate how the meteorological conditions can affect the atmospheric Hg cycle. This study is based on a comparison between the North Atlantic Ocean, North Pacific Ocean, a coastal site and an urban environment.

# Development of a Prototype Biogenic Mercury Emission Processor in BEIS3 for Comprehensive Atmospheric Mercury Modeling

CHE-JEN LIN<sup>1</sup>, STEVE E. LINDBERG<sup>2</sup>, HENG YANG<sup>3</sup>, THOMAS C. HO<sup>4</sup> & HSING-WEI CHU<sup>5</sup>

<sup>1</sup>Department of Civil Engineering, <sup>3</sup>Department of Computer Science,  
<sup>4</sup>Department of Chemical Engineering, <sup>5</sup>Department of Industrial Engineering,  
Lamar University, Beaumont, TX, USA. Email: [lincx@hal.lamar.edu](mailto:lincx@hal.lamar.edu)  
<sup>2</sup>Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN, USA  
Email: [sll@ornl.gov](mailto:sll@ornl.gov)

**Abstract:** We have developed a prototype emission processor for biogenic mercury emission within the framework of Biogenic Emission Inventory System Version 3.11 (BEIS3). In this development, 230 categories of USGS landuse/landcover data were utilized to generate the normalized vegetation-specific Hg emission in a 36-km Lambert Conformal grid covering the continental United States. Surface temperature and cloud-cover corrected solar radiation were used for temperature and photosynthetic active radiation (PAR) corrections to calculate the diurnal emission cycle. The implemented Hg emission factors were either evaluated from the published Hg flux data, or assumed for the tree species without flux data. The output is hourly resolved gridded emission in netCDF format ready for applications in Eulerian-based chemical transport models. The simulation results show that the biogenic Hg emission exhibits strong diurnal variation with an average emission flux up to 32 ng m<sup>-2</sup> hr<sup>-1</sup> in southeast US during the modeling period representing a hot summer day. Compared to the anthropogenic source, biogenic Hg emission has generally lower emission intensity but covers a much broader region. During the modeling period, the modeled 24-hr biogenic Hg emission constitutes about 72 % of the total mercury (i.e., natural and anthropogenic) emission. However, the biogenic emission should decrease significantly during winter due to the much lower leaf mass, temperature and PAR. Additional Hg flux measurement data are needed to resolve the emission for more vegetation species.

**Key words:** emission inventory, BEIS3, biogenic source, emission modeling.

## INTRODUCTION

Emission inventory is one of the required input fields for the comprehensive chemical-transport modeling of atmospheric mercury. Accurate emission inventory is critical to reduce model uncertainties<sup>[1]</sup>. However, mercury emission from biogenic (natural) sources has not been treated rigorously in previous modeling efforts of atmospheric mercury<sup>[2-3]</sup>.

Several studies have indicated that the biogenic emission of mercury may dominate that from anthropogenic sources, and there is a need to reassess the this diffuse emission contribution<sup>[4]</sup>. More recently, it is reported that the biogenic mercury emission exhibits a strong diurnal variation<sup>[5]</sup>. In the atmosphere, biogenic mercury emission may play an important role in the concentration and deposition of mercury due to its predomi-

nant mercury input, especially in summer. However, there is not a modeling tool for biogenic mercury emission to address the modeling need and emission estimates.

The objective of this study is to develop a prototype processor for biogenic mercury emission in the framework of Biogenic Emission Inventory System Version 3 (BEIS3)<sup>[6]</sup>. BEIS3 is a flexible modeling system for estimating the emission inventory of volatile organic compounds (VOCs) for comprehensive air quality models that have incorporates the simulations of transport, reactions and deposition of atmospheric mercury in recent model studies.

## RESULTS AND DISCUSSION

The version of BEIS3 used in this development is V3.11, a stand-alone research version on UNIX/Linux platform. The 1-km-resolution, 230-category USGS Biogenic Emissions Landcover Data Version 3 (BELD3) were utilized to generate the normalized vegetation-specific mercury emis-

sion in a 36-km Lambert Conformal grid covering the entire continental United States. The surface temperature and cloud-cover corrected solar radiation from a mesoscale meteorological model (MM5) were retrieved and converted into model-ready format using a Meteorology-Chemistry Interface Processor (MCIP2). The converted data were then used for temperature and photosynthetic active radiation (PAR) corrections to calculate the diurnal variation of biogenic Hg emission for each landuse category. Guenther Algorithm<sup>[7]</sup> for biogenic VOC emission was assumed since a similar emission-temperature-PAR relationship is not yet available for mercury. A mercury emission factor table was created. The implemented emission factors were either evaluated from the published mercury flux data for selected tree species and wetland, or assumed at a background level for the tree species without mercury flux data. The output from the model is temporally (hourly) and spatially resolved gridded emission in netCDF format ready for applications in Eulerian-based chemical transport models including CMAQ-Hg and CAMx. Figure 1 shows the data flow of the

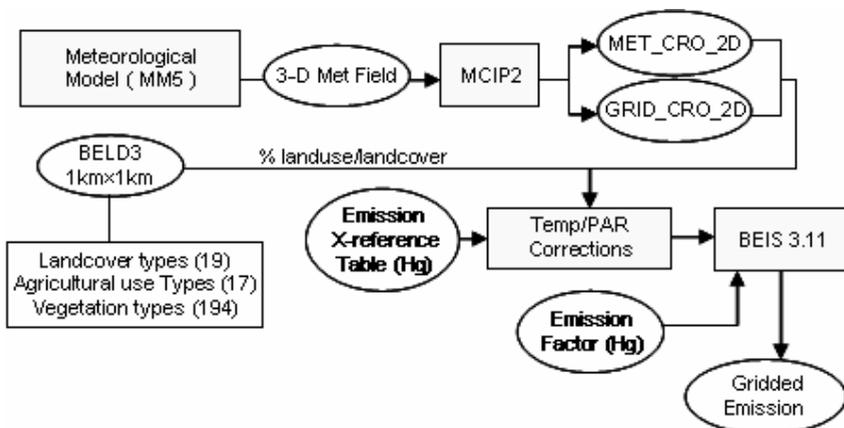
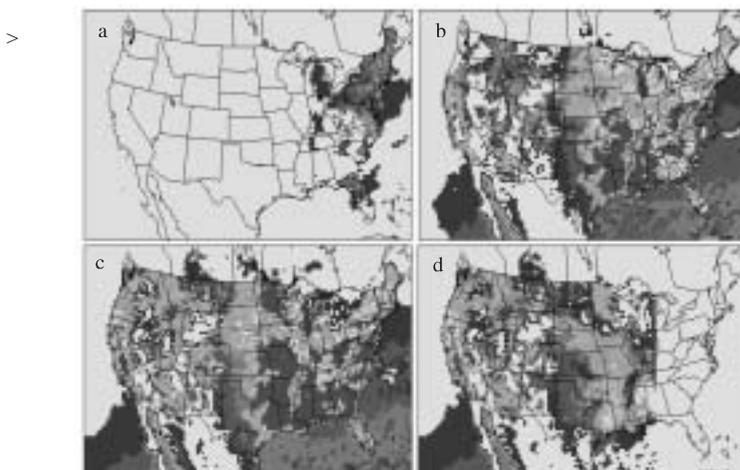


Figure 1. Data flow for developing biogenic mercury emission processor.

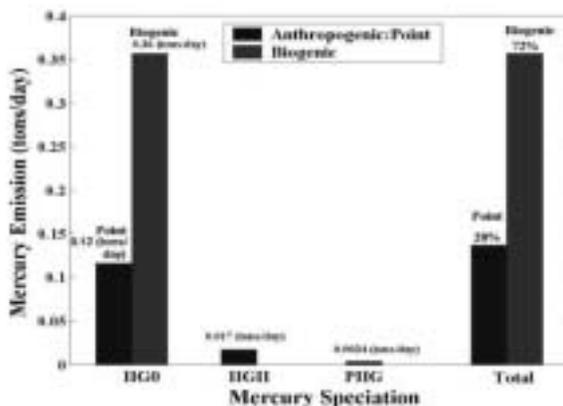
model processing. The source codes of BEIS3 were modified to include gaseous elemental mercury (Hg<sup>0</sup>) as one of the emitted species.

Figure 2 show the output of the modeled biogenic mercury emission at (a) 7 am, (b) 11 am, (c) 3 pm, and (d) 7 pm during a 24-hour modeling period on August 22, 2000 (all times are of US Eastern Time). Note that the emission unit is expressed as mole/hr in each 36×36 km grid cell (1 mole/hr

≈ 155 ng/hr/m<sup>2</sup> in each model grid). It can be clearly seen that the simulated biogenic mercury emission starts from the east coast and gradually “migrates” to the west coast according to the change of solar intensity. During the daytime, the strongest emission occurs in the southeastern US due to the high temperature and vegetation coverage of the land surface. The greatest emission flux occurs at 2 pm at 0.21 mole/hr in the corresponding model grids.



**Figure 2.** The simulated biogenic mercury emission (a) 7 am, (b) 11 am, (c) 3 pm, and (d) 7 pm (US Eastern Time) on August 25, 2000.



**Figure 3.** Comparison of 24-hour anthropogenic and biogenic mercury emission on August 25, 2000.

The estimated biogenic emission was compared to the anthropogenic mercury emission during the same modeling period (Figure 3). The anthropogenic emission was calculated based on temporally and spatially allocated USEPA speciated mercury emission inventory in the continental US model domain. As seen in Figure 3, the biogenic mercury emission dominates the total emission of the modeling period, constituting 72 % of the total mercury emission. However, the biogenic emission may decrease significantly during winter due to the much lower leaf mass, surface temperature and PAR, leaving anthropogenic source as the predominant mercury emission source. Ongoing annual simulation is underway to verify this hypothesis.

## CONCLUSIONS

A biogenic mercury emission processor in BEIS3 framework has been developed. The developed model can be used for estimating biogenic mercury emission at high temporal and spatial resolutions. This will improve the modeling analysis of atmospheric mercury. In this development, the emission factors were implemented only for a limited number of vegetation species. Additional mercury flux data with a detailed relationship between the emission quantity and temperature/PAR are needed to for further model implementation of more vegetation species.

## ACKNOWLEDGEMENTS

This work was supported by the in part by Gulf Coast Hazardous Substance Research Center and by Texas Commission on Environmental Quality under Contract number 582-4-64582. The financial support is gratefully acknowledged.

## REFERENCES

- [1] BULLOCK O. R. JR. AND BREHME K. A. (2002): Atmospheric mercury simulation using the CMAQ model: formulation description and analysis of wet deposition results, *Atm. Environ.* 36, pp. 2135-2146.
- [2] RYABOSHAPKO A, BULLOCK R., EBINGHAUS R., ILYIN I., LOHMAN K., MUNTHE J., PETERSEN G., SEIGNEUR C. AND WANGBERG I. (2002): Comparison of mercury chemistry models, *Atm. Environ.* 36, pp. 3881-3898.
- [3] SEIGNEUR C., LOHMAN K., VIJAYARAGHAVAN K., AND SHIA R.-L. (2003): Contribution of global and regional sources to mercury deposition in New York State, *Env. Pollut.* 123, pp. 365-373.
- [4] LINDBERG S. E., HANSON P. J., MAYERS T. P. AND KIM K.-H. (1998): Air/surface exchange of mercury vapor over forest – the need for reassessment of continental biogenic emissions, *Atm. Environ.* 32, pp. 895-908.
- [5] LINDBERG S. E., DONG W. AND MEYERS T. (2002): Transpiration of gaseous elemental mercury through vegetation in a subtropical wetland in Florida, *Atm. Environ.* 36, pp. 5207-5219.
- [6] LAMB B., GAY D. AND WESTBERG H. (1993): A biogenic hydrocarbon emission inventory for the USA using a simple forest canopy model, *Atm. Environ.* 27A, pp. 1673-1690.
- [7] GUENTHER, A., W. BAUGH, P. ZIMMERMAN, L. KLINGER, P. HARLEY, H. WESTBERG, L. VIERLING, B. LAMB, E. ALLWINE, S. DILTS, D. BALDOCCHI, C. GERON, AND T. PIERCE (1996): Isoprene fluxes measured by enclosure, relaxed eddy accumulation, surface-layer gradient, mixed-layer gradient, and mass balance techniques, *J. Geophys. Res.* 101, pp. 18555-18568.

## Atmospheric Mercury Speciation: diurnal and seasonal patterns in Detroit, Michigan, USA

BIAN LIU

**Abstract:** Speciation is critical to understand the distribution, transport, and biological cycle of atmospheric mercury. As part of the Michigan Atmospheric Mercury Monitoring Network, whose objective is to investigate the spatial and temporal distributions and depositions of mercury, three mercury species ( $Hg_0$ , Hg-II, and Hg-P) have been measured in Detroit since September 2002 using automated Hg speciation instruments. Analysis of data over a one-year period indicates a clear seasonal trend for all three mercury species with higher mercury concentrations appearing in warm months than cold months. The average concentrations for  $Hg_0$ , Hg (II), and Hg-P are  $2.3 \text{ ng/m}^3$ ,  $21.3 \text{ pg/m}^3$ , and  $16.1 \text{ pg/m}^3$  respectively. Stronger concentration variations were observed in Hg-II and Hg-P than  $Hg_0$  partly due to their efficient removal during low dew point temperature, high relative humidity, and precipitation episodes. The coincidence of high mercury concentrations for all three species occurred when winds were blowing from southwest and south sectors suggests the existence of a common source. The three mercury species also experienced high degree of diurnal fluctuations. While similar morning peaks (7-9 a.m.) appeared for all three mercury species, decoupling of Hg-II with  $Hg_0$  occurred in the afternoon. This phenomenon is more pronounced during the summer when ozone concentration was high. The interspecies variations of mercury concentrations observed here suggest mercury deposition could be strongly influenced by the photochemically related process in which  $Hg_0$  is oxidized to Hg-II.

**Key words:** speciation, atmospheric mercury, diurnal and seasonal patterns

## How to measure dry deposition of mercury? - Some questions and critical remarks.

MARTIN LODENIUS<sup>1</sup>, CARMO FREITAS<sup>2</sup>, MILENA HORVAT<sup>3</sup>, EILIV STEINNES<sup>4</sup>

<sup>1</sup>Environmental Protection Science, POB 27, FIN-00014 University of Helsinki, Finland;  
E-mail: martin.lodenius@helsinki.fi.

<sup>2</sup>ITN, Estrada Nacional 10, Apartado 21, P-2686-953 Savacém, Portugal; E-mail: cfreitas@itn.pt.

<sup>3</sup>Josef Stefan Institute, Jamova 39, 1001 Ljubljana, Slovenia; E-mail: milena.horvat@ijs.si.

<sup>4</sup>Department of Chemistry, Norwegian University of Science and Technology,  
N-7491 Trondheim, Norway; E-mail: Eiliv.Steinnes@chem.ntnu.no.

**Abstract:** Dry deposition is an important pathway between air and terrestrial systems. The net deposition is affected by many factors including Hg concentration in air, temperature, light, and receiving landscape surfaces. The measurement of dry deposition using technical and biological methods is associated with many difficulties. The main problem is that the absorption process probably is different for different parts of a complex ecosystem including leaves, needles, bark, mushrooms, mosses, soil etc. The biological structure and physiology include different surfaces and cell structures and different physiological processes. Mercury is strongly bound to a plant material but the binding sites of mercury are not known: surface of the plants or inside the plant cells. For these reasons it would be very important to carry out a well designed comparison between data obtained by different techniques and propose the basis for standardized methodology to quantify dry deposition of mercury.

**Key words:** mercury, dry deposition, bio-monitoring, vegetation

### INTRODUCTION

Dry deposition and re-emission are important pathway between air and terrestrial systems and these processes are affected by many factors. Dry deposition includes particulate deposition on soil, plants and other surfaces and uptake of gaseous mercury mainly by plants. Dry deposition has a very important influence on Hg fluxes. It can be seen as throughfall, litterfall and foliar leaching (REA ET AL., 2000, 2001). In one experiment twice as much Hg was deposited in a forested watershed compared to an open area. Conifer canopies were more efficient filters of airborne particulates

than deciduous canopies (KOLKA ET AL., 1999). In a moss bag experiment near a chlor alkali plant two-thirds of the total monthly deposition ( $130 \text{ ng g}^{-1}$ ) was estimated to be dry deposition (LODENIUS, 1998) while e.g., IVERFELDT (1991) estimated wet deposition ( $12 \mu\text{g m}^{-2} \text{ a}^{-1}$ ) to dominate over the dry deposition ( $4\text{--}7 \mu\text{g m}^{-2} \text{ a}^{-1}$ ). In a northern mixed hardwood forest the annual throughfall was estimated to be greater ( $10.5 \mu\text{g m}^{-2}$ ) than the precipitation flux ( $8.7 \mu\text{g m}^{-2}$ ; REA ET AL., 2001). Depending on ambient concentrations, foliar surfaces in terrestrial forest landscapes may be a dynamic exchange surface that can function as a source or sink of mercury (HANSON ET AL., 1995).

There may also be considerable plant-to-atmosphere emissions which are greater in the light and at higher temperature (TODD ET AL., 1998a, 1998b). In a wetland in Florida LINDBERG ET AL. (2002) found that the predominant flux of  $Hg^0$  in daytime was emission, greater in summer than in winter. Night-time fluxes approached zero. As the  $Hg^0$  flux correlated best with water vapour, the authors found it appropriate to define the  $Hg^0$  flux as transpiration.

Another critical question is the temporal variation (diurnal, seasonal) which may be related to temperature and possibly other meteorological factors and to the occurrence of other chemical compounds, e.g., oxidants. The relation between dry and wet deposition of mercury is determined by meteorological factors but probably also by biological factors such as the occurrence of suitable biological structures. Estimation of total, dry and wet deposition under natural conditions is a difficult task and many previous attempts may have been based on too simplified calculations.

The objective of this paper is to outline experimental difficulties to accurately assess or monitor the amount of mercury deposited by the process of dry deposition and its importance for better understanding of mercury cycling.

#### **FACTORS AFFECTING THE EXCHANGE OF MERCURY BETWEEN AIR AND VEGETATION**

For dry deposition, one problem is to differentiate between: mercury(II) adsorbed or bound on dry particles and mercury(0) that

can be adsorbed on the surface of biomonitors (and/or collectors) and/or oxidized and then bound on the surface. Although there are many attempts to determine the Hg species in air, a number of techniques are subjected to artefacts, mainly due to sampling procedures. E.g. collecting gaseous mercury in vessels of glass or teflon or by trapping on amalgam can not describe the uptake in plant tissues. Estimating dry deposition by using non-biological methods will not necessarily give accurate results. In order to have harmonized procedures that will produce comparable results it is necessary to accept a common protocol that represent real and undisturbed situation. The cost-effectiveness of methods proposed should be taken into consideration as well.

The dominant form of mercury in the atmosphere is  $Hg^0$  which can be taken up by vegetation through stomata. We do not know if it is transformed to a water soluble form such as  $Hg^{2+}$  or attached directly to particles or to cell walls. AMADO FILHO ET AL. (2002) studied the moss *Tillandsia usneoides* in a contaminated environment using analytical scanning electron microscopy. They found no mercury in the mesophyll or vascular system cells and only small amounts in epidermal cells. Mercury was mostly absorbed by scales, stems and leaf surfaces. To some extent it was also attached to atmospheric particles deposited on the plant surfaces. In a laboratory experiment (LODENIUS ET AL., 2003) mercury was strongly attached to the tissues of both moss and grass with almost no leaching or evaporation in the temperature range +10 °C to +60 °C.

Absorption is most probably different for different parts of complex ecosystems in-

cluding leaves, needles, bark, mushrooms, mosses, soil etc. The biological structure and physiology include different surfaces and cell structures and different physiological processes. Certainly this biological absorption is different from deposition measured by technical collectors. Perhaps it is not possible to get a reliable estimate of dry deposition to a terrestrial ecosystem by using technical collectors. Mercury is strongly bound to plant material but we do not know the binding sites of mercury: surface of the plants or inside the plant cells. Nor do we know the biochemical binding mechanisms. For these reasons it would be very important to carry out a critical comparison between data obtained by different techniques. This comparison should include technical collectors and key components of terrestrial ecosystems. We also recommend that investigations should be carried out by using enriched stable isotope under experimental conditions as close to natural environment as possible. This may explain mechanisms of uptake and distribution of mercury in biomonitors.

## CONCLUSIONS

Natural ecosystems are complex including many different species with different surfaces. Depending on factors such as temperature, light and ambient Hg concentrations the plants may take up or release mercury. Weather conditions greatly influences the routes for mercury: dry or wet deposition, absorption, leaching or evaporation. Consequently there are considerable temporal fluctuations in mercury fluxes. The binding of mercury to plant surfaces and transport processes of mercury within the plants are poorly known. Atmospheric mercury and dry deposition of mercury may be monitored using biological or technical methods giving results that, due to a complex biogeochemical behaviour of mercury, are not completely comparable. In routine monitoring of mercury or when interpreting results concerning concentrations or fluxes we should be aware of the factors influencing the results. It is recommended, therefore, that well structured studies are implemented in order to harmonize procedures for the determination of dry deposition of mercury.

## REFERENCES

- AMADO FILHO, G. M., ANDRADE, L. R., FARINA, M. & MALM, O. (2002): Hg localisation in *Tillandsia usneoides* L. (Bromeliaceae), an atmospheric biomonitor; *Atmos Environ.* Vol. 36, pp. 881-887.
- FERRARA, R., MASERTI, B. E., ANDERSSON, M., EDNER, H., RAGNARSON, P. & SVANBERG, S. (1997): Mercury degassing rate from mineralized areas in the mediterranean basin; *Water Air Soil Pollut.* Vol. 93, pp. 59-66.
- HANSON, P. J., LINDBERG, S. E., TABBERER, T. A., OWENS, J. G. & KIM, K. H. (1995): Foliar exchange of mercury vapor: Evidence for a compensation point; *Water Air Soil Pollut.* Vol. 80, pp. 373-382.
- IVERFELDT, L. (1991): Mercury in forest canopy throughfall water and its relation to atmospheric deposition; *Water Air Soil Pollut.* Vol. 56, pp.553-564.
- KOLKA, R. K., NATER, E. A., GRIGAL, D. F. & VERRY, E. S. (1999): Atmospheric inputs of mercury and organic carbon into a forested upland bog watershed; *Water Air Soil Pollut.*, Vol. 113, pp. 273-294.
- KONDOH, M., FUKUDA, M., AZUMA, M., OOSHIMA, H. & KATO, J. (1998) Removal of mercury ion by the moss *Pohlia flexuosa*; *J. Ferment. Bioengin.* Vol. 86, pp.197-201.
- LINDBERG, S. E., DONG, W. & MEYERS, T. (2002): Transpiration of gaseous mercury through vegetation in a subtropical wetland in Florida; *Atmos. Environ.* Vol. 36, pp. 5207-5219.
- LINDBERG, S. E., HANSON, P. J., MEYERS, T. P. & KIM, K. H. (1998): Air/surface exchange of mercury vapor over forests - The need for a reassessment of continental biogenic emissions; *Atmos. Environ.* Vol. 32, pp. 895-908.
- LODENIUS, M. (1998): Dry and wet deposition of mercury near a chlor-alkali plant; *Sci. Tot. Environ.* Vol. 213, pp.53-56.
- LODENIUS, M., TULISALO, E. & SOLTAPOUR-GARGARI, A. (2003): Exchange of mercury between atmosphere and vegetation under contaminated conditions; *Sci. Total Environ.*, Vol. 304, pp. 169-174.
- REA, A. W., LINDBERG, S. E. & KEELER, G. J. (2000): Assessment of dry deposition and foliar leaching of mercury and selected trace elements based on washed foliar and surrogate surfaces; *Environ. Sci. Technol.* Vol. 34, pp. 2418-2425.
- REA, A. W., LINDBERG, S. E. & KEELER, G. J. (2001): Dry deposition and foliar leaching of mercury and selected trace elements in deciduous forest throughfall; *Atmos. Environ.* Vol. 35, pp. 3453-3462.
- TODD, L. L., TAYLOR, G. E. JR., GUSTIN, M. S. & FERNANDEZ, G. C. I. (1998a): Mercury and Plants in Contaminated Soils: I. Uptake, Partitioning, and Emission to the Atmosphere; *Environ. Toxicol. Chem.* Vol. 17, pp. 2063-2071.
- TODD, L. L., TAYLOR, G. E. JR., GUSTIN, M. S. & FERNANDEZ, G. C. I. (1998b): Mercury and plants in contaminated soils: 2. Environmental and Physiological factors governing mercury flux to the atmosphere; *Environ. Toxicol. Chem.* Vol. 17, pp. 2072-2079.

# Modeling Mercury Transformation in Power Plant Plumes

KRISTEN LOHMAN<sup>1</sup>, CHRISTIAN SEIGNEUR<sup>1</sup> & JOHN JANSEN<sup>2</sup>

<sup>1</sup>Atmospheric & Environmental Research, Inc., San Ramon, CA, USA; E-mail: lohman@aer.com

<sup>2</sup>Southern Company, Birmingham, AL, USA

**Abstract:** A reactive plume model, ROME, is used to simulate the evolution of mercury concentrations and speciation in power plant plumes. Plume simulations are compared with data collected at ground-level downwind of the power plants (EDGERTON ET AL., 2003). This comparison suggests that the observed reduction of Hg(II) to Hg(0) in the power plant plumes is not reproduced by our current understanding of mercury chemistry.

**Key words:** mercury speciation, power plants, atmospheric chemistry, plume model

## INTRODUCTION

Several recent experimental studies provide circumstantial and direct evidence of reduction of Hg(II) to Hg(0) in power plant plumes. First, the Mercury Deposition Network (MDN) data along a west-to-east transect from Minnesota to Pennsylvania show no significant spatial gradient in mercury annual wet deposition although the Ohio Valley includes several large mercury emission sources located, under prevailing wind conditions, upwind of Pennsylvania (SEIGNEUR ET AL., 2003). Model simulations conducted with lower Hg(II)/Hg(0) ratios for power plant emissions showed improved model performance when compared to MDN data (VIJAYARAGHAVAN ET AL., 2004). Second, experiments conducted with a Teflon-lined dispersion chamber where the exhaust flue gases from a coal-fired power plant stack are sampled, diluted and analyzed, showed a lower Hg(II)/Hg(0) ratio in the chamber than in the stack (Laudal, 2001). Third, aircraft measurement campaigns performed near

the Bowen plant in Georgia and the Pleasant Prairie plant in Wisconsin indicate that some conversion of Hg(II) to Hg(0) takes place in power plant plumes. Finally, ambient sampling of Hg species (Hg(II), Hg(0), and Hg(p)), NO<sub>x</sub> and SO<sub>2</sub> was conducted with continuous monitors downwind of coal-fired power plants in the Atlanta region (EDGERTON ET AL., 2003). The SO<sub>2</sub>/NO<sub>x</sub> ratio was used as a signature of individual power plants assuming that there is little oxidation and deposition of SO<sub>2</sub> and NO<sub>x</sub> between the stacks and the sampling site. Then, the corresponding speciated mercury measurements were compared with the estimated mercury speciated emissions. The results from that study suggest that the Hg(II)/Hg<sub>T</sub> ratio (where Hg<sub>T</sub> is the sum of Hg(0), Hg(II) and Hg(p)) downwind from several power plants is lower than the Hg(II)/Hg<sub>T</sub> ratio estimated for the stack emissions while Hg<sub>T</sub> does not vary significantly between the two locations. We investigate here whether our current understanding of the atmospheric chemistry of mercury can explain the changes in

Hg(II)/Hg<sub>T</sub> speciation observed by EDGERTON ET AL. (2003). To that end, we simulate the evolution of the Hg(II)/Hg<sub>T</sub> ratio from the stack to the monitoring site using a reactive plume model and compare the results with the observations.

## DESCRIPTION OF THE REACTIVE PLUME MODEL

The Reactive & Optics Model of Emissions (ROME) is a reactive plume model that includes state-of-the-science formulations of plume rise and dispersion, atmospheric transformations, and wet and dry deposition processes (SEIGNEUR ET AL., 1997). Plume rise is calculated according to the initial momentum and buoyancy of the stack gases. Plume transport is simulated in a Lagrangian framework according to the mean wind speed and direction. Plume dispersion in the crosswind directions can be simulated using several options; here, we used the option of selecting user-input values of the horizontal and vertical coefficients because the measured concentrations of SO<sub>2</sub> and NO<sub>x</sub> could be used to characterize plume dilution. Chemical transformations include gas-phase reactions of VOC, NO<sub>x</sub> and SO<sub>2</sub> simulated with the Carbon-Bond Mechanism (CBM-IV), aqueous-phase oxidation of SO<sub>2</sub> and NO<sub>x</sub> simulated with 30 reactions and 31 equilibria, and gas-phase and aqueous-phase reactions of mercury (Hg) species. Mercury transformations are simulated with the AER mechanism (SEIGNEUR ET AL., 2004).

## PLUME MODEL SIMULATIONS

Plume simulations were conducted for 3 plume episodes sampled by EDGERTON ET AL. (2003). Power plant emissions were obtained from Southern Company. The mercury emission rates and speciation were estimated from the Information Collection Request (ICR) database. Meteorological data collected at the site were used to calculate the ROME trajectories (EDGERTON ET AL., 2003).

## COMPARISON OF MODEL RESULTS WITH OBSERVATIONS

We compare in Table 1 the Hg(II)/Hg<sub>T</sub> ratios estimated for the power plant emissions, observed at the downwind ambient receptor site, and simulated with ROME. As discussed by EDGERTON ET AL. (2003), the Hg(II)/Hg ratios measured at the ambient site are much lower than those estimated for the emissions. The ROME simulations show Hg(II)/Hg<sub>T</sub> ratios that are slightly lower than those of the emissions, due to some reduction of Hg(II) to Hg(0) and some dry deposition of Hg(II). However, these simulated ratios are very different from the observed ratios. As a sensitivity, increasing the dry deposition velocity of Hg(II) in ROME by an order of magnitude leads to lower simulated Hg(II)/Hg<sub>T</sub> ratios because of faster depletion of plume Hg(II). Nevertheless, the simulated Hg(II)/Hg<sub>T</sub> ratios are still larger than the observed ratios.

These results suggest that some reaction reducing Hg(II) to Hg(0) occurs in power plant plumes but is not simulated in the state-of-the-science mechanism of ROME. YUSUF ET AL. (2003) reported the possible heterogeneous reduction of HgO(p) by SO<sub>2</sub>. Most Hg(II) emitted from power plants is believed to be HgCl<sub>2</sub> rather than HgO. However, the possibility of the reduction of HgCl<sub>2</sub> adsorbed on particulate matter cannot be ruled out as a pathway for Hg(II) reduction in power plant plumes. Laboratory studies should be conducted to investigate such reaction pathways.

## CONCLUSIONS

A comparison of plume model simulations with ground-level measurements of speciated Hg downwind of power plant plumes sug-

gests that the Hg(II)/Hg(0) ratio decreases from the stack to the downwind receptor. Sensitivity studies indicate that dry deposition of Hg(II) alone cannot account for this change in Hg speciation. Consequently, we propose the hypothesis that some reaction that reduces Hg(II) to Hg(0) occurs in power plant plumes and that it is not currently treated in atmospheric mercury models. Furthermore, these results suggest that current models of atmospheric mercury deposition may overestimate the local deposition of mercury emissions from power plants.

## Acknowledgements

This work was supported by Southern Company under a contract with Atmospheric Research & Analysis, Inc. and subcontract to Atmospheric & Environmental Research, Inc.

## REFERENCES

- EDGERTON, E., JANSEN, J & HARTSELL, B. (2003): Field observations of mercury at a rural/urban pair of sites near Atlanta, Georgia, USA; *International Conference on Air Quality IV*, 22-24 September, Arlington, VA, USA.
- LAUDAL, D. (2001): Final Report for JV Task 24 – Investigation of the Fate of Mercury in a Coal Combustion Plume Using a Static Plume Dilution Chamber, Cooperative Agreement No. DE-FC26-98FT40321; UND Fund 4727.
- SEIGNEUR, C., WU, X. A., CONSTANTINOU, E., GILLESPIE, P., BERGSTROM, R. W., SYKES, I., VENKATRAM, A. & KARAMCHANDANI, P. (1997): Formulation of a second-generation reactive plume & visibility model; *J. Air Waste Manage. Assoc.*, Vol. 47, pp. 176-184.
- SEIGNEUR, C., KARAMCHANDANI, P., VIJAYARAGHAVAN, K., LOHMAN, K. & YELLURU, G. (2003): *Scoping Study for Mercury Deposition in the Upper Midwest*, www.ladco.org.
- SEIGNEUR, C., VIJAYARAGHAVAN, K., LOHMAN, K., KARAMCHANDANI, P. & SCOTT, C. (2004): Global source attribution for mercury deposition in the United States; *Environ. Sci. Technol.*, Vol. 38, pp. 555-569.
- VIJAYARAGHAVAN, K., SEIGNEUR, C., LOHMAN, K., KARAMCHANDANI, P., LEVIN, L. & JANSEN, J. (2004): Modeling the impact of mercury speciation in power plant plumes on mercury deposition over the eastern U.S.; *7<sup>th</sup> Electric Utilities Environmental Conference*, 19-22 January, Tucson, AZ, USA.
- YUSUF, H., LAHOUTIFARD, N., MAUNDER, K. & SCOTT, S. (2003): *Homogeneous and heterogeneous reactions of atmospheric mercury (II) with sulfur (IV)*, 12<sup>th</sup> International Conference on Heavy Metals in the Environment, 26-30 May, Grenoble, France.

**Table 1.** Comparison of observed and simulated Hg(II)/Hg<sub>T</sub> ratios<sup>a</sup>.

Plume event	Power plant	Emissions <sup>b</sup> Hg(II)/Hg <sub>T</sub>	Downwind plume Hg(II)/Hg <sub>T</sub> <sup>c</sup>		
			Observed	Simulated	Simulated with dry deposition x 10
20 July 2001	Bowen	0.59	0.06	0.59	0.48
29 December 2001	Hammond	0.44	0.13	0.40	0.18
13 December 2001	Wansley	0.55	0.07	0.53	0.40

(a)  $Hg_T = Hg(0) + Hg(II) + Hg(p)$

(b) estimated from the Information Collection Request (ICR) database

(c) concentrations above the ambient background

## Transformation and distribution of mercury species in the atmosphere

JULIA Y. LU<sup>1</sup>, JAMES J. LU<sup>1</sup>, D. CONRAD GRÉGOIRE<sup>2</sup>

<sup>1</sup>Department of Chemistry and Biology, Ryerson University, 350 Victoria Street, Toronto, Ontario, M5B 2K3 Canada, Email: julialu@Ryerson.ca

<sup>2</sup>Analytical Chemistry Research Laboratory, Geological Survey of Canada, 601 Both Street, Ottawa, K1A 0E8 Canada

**Abstract:** Mercury in the atmosphere can be either in the gas phase or associated with particulate matter. In each phase, mercury can be present in elemental or oxidized form. Oxidized mercury, mainly as Hg(II) in the atmosphere, can combine with various anions present in the atmosphere. Our studies of mercury speciation in atmospheric aerosol samples reveal that: (1) the oxidation of atmospheric gaseous elemental mercury (GEM) in the Arctic each Spring leads to the formation of (mainly) water soluble mercury species; (2) mercury species associated with airborne particulate matter appear to be a mixture of elemental and soluble mercury species and the distribution of these species in the particulate phase varies with location; (3) mercury species associated with suspended particles in rainwater are mainly present as non-soluble forms. This study identified a new chemical transformation pathway of mercury in the atmosphere.

**Key words:** Mercury, Mercury species, Atmosphere, Particulates, chemical transformation

### INTRODUCTION

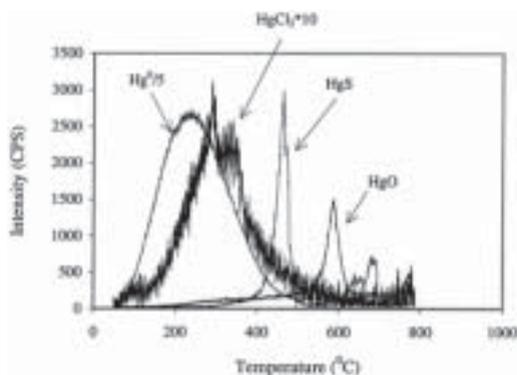
The atmosphere receives more than 90 % of its mercury in the form of emissions<sup>[1, 2]</sup> and thus becomes the primary source of mercury input to water bodies and land. Mercury in the atmosphere can be divided into gaseous and particulate phase mercury. In each phase, mercury can be sub-divided into elemental and oxidized forms. Oxidized mercury can be in different forms of inorganic and/or organic species. Recent studies have uncovered evidence supporting mercury transformation in the atmosphere<sup>[3, 4]</sup> and highlighted the important role of mercury species in determining the movement of this element in the environment<sup>[3-5]</sup>, its bioavailability and toxicity<sup>[6]</sup>. In this study, mercury species as-

sociated with atmospheric particulate matter, collected using the technique developed by LU ET AL.<sup>[7]</sup>, from industrial (near Toronto, Ontario and Rouyn-Noranda, Quebec, Canada), urban (downtown Toronto, Canada) and remote (Arctic) sites (Alert, Canada) were analyzed using a methodology that combines thermal release for separation of mercury species with ICP-MS for mercury detection<sup>[8]</sup>.

### RESULTS AND DISCUSSION

The thermograms obtained for the baked fly-ash matrices spiked with mercury compounds are shown in Figure 1. The temperature of the furnace was programmed at a lin-

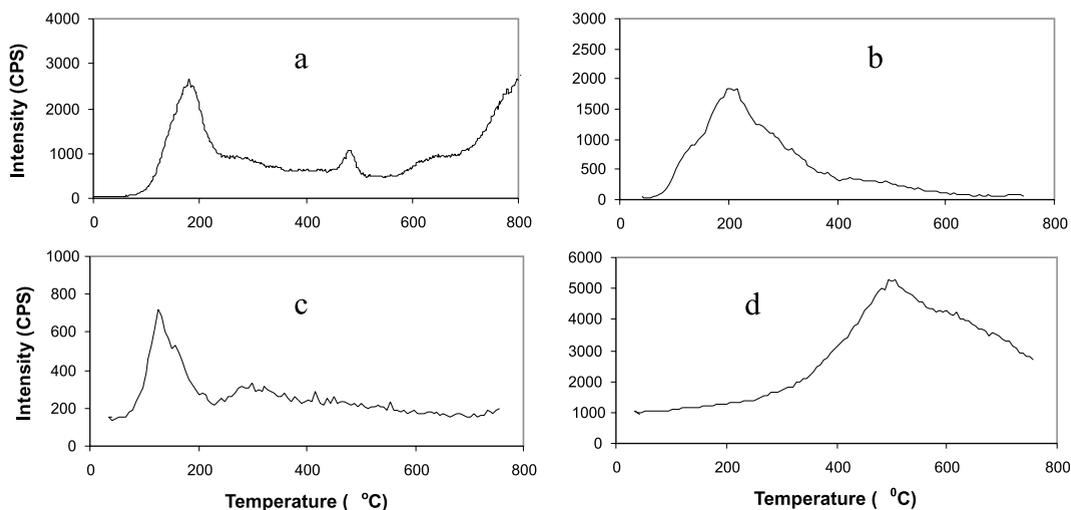
ear increase rate of  $50\text{ }^{\circ}\text{C min}^{-1}$ . As shown in Figure 1, the mercury baseline was elevated in high temperature regions, which is caused by thermal desorption of mercury from the transport line leading from the furnace downstream to the argon plasma. It can be seen that, at this heating rate, the temperature corresponding to the emergence of Hg peaks varied significantly for different mercury



**Figure 1.** Thermograms of mercury compounds in coal fly-ash matrix

compounds, indicating the validity of the method for speciating mercury. It was previously demonstrated that different species of Hg from solid samples is released as  $\text{Hg}^0$  during the heating process<sup>[9]</sup>. Therefore different mercury species contained in the fly-ash matrices will be converted to  $\text{Hg}^0$  at different temperatures.

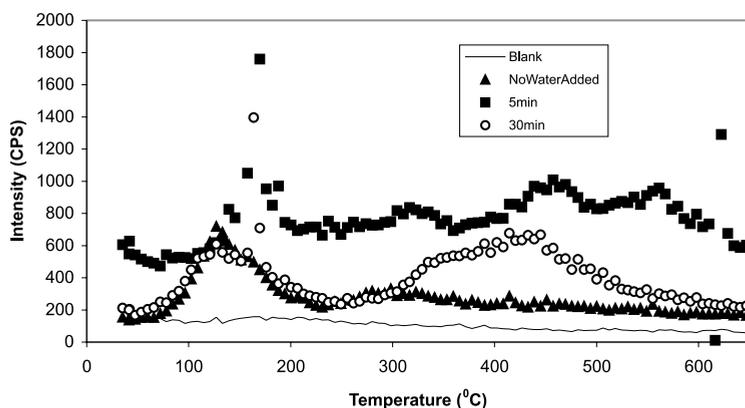
Figure 2 contains thermograms obtained during the analysis of atmospheric particulate matter. Comparison of these thermograms with those in Figure 1 reveals that elemental mercury and  $\text{HgCl}_2$  are present in all the samples of airborne particulate matter but the distribution of these two mercury species varies with sampling location (see Figure 1 (a), (b), and (c)). The appearance of the peaks at temperatures higher than  $400\text{ }^{\circ}\text{C}$  (Figure 1 (a)) suggests the presence of HgS and HgO in the particulate matter collected from an industrial area. The mer-



**Figure 2.** Analysis of mercury species associated with (a) airborne particulate matter from an industrial area near Toronto, Canada; (b) airborne particulate matter from the Arctic at Alert, Canada; (c) airborne particulate matter from downtown Toronto; (d) suspended particles in rain water from Rouyn-Noranda, Canada

cury species associated with suspended particle in rainwater, as shown in Figure 1 (d), are however, different from those present in the samples of airborne particulate mater and are a mixture of HgO and HgS. The above-presented results suggest that rainwater/moisture may have led to the transformation of mercury species that are associated with airborne particulate matter. Laboratory experiments were carried out to either confirm or rule out the hypothesis of chemical trans-

formation. A batch of samples of airborne particulate matter was collected in downtown Toronto. Before the analysis, snowmelt was added to two of the samples and the samples were let to stand for 5 and 30 minutes, respectively. The results shown in Figure 3 clearly indicate the effect of water/moisture on mercury species that are associated with airborne particulate matter and the occurrence of the chemical transformation of mercury species.



**Figure 3.** Effect of rain on mercury species associated with airborne particles

## CONCLUSIONS

This research demonstrates that chemical speciation can be used as a powerful tool to study source of emission and transformation of mercury in the atmosphere. It also demonstrates the power of the thermal desorption coupled with ICP mass spectrometry as a viable approach for the solid state speciation of inorganic mercury species in a variety of environmental samples. Further, coupling of the thermal desorption technique with the high precision measurement of mercury isotopes by multi-collector inductively

coupled plasma mass spectrometry may provide clues to the various sources of mercury species present in samples. This avenue of research is now being actively pursued in our laboratories.

## Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC), the Metals in the Environment Research Network (MITE-RN), the Premier's Research Excellence Awards Program, and Ryerson University.

## REFERENCES

- [1] LAUDAL, D. ET AL. (1999): In *Proceedings of a Special Conference on Mercury in the Environment*; Minneapolis, Minnesota, USA, September 15-17, 1999; p. 340.
- [2] FRIEDLI, H. R., RADKE, L. F., LU, J. Y., BANIC, C. M., LEAITCH, W. R., MACPHERSON, J. I. (2003): Mercury emissions from burning of biomass from temperate North American forests: laboratory and airborne measurements; *Atmospheric Environment* 37, pp. 253–267.
- [3] LU, J. Y., SCHROEDER, W. H., BARRIE, L. A., STEFFEN, A., WELCH, E. H., MARTIN, K., LOCKHART, W. L., HUNT, R. V., BOILA, G., RICHTER, A. (2001): Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry; *Geophysical Research Letter* 28, pp. 3219-3222.
- [4] LINDBERG, S. E., BROOKS, S., LIN, C. J., SCOTT, K. J., LANDIS, M. S., STEVENS, R. K., GOODSITE, M., RICHTER, A. (2002): Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise; *Environmental Science and Technology* 36, pp. 1245-1256.
- [5] KEELER, G., GLINSORN, G., PIRRONE, N. (1995): Particulate mercury in the atmosphere: its significance, transport, transformation and sources; *Water Air and Soil Pollution* 80, pp. 159-168.
- [6] MAHAFFEY K. R. (1999): Methylmercury: A new look at the risks; *Public Health Report* 114, pp. 397- 415.
- [7] LU, J. Y., SCHROEDER, W. H., BERG, T., MUNTHE, J., SCHNEEBERGER, D., SCHAEDLICH, F. (1998): A device for sampling and determination of total particulate mercury in ambient air; *Analytical Chemistry* 70, pp. 2403-2408
- [8] FENG, X., LU, J. Y., GREGOIRE, D. C., HAO, Y., BANIC, C., SCHROEDER W. H. (2004): Thermal release coupled with ICP-MS detection for analysis of mercury species associated with airborne particulate matter – method development; *Analytical and Bioanalytical Chemistry*, submitted (MS#: ABC-00219-2004).
- [9] BIESTER, H., SCHOLZ, C. (1997): Determination of mercury binding forms in contaminated soils: Mercury pyrolysis versus sequential extractions; *Environmental Science Technology* 31, pp. 233-239.

## Source Receptor Relationships for Speciated Mercury in the Urban Environment

MARY M. LYNAM<sup>1</sup> & GERALD J. KEELER<sup>1</sup>

<sup>1</sup>The University of Michigan Air Quality Laboratory, Ann Arbor, MI 48109-2029, USA

**Abstract:** The need for speciated mercury measurements at receptor locations has been articulated by many as an obligatory requirement to adequately describe the biogeochemical cycling of mercury in the environment as well as ensure continued success in advancing the state of the science for mercury research in the 21st century

The objective of this research was to better understand the biogeochemical cycling of mercury in the urban environment by utilization of state of the art sampling and analytical techniques. This was achieved by automated speciated mercury monitoring with the Tekran 1130/1135 system to obtain higher resolution data thus providing potential for a greater understanding of the atmospheric dynamics of mercury.

Mercury speciation measurements were made from 1999-2002 at Dexter, Ann Arbor and Detroit, MI representing rural, suburban and urban environments, respectively. Ancillary measurements including meteorological variables as well as chemical parameters were also measured at these sites.

The results reveal a concentration gradient in the observed values for elemental and reactive gaseous mercury on going from the rural to the urban sites. Ranges for elemental mercury were 1.03-4.09 ng/m<sup>3</sup> (Dexter), 1.08-11.94 ng/m<sup>3</sup> (Ann Arbor) and 1.17-40.33 ng/m<sup>3</sup> (Detroit). Ranges for reactive gaseous mercury were 0.18-37.51 pg/m<sup>3</sup> (Dexter), 0.14-308.95 pg/m<sup>3</sup> (Ann Arbor), and 0.62-281.32 pg/m<sup>3</sup> (Detroit).

Principal Component Analysis (PCA), was carried out for the speciated mercury data collected in Dexter and Detroit. Analysis of the data from the rural location shows that elemental mercury and reactive gaseous mercury are located on different factors suggesting that these species are not highly correlated at this site. The Detroit data show some common factors for both elemental and reactive gaseous mercury. Elemental mercury was strongly associated with CO and NO suggesting a combustion factor. Reactive gaseous mercury was associated with ozone suggesting a photochemistry factor, primary emissions from coal combustion sources, and particulate phase mercury independent of elemental mercury.

The results of this analysis reveal that mercury species in urban environments can result from a complex mix of factors including primary emissions from combustions sources, photochemistry related to local automobile sources and regional photochemistry.

**Key words:** Speciated mercury, urban monitoring, source receptor relationships

# Atmosphere - Soil Exchange of Mercury in the Negro River Basin, Amazon: Influences of the Vegetal Covering

GABRIELLA MAGARELLI AND ANNE HÉLÈNE FOSTIER

Institute of Chemistry, State University of Campinas, P.O. Box 6154, 13084-971, Campinas, SP, Brazil; E-mail: gmagarelli@iqm.uicamp.br

**Abstract:** An investigation of air/surface exchange of mercury, performed at the Negro River Basin, (Amazon region) in January 2003, is presented. Three sites were investigated: a flooding primary forest, a non-flooding primary forest and a deforested area. The fluxes were estimated by using a dynamic flux chamber with sampling times varying between 6 and 12 h. At the two forest sites (flooding and non-flooding), low mercury fluxes, which varied in a diurnal cycle, were observed with positive values during the day (maximum: 3 pmol m<sup>-2</sup> h<sup>-1</sup>) and negative values at night (minimum: -1 pmol m<sup>-2</sup> h<sup>-1</sup>). However at the deforested site, the mercury fluxes were higher and always positive throughout the diurnal cycle, with values reaching 26 pmol m<sup>-2</sup> h<sup>-1</sup> during the day and 17 pmol m<sup>-2</sup> h<sup>-1</sup> at night. Our results showed that deforestation could be responsible for significantly increasing soil Hg emissions, mainly because of the high soil temperatures reached in deforested sites.

**Key words:** Mercury fluxes, atmosphere-soil exchange, flux chamber.

## INTRODUCTION

An investigation of the air/surface exchange of mercury is of particular interest in studying the global biogeochemical cycling of mercury<sup>[1]</sup>. It has been estimated that approximately 95 % of the 200,000 tons of Hg mobilized since 1890 are currently accumulated in superficial deposits<sup>[2]</sup>. The re-emission of a portion of this supply would be equivalent to the total of the anthropogenic emissions of the United States<sup>[3]</sup>. The forests cover approximately 4x10<sup>9</sup> ha of the terrestrial surface, and the destination of the stored Hg, whether on the ground or in the vegetation, is still widely unknown. Considering that the Brazilian Amazon is covered by 0.4x10<sup>9</sup> ha of forest<sup>[4]</sup>, 10 % of the area covered by forests on the planet, the importance of studying the transfer processes of Hg in this eco-

system becomes important. The Hg emissions from contaminated and background soils have already been reported<sup>[5]</sup>. Many factors can influence Hg emissions from soil measured *in situ*, e.g., soil and air temperature, soil Hg concentration, solar radiation, vegetal covering, soil moisture, etc.

## RESULTS AND DISCUSSION

Mercury fluxes in the interface soil-atmosphere were measured at three sites located along the Negro river basin (Amazon): a flooding primary forest (Igapó) (ARA-1), a non-flooding area covered by primary forest (CARV-1) and an open field site (CARV-2) resulting from the deforestation of part of CARV-1 and where "slash and burn" was practiced for local agriculture purposes. The

fluxes of Total Gaseous Mercury (TGM) were estimated by using a rectangular acrylic dynamic flux chamber (DFC) (20 x 20 x 60 cm) with nine holes (2.5 cm i.d.) at the inlet face and one outlet hole connected to a Teflon tube. The outlet tube was connected to a T-junction going to a pump for flushing (3.2 L min<sup>-1</sup>) and the other tube leading to the sampling line (0.3 L min<sup>-1</sup>). A flow regulator was used to monitor the airflow rate through the chamber. Mercury vapor concentrations at both inlet and outlet of the chamber were measured by using gold trap amalgamation and subsequent analysis with a Brooks Rand CVAFS instrument. Sampling time varied between 6 and 12 h. Mercury fluxes ( $F$ : pmol Hg m<sup>-2</sup> h<sup>-1</sup>) were calculated by the equation  $F = Q(C_o - C_i)/A$ , where  $C_o$  and  $C_i$  are the Hg concentrations at the outlet and inlet of the DFC (pmol Hg m<sup>-3</sup> h<sup>-1</sup>), respectively, and  $A$  (m<sup>2</sup>) is the soil area covered by the DFC. The meteorological parameters were measured in parallel to the measurement of Hg fluxes, using a compact meteorological station "Total Solus Weather System" (Texas Instruments). In order to check measurement precision, two DFC were operated simultaneously at ARA 1. DFC blanks were also measured by determining Hg concentration in the outlet air when an acrylic plate was placed on the bottom of the chamber.

At the two forest sites (CARV-1 and ARA-1), low mercury fluxes were observed with positive values during the day (maximum: 3 pmol m<sup>-2</sup> h<sup>-1</sup>), indicating a slight evasion of gaseous Hg from the soil to the atmosphere. At night, null or negative fluxes were observed (minimum: -2.5 pmol m<sup>-2</sup> h<sup>-1</sup>). These results agree well with data reported in the literature, also presenting fluxes with similar diurnal variance<sup>[7]</sup>. In the flooding forest, the concentrations of atmospheric Hg appeared to be correlated with the Hg fluxes, in contrast to the non-flooding forest (Figure 1). On the other hand, Hg fluxes at the open field site were clearly higher and always positive along the diurnal cycle, with values reaching 26 pmol m<sup>-2</sup>h<sup>-1</sup> during the day and 17 pmol m<sup>-2</sup> h<sup>-1</sup> at night. At this site, no correlation was observed between the Hg fluxes and atmospheric Hg concentrations (Figure 2).

When considering the three sites studied, the Hg fluxes were positively correlated with solar radiation, air and soil temperature and presented negative correlations with air humidity. For the forest sites, this trend was expected with the highest fluxes measured during the day and the lowest at night. Figure 3 shows the profile of the meteorological parameters in the areas studied during the

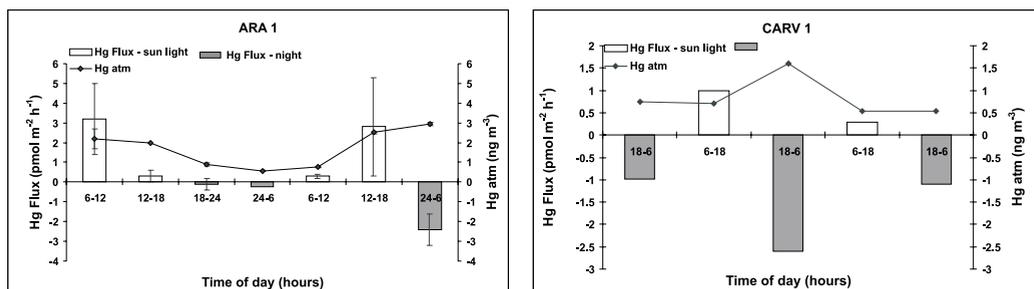
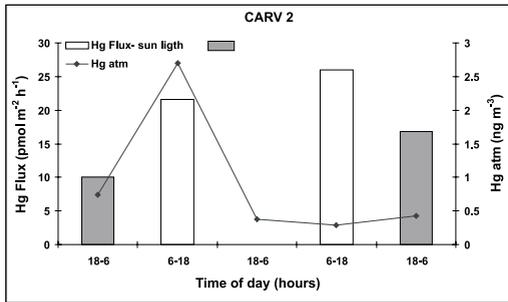


Figure 1. Hg fluxes and concentrations of atmospheric Hg at the forest sites.



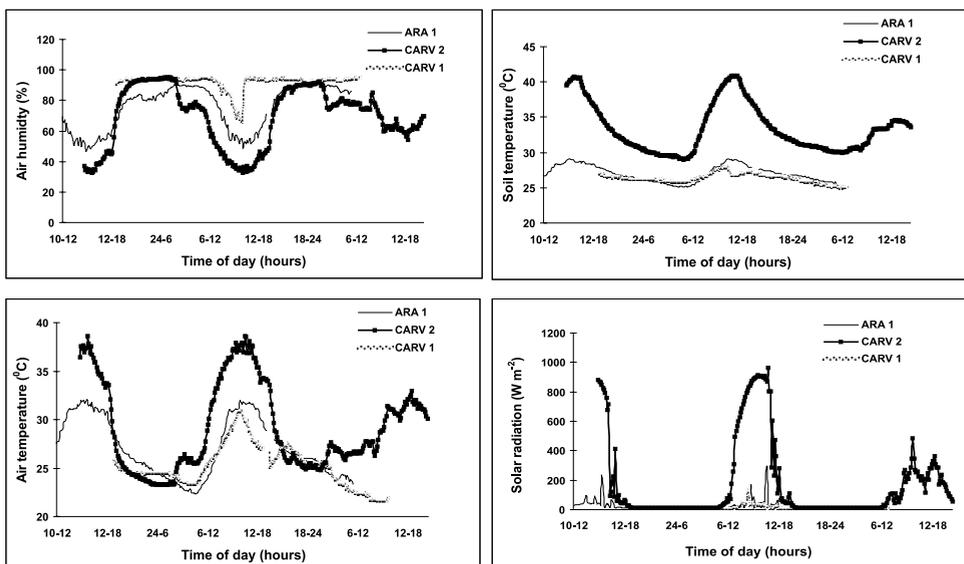
**Figure 2.** Hg fluxes and concentrations of atmospheric Hg at the deforested site (CARV-2).

diurnal cycle. In the deforested area the intensities of solar radiation, air temperature and mainly soil temperature were higher than in the forest areas, which can be attributed to the lack of vegetal covering. All of the four factors studied have already been pointed out as influences on soil Hg emission<sup>[5, 6]</sup>. Nevertheless, in our study the soil temperature was the only factor, which differed significantly at night between the forest and deforested sites, pointing out its

strong contribution in to higher Hg emissions observed at night in the deforested area.

According to literature data, a high soil temperature contributes to increasing vapor pressure for the different mercury compounds, especially those species that are highly volatile, such Hg<sup>0</sup> and (CH<sub>3</sub>)<sub>2</sub>Hg. This would also explain the diurnal and seasonal variation of the Hg soil emissions<sup>[5, 8]</sup>. Although high soil temperatures should also strongly promote the Hg emissions at the deforested site during the day, photoinduced formation mechanisms of Hg<sup>0</sup> could also significantly enhance Hg emissions<sup>[5, 6]</sup>.

Some physical and chemical parameters were also determined in superficial soil (0-10 cm) (Table 1). The higher Hg concentration was found at ARA-1 (159 ng g<sup>-1</sup>), indicating that total Hg concentration did not directly influence Hg emission from soil at the sites studied. Also the granulometric



**Figure 3.** Meteorological parameter profiles in the areas studied during the diurnal cycle.

composition did not show any direct correlation with Hg emission. On the other hand, the highest organic matter concentration was found at CARV-2 (27 %), where the highest Hg emissions were also observed. Although these parameters could have an effect on the Hg emission, some other parameters, such as Fe and Al (oxy) hydroxides, C/N ratio, soil humidity and porosity, have also been pointed out as important factors and so have to be considered in our study.

## CONCLUSIONS

The Hg fluxes at forest sites were low but coherent with those reported for background soils. However at the open field site, the mercury fluxes were significantly higher,

showing that deforestation could be responsible for significantly increasing Hg soil emissions, mainly because of the high soil temperatures reached at the deforested sites. Total mercury concentration in the soil did not appear to enhance Hg emissions. Some other physical and chemical soil parameters that could influence the Hg fluxes have to be better investigated in order to better understand the mechanisms, which govern Hg emission in this region. In this way, complementary measurements of Hg fluxes at other sites in the Negro river basin, as well as laboratory experiments, are now being performed.

## Acknowledgements

This work was supported by the CNPq and FAPESP

## REFERENCES

- [1] SCHROEDER, W. H., MUNTHE, J., LINDQVIST, O. (1989): Cycling of Mercury Between Water, Air, And Soil Compartments of the Environment; *Water Air And Soil Pollution* 48(3-4), pp. 337-347.
- [2] Expert Panel on Mercury Atmospheric Processes (1994): Mercury atmospheric processes: a synthesis report; *EPRI/TR-104214*, Tampa, Florida, September 1994.
- [3] PORCELLA, D. B., CHU, P., ALLAN, M. A. (1996): Inventory of North America Hg emissions to the atmosphere; In *Global and regional mercury cycles: sources, fluxes and mass balances* (Baeyens, Ed.), NATO ASI Series.
- [4] INPE (1999): *Monitoramento da floresta amazônica por satélite, 1997-1998*; Instituto Nacional de Pesquisas Espaciais/Ministério da Ciência e Tecnologia. Homepage: <http://www.grid.inpe.br/amz/>.
- [5] ZHANG, H., LINDBERG, S. E. (1999). Processes influencing the emission of mercury from soils: A conceptual model; *Journal of Geophysical Research* 104, D17, pp. 21,889-21,896.
- [6] BAHLMANN, E., EBINGHAUS, R. (2003): Process studies on mercury fluxes over different soils with a Laboratory Flux Measurement System (LFMS); *Journal de Physique IV* 107, pp. 99-102.
- [7] KIM, K. H., LINDBERG, S. E., MEYERS, T. P. (1995): Micrometeorological Measurements of Mercury-Vapor Fluxes over Background Forest Soils in Eastern Tennessee; *Atmospheric Environment* 29(2), pp. 267-282.
- [8] SCHLUTER, K. (2000): Review: evaporation of mercury from soils. An integration and synthesis of current knowledge; *Environmental Geology* 39(3-4), pp. 249-271.

## A Receptor-based Approach to Understanding Sources of Reactive Mercury in the Atmosphere

HELEN MANOLOPOULOS, JAMES SCHAUER<sup>1</sup>, TODD RUDOLPH<sup>2</sup>, MARK OLSON<sup>3</sup>,  
DAVE KRABBENHOFT<sup>3</sup>, JAY TURNER<sup>4</sup> & BRUCE RODGER<sup>5</sup>

<sup>1</sup>University of Wisconsin, 660 N. Park St., 53706, Madison, USA, e-mail: jschauer@engr.wisc.edu

<sup>2</sup>University of Wisconsin, 660 N. Park St., 53706, Madison, USA

<sup>3</sup>U. S. Geological Survey, 8505 Research Way, 53562, Middleton, USA

<sup>4</sup>Washington University, One Brooking Dr., 63130, St. Louis, USA

<sup>5</sup>Wisconsin Department of Natural Resources, 101 S. Webster St., 53707, Madison, USA

**Abstract:** Data on atmospheric mercury species were collected at two remote sites at Devil's Lake State Park and Mt. Horeb, WI, and one heavily industrialized site at East St. Louis, IL, to assess sources of reactive mercury in the atmosphere. Sampling periods varied with location. Monitoring at Devil's Lake has been continuous since April, 2003, and will proceed through 2004 as part of an ongoing study. Short-term monitoring was conducted at Mt. Horeb, located about 65 km from the Devil's Lake site, in June and July, 2003, to provide a regional comparison to Devil's Lake. In addition, sampling was conducted in East St. Louis through November, 2002. Supplementary data on atmospheric gases (SO<sub>2</sub>, NO<sub>x</sub>, O<sub>3</sub>) and meteorological parameters were measured at Devil's Lake. These same measurements, along with semi-continuous hourly fine particle (PM<sub>2.5</sub>) mass, ions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>), and organic and elemental carbon (OC, EC) measurements were obtained at the East St. Louis site.

The most striking aspect of the East St. Louis data set was the exceptionally high levels of all mercury forms, with concentrations of elemental (Hg<sub>0</sub>) and reactive (RGM + PHg) mercury reaching 235 ng m<sup>-3</sup> and 36000 pg m<sup>-3</sup>, respectively. Step-wise multiple regression analysis indicated that OC may influence the gas/particle partitioning of reactive mercury (K<sub>p</sub>,Hg) at East St. Louis (for RGM and PHg < 500 pg m<sup>-3</sup>) relative to other aerosol components such as EC, SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>. The dependence of the K<sub>p</sub>,Hg with aerosol OC varied with wind direction and suggests that different OC sources impact reactive mercury partitioning differently. Organic carbon content explained about 50 % of the variability observed in K<sub>p</sub>,Hg when data from a north-east plume was analyzed. Concentrations at Devil's Lake were generally at background levels with Hg<sub>0</sub> ranging between 1.0 and 2.0 ng m<sup>-3</sup>, while RGM and PHg were typically less than 15 pg m<sup>-3</sup>. Even during high events, concentrations at Devil's Lake never exceeded 10 ng m<sup>-3</sup> for Hg<sub>0</sub> and 150 pg m<sup>-3</sup> for reactive mercury.

Atmospheric mercury species measured simultaneously at Devils Lake and Mt. Horeb revealed remarkably similar concentrations indicating a regional source common to both locations. Furthermore, Hg<sub>0</sub> appeared to be affected by common processes at both sites resulting in similar concentration patterns and trends such as diurnal cycles. Regional concentrations of reactive mercury were generally observed at both sites, but occasional spikes in RGM and SO<sub>2</sub> indicated an additional local source to Devil's Lake. Concurrent increases in Hg<sub>0</sub> with RGM were not evident at Devil's Lake. This suggests that, either the amount of Hg<sub>0</sub> co-emitted with RGM is not enough to increase Hg<sub>0</sub> concentrations above background levels (ng m<sup>-3</sup>), or RGM is formed in the atmosphere following emission from the oxidation of Hg<sub>0</sub> by SO<sub>2</sub> or another oxidant present in the plume.

**Key words:** Atmosphere, reactive mercury, sources

## The Air-Surface Exchange of Gaseous Mercury over a Mixed Sawgrass-Cattail Stand within the Florida Everglades

FRANK MARIK

**Abstract:** Micrometeorological and dynamic flux chamber techniques were used to study the air-surface exchange of vapor-phase mercury over a mixed sawgrass/cattail stand within the Florida Everglades during two measurement periods: February/March 1999 and June 2000. Supporting meteorological and chemical measurements were also conducted to investigate the potential role of other environmental parameters in controlling these fluxes.

The 1999 study results suggest that, on average, vapor-phase mercury was emitted from the ecosystem during the daytime ( $18 \pm 37 \text{ ng m}^{-2} \text{ hr}^{-1}$ ), with deposition to the canopy observed at night ( $-1 \pm 3 \text{ ng m}^{-2} \text{ hr}^{-1}$ ). Similar results were obtained during the 2000 intensive, with emission observed during the daytime ( $16 \pm 35 \text{ ng m}^{-2} \text{ hr}^{-1}$ ) and deposition observed at night ( $-2 \pm 8 \text{ ng m}^{-2} \text{ hr}^{-1}$ ). The measured fluxes followed a diurnal pattern and were positively correlated with ambient temperature, solar radiation and water vapor fluxes and negatively correlated with carbon dioxide fluxes. Limited dynamic flux-chamber measurements suggest that vapor-phase mercury fluxes over open-water within the Everglades also followed a diurnal pattern, with daytime emissions typically less than  $5 \text{ ng m}^{-2} \text{ hr}^{-1}$ . This latter result underscores the important role of vegetation in the air-surface exchange of vapor-phase mercury in this ecosystem.

**Key words:** air-surface exchange, Florida Everglades, biogeochemical cycling

## The Role of Reactive Gaseous Mercury in Air-Ocean Mercury Exchange and to the Global Mercury Cycle

ROBERT MASON, FABIEN LAURIER, NICOLA PIRRONE & IAN HEDGECK

**Abstract:** Atmospheric deposition is the dominant source of Hg to many environments. Recent studies have highlighted the importance of dry deposition of reactive (ionic) gaseous mercury (RGHg) in contributing to Hg deposition in both remote and urban environments. The source of RGHg is both point source inputs to the atmosphere and through elemental mercury (Hg<sup>0</sup>) oxidation in the atmosphere. In the marine boundary layer and in coastal regions, a number of studies have now reported elevated RGHg concentrations, as have studies in polar regions during polar sunrise. For example, our measurements using the Tekran Hg speciation system showed high levels of RGHg in the equatorial Pacific Ocean boundary layer, and a strong diurnal cycle. Further, our estimates for the equatorial Pacific Ocean suggest that dry RGHg deposition can be as important as wet deposition in contributing Hg to the surface ocean. This is not the case, however, for more temperate latitudes. In addition, measurements in the Atlantic Ocean and at CBL, in coastal Maryland, USA show differing amounts of atmospheric RGHg, and provide a better understanding of the factors controlling RGHg formation, and those determining its rate of deposition. In all the remote locations where RGHg has been measured, elevated concentrations of reactive halogen species and the hydroxyl radical, reactants that rapidly oxidize Hg, are found, or estimated to be present. Given this new information of RGHg concentrations over oceanic regions, it is necessary to amend and update estimates of atmospheric deposition to various ecosystems. We have revised our flux estimates based on the recent data, and computer modeling, and use this information to provide an updated estimate of the cycling of Hg at the air-sea interface, and in the upper ocean. Overall, based on the revised model, and in conjunction with recent and historic measurements of Hg in surface and deep ocean waters, we make predictions of how Hg concentrations in the ocean have increased due to man's activities in the last century.

**Key words:** deposition, ocean, reactive gaseous mercury

## Suitableness of the $k_0$ -method of neutron activation analysis for the determination of total Hg concentration in sediments

MARIA ÂNGELA DE B. C. MENEZES<sup>1</sup>, RADOJKO JAČIMOVIĆ<sup>2</sup>, HELENA E. L. PALMIERI<sup>1</sup>,  
LUCIANA V. CRUZ<sup>3</sup> & HERMÍNIO A. NALINI JR.<sup>3</sup>

<sup>1</sup>Nuclear Technology Development Centre/ National Commission for Nuclear Energy  
Belo Horizonte, Minas Gerais, Brazil; E-mail: menezes@cdtn.br

<sup>2</sup>Jožef Stefan Institute, Department of Environmental Sciences, Group for Radiochemistry and  
Radioecology, Ljubljana, Slovenia; E-mail: radojko.jacimovic@ijs.si

<sup>3</sup>Federal University of Ouro Preto, Geological Department, Minas Gerais, Brazil

**Abstract:** The Instrumental Neutron Activation Analysis, specifically the  $k_0$ -standardization method, is a non-destructive and a multi-elemental technique suitable for the determination of trace elements in several matrices, covering a large range of concentration. This work is related to the application of  $k_0$ -method by two groups, Jožef Stefan Institute, Slovenia, and Nuclear Technology Development Centre (CDTN/CNEN), Brazil, on assessing the elemental concentrations in sediment samples focusing on total Hg concentration. The samples were collected from streams that cross the Ecological Station of Tripuí in Minas Gerais, Brazil. The assessment was carried out aiming at evaluating the possible contamination from mineral exploration and correlated activities in the surroundings of this area, including the 'garimpo'- small scale gold mining. The results for total-Hg are higher than the values established and suggest further studies to elucidate if they reflect environmental contamination or natural occurrence. The  $k_0$ -method applied by both Institutes presented good agreement. As the detection limit for Hg in sediment is  $1 \text{ mg}\cdot\text{kg}^{-1}$  (reached by CDTN/CNEN), this method should be applied to screen the samples for other more suitable techniques.

**Key words:** Instrumental Neutron Activation Analysis,  $k_0$ - standardisation, Hg, sediment

### INTRODUCTION

Mercury has been calling attention of all study fields and one reason is "no other metal illustrates the diversity of effects caused by different chemical species than does Hg"<sup>[1]</sup>. This sentence compiles the importance of more knowledge about Hg in all sense. In analytical field, several techniques<sup>[2]</sup> have been employed on low level concentration total - Hg determination and the most frequently applied are: CV AFS (cold vapour atomic fluorescence spectrophotometry), CV

AAS (cold vapour atomic absorption spectrophotometry), ICP-MS (Inductively-Coupled Plasma-Mass Spectrometry), Electrochemical Methods, AAS-Hydride Generator (Atomic Absorption Spectrophotometry With Hydride Generator), XRF (X-Ray Fluorescence), INAA (Instrumental Neutron Activation Analysis). Most of these methods require preliminary digestion of the solid sample and in sequence submitted to one type of a chemical process, except XRF and INAA. It brings about all probable consequences involved when a sample is subjected

to several chemical steps, mainly contamination and loss of material and mercury. The quasi-ideal technique is just the one that does not require any chemical process neither during preparation nor during the analysis with low level elemental concentration determination. The non-destructive INAA<sup>[3, 4]</sup> attends this important characteristic.

This work is related to the application of  $k_0$ -method by two groups – Group for Radiochemistry and Radioecology, Jožef Stefan Institute (JSI) in Ljubljana, Slovenia and Laboratory for Neutron Activation Analysis, Nuclear Technology Development Centre (CDTN/CNEN), Belo Horizonte, Brazil – to verify the suitability on the application of INAA  $k_0$ -standardization on assessing the elemental concentrations in sediment samples focusing on total Hg concentration.

Activation differs from most other methods of chemical analysis in that it is based on the properties of nuclei and not on the behaviour of the outer electrons. It means that it is purely a method of elementary analysis. Basically, the activation process involves exposure to a source of particles or photons of sufficient energy to react with the constituent nuclei. In this work the activation was carried out by neutrons in nuclear reactors. The chemical elements are then identified and assayed after irradiation by measurement – gamma spectrometry - of characteristic radiation emitted from radionuclides formed in the  $(n, \gamma)$  reaction. The INAA, specifically the  $k_0$ -standardization method (INAA- $k_0$ )<sup>[3, 4]</sup> applied in this current work, is a “quasi” absolute technique in which instead of standards, neutron fluence rate monitor are used and the nuclear data which are unknown are replaced by a compound nuclear constants characterising the

nuclides, the so-called  $k_0$  factors. In addition, it also requires good knowledge of spectral parameters of the neutron fluence rate in irradiation channels of the reactor.

The sediment samples<sup>[5]</sup> were collected from streams that cross the Ecological Station of Tripuí, close to Ouro Preto city, located in Minas Gerais, Brazil. The Station is inserted in the Iron Quadrangle considered one of the richest mineral ore-bearing regions in the world. This Ecological Station presents a diversified fauna and there are several animals and some of them are included among the animals under risk of extinction. The assessment was carried out aiming at evaluating the possible streams contamination from mineral exploration and correlated activities in the surroundings of this area, including the ‘garimpo’- small scale gold mining where metal Hg is used to concentrate gold. The stream soil sediments were collected at points along the three streams and their tributaries. The sampling was carried out in the central part of the streams using a shovel and the material was kept in plastic bags. At the laboratory, the samples were air-dried, sieved in five granulometric fractions. The finest-grained fraction, < 63  $\mu\text{m}$  consisting of silt and clay, was analysed.

The analytical technique applied on Hg elemental determination in both laboratories - INAA- $k_0$  - followed the same procedure after each sample had been weighed in polyethylene vial suitable for neutron irradiation. At the Jožef Stefan Institute (JSI), the irradiations were performed in the carousel facility (CF) of the 250 kW TRIGA Mark II reactor with thermal neutron fluence rate of  $1.1 \times 10^{12}$  neutrons  $\text{cm}^{-2} \text{s}^{-1}$ ; and alpha, -0.014 for the specific irradiation channel in

the CF. The gamma spectrometry was performed in gamma counting system HPGe, 20 % efficiency. In Brazil, the irradiations were carried out in the same type reactor, TRIGA Mark I IPR-R1, located at CDTN/CNEN at 100 kW with thermal neutron fluence rate of  $6.6 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ ; alpha, 0.025. The gamma spectrometry was performed in gamma counting system HPGe, 15 % efficiency. In both laboratories, the samples were co-irradiated with fluence rate monitor disks of Al-Au 0.1 % from Central Bureau for Nuclear Measurements, Geel, Belgium. After suitable cooling time, the gamma spectra were obtained and evaluated by HyperLab PC software<sup>[6]</sup>. The concentra-

tion was calculated using the KAYZERO/SOLCOI software<sup>[7]</sup>.

## RESULTS AND DISCUSSION

Table 1 presents the total Hg concentration determined in sediment samples by both laboratories. The results obtained from JSI presented lower detection limits when compared with those from CDTN/CNEN. It is because not only the thermal neutron fluence rate is higher than in CDTN/CNEN but also the gamma counting system is more efficient. The Brazilian legislation<sup>[8]</sup> has not established limit values for sediment but it foresees them for soil. Basing on the limit established for Hg in soil,  $0.5 \text{ mg kg}^{-1}$ , several results exceeded the limit.

**Table 1.** Total Hg concentration ( $\text{mg kg}^{-1}$ ) in sediment samples

Sample	JSI	CDTN/CNEN
1	$0.55 \pm 0.09$	< 1
2	$0.84 \pm 0.09$	< 1
3	$0.71 \pm 0.06$	< 1
4	$0.39 \pm 0.08$	< 1
5	$0.45 \pm 0.08$	< 1
6	$0.62 \pm 0.07$	< 1
7	$2.62 \pm 0.12$	$2.2 \pm 0.2$
8	$0.71 \pm 0.11$	< 1
9	< 0.5	< 1
10	< 0.5	< 1
11	$0.37 \pm 0.07$	< 1

## CONCLUSIONS

The results achieved show that total Hg was increased and exceeded the limit value established by the Brazilian legislation<sup>[8]</sup>. These results suggest the need to carry out further studies in order to elucidate if the Hg values come from mineral activities, characterising

environmental contamination, or from natural occurrence.

The INAA- $k_0$  was suitable to determine the total Hg in concentration level higher than  $0.5 \text{ mg kg}^{-1}$  at IJS and  $1 \text{ mg kg}^{-1}$  at CDTN/CNEN according to local conditions of irradiations and measurements. The technique

is theoretically suitable to determine total Hg concentrations attending the Brazilian Legislation since the analysis condition is optimised. Although at the present moment the instrumental technique at CDTN/CNEN is not suitable to determine lower concentration, it is extremely useful as a screening technique determining the samples (total Hg concentration < detection limit) to other more suitable techniques. The importance of this selection is to avoid that samples with higher total Hg concentration are analysed using techniques indicated for lower Hg concen-

trations. It would avoid, for example, the apparatus contamination.

The results for total Hg concentration obtained by the  $k_0$ - standardisation method applied by both Institutes presented good agreement.

### Acknowledgements

Dr. Radojko Jaćimović, Jožef Stefan Institute, for technical support on optimisation of the INAA- $k_0$  at Laboratory for Neutron Activation Analysis, CDTN/CNEN.

### REFERENCES

- [1] GOYER, R. A. (1991): Toxic effects of metals; In (CASARETT, L. J., DOULL, J., Eds.) *Toxicology: the basic science of poisons*, New York: Pergamon Press (4<sup>th</sup> ed.), pp. 623-680.
- [2] HORVAT, M. (1989): *Development and study of analytical methods for determination of low level mercury concentration and its application in analysis of biological and other environmental samples*; Ph.D. Thesis, University of Ljubljana, Slovenia.
- [3] JAĆIMOVIĆ, R., STIBILJ, V., BENEDIK, L., SMODIŠ, B. (2003): Characterisation of the neutron flux gradients in typical irradiation channels of a TRIGA Mark II reactor; *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 257, No. 3, pp. 545-549.
- [4] MENEZES, M. Â. B. C., SABINO, C. V. S., FRANCO, M. B., KASTNER, G. F., MONTOYA, E. H. R. (2003):  $K_0$  - Instrumental Neutron Activation establishment at CDTN, Brazil: a successful story; *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 257, No. 3, pp. 627-632.
- [5] CRUZ, L. V. (2002): *Avaliação Geoquímica ambiental da Estação Ecológica do Tripuí e adjacências, sudeste do Quadrilátero Ferrífero, MG*; M.Sc. Thesis, Federal University of Ouro Preto, Brazil.
- [6] HyperLab 2002 System: Installation and Quick Start Guide, HyperLab Software Budapest Hungary, 57 p.
- [7] KAYZERO/SOLCOI (2003): User's Manual, for reactor neutron activation analysis (NAA) using the  $k_0$  standardisation method, Ver. 5a, February.
- [8] Conselho Nacional do Meio Ambiente. Proposta de resolução versão 11/09/03. Dispõe sobre diretrizes e procedimentos para a proteção da qualidade do solo e o gerenciamento de áreas contaminadas. [<http://www.mma.gov.br/port/conama>.]

## Atmospheric mercury monitoring in a highly industrialized Brazilian region (Paulinia, São Paulo State)

PAULA A. M. MICHELAZZO AND ANNE HÉLÈNE FOSTIER

State University of Campinas (Unicamp), Institute of Chemistry, PO Box 6154, Campinas, SP, 13084-971, Brazil - e-mail: fostier@iqm.unicamp.br.

**Abstract:** The concentrations of total atmospheric gaseous mercury (TGM) and total particulate mercury (TPM) have been monitored at two sites (industrial and residential) in one of the more industrialized Brazilian region. The monitoring was done during both the dry and wet seasons of 2003. The mean concentrations of TGM were  $6.9 \pm 4.4 \text{ ng m}^{-3}$  (dry season) and  $5.8 \pm 3.3 \text{ ng m}^{-3}$  (wet) at the industrial site and  $4.5 \pm 3.0 \text{ ng m}^{-3}$  (dry) and  $10.8 \pm 8.6 \text{ ng m}^{-3}$  (wet) at the residential site. The analysis of the diurnal TGM variability showed the occurrence of higher concentrations during the day. The mean concentrations of particulate mercury were  $437 \pm 473 \text{ pg m}^{-3}$  and  $593 \pm 232 \text{ pg m}^{-3}$  for the dry season and  $228 \pm 165 \text{ pg m}^{-3}$  and  $337 \pm 219 \text{ pg m}^{-3}$  for the wet season (industrial and residential sites respectively). The concentrations of TGM and TPM are comparable with those found in literature for regions that are affected by anthropogenic mercury sources.

**Key words:** Atmosphere, mercury speciation, anthropogenic emissions.

### INTRODUCTION

Recently, a number of studies have been performed in order to evaluate the impact of anthropogenic activity on atmospheric mercury concentrations in highly industrialized regions of the Northern Hemisphere. In Brazil, as in the other countries of the Southern Hemisphere, mining activities (gold and silver) have been considered as the main mercury sources and studies were mainly performed for the Amazonian region. Data about atmospheric Hg concentrations and anthropogenic emission sources are scarce. Nevertheless, considering that the productive capacity of several developing countries, mainly located in the Southern Hemisphere, has grown significantly over the last decade, their contribution to the Global Mercury Cycle needs to be better investigated. As part

of a more extended work aiming to evaluate the natural and anthropogenic Hg emission sources in Brazil<sup>[1]</sup>, the purpose of this work was to evaluate the total gaseous mercury (TGM) and total particulate mercury (TPM) concentrations in one of the more industrialized Brazilian regions.

The Paulínia municipality, located in the Campinas Metropolitan Region (São Paulo State, Brazil) has a very expressive industrial area with potential Hg emission sources, such as the largest Brazilian petroleum refinery, petrochemical and chemical industries, oil derivation distributors, an Hg recycling industry, incinerators, etc.<sup>[2]</sup> In 2000, the daily emissions of SO<sub>2</sub>, NO<sub>x</sub> and particulate matter were estimated to be 73.9 t, 15.8 t and 5.8 t, respectively. In the last decade the population growth rate, in the Campinas

Metropolitan, Region was 2.2 % yr<sup>-1</sup>, a little higher than the rate of 1.9 % yr<sup>-1</sup> reported for the entire São Paulo State. During the same period, energy consumption by industrial activities increased 4.0 % yr<sup>-1</sup>, also faster than the 2.8 % observed for São Paulo State.

## RESULTS AND DISCUSSION

Two sampling points were selected according to the dominant wind direction, which in this region is from southeast to northwest. The first point was located on the campus of the Campinas State University (Unicamp), which is surrounded by a residential area. The second point, about 15 km northwest from the first point, is near the Paulínia industrial district, and directly receives atmospheric emissions from the industrial district<sup>[3]</sup>. The monitoring was performed during both the 2003 dry and wet seasons for five-days at each site. Atmospheric parameters were also recorded. For TGM, six 2-hour samples were collected daily on gold-coated glass traps at a nominal flow rate of 0.3 L min<sup>-1</sup> and Hg detection was made by Cold Vapor Atomic Fluorescence Spectrometry, CVAFS. The sampling of particulate Hg was carried out through quartz fiber filters (30 L min<sup>-1</sup>, 24 h sampling time) according to the US-EPA IO-5 method<sup>[4]</sup>. After digestion of the filters with BrCl and reduction with SnCl<sub>2</sub>, Hg was quantified by CVAFS<sup>[5]</sup>.

The TGM data obtained for both sampling sites and both seasons are presented in Table 1. The mean TGM concentration calculated for the total period of measurements was 8 (± 12) ng m<sup>-3</sup> for Unicamp and 8 (± 7) ng m<sup>-3</sup> for Paulínia, without any significant difference (p < 0.05).

In Brazil, background TGM concentrations measured in the Negro River basin were 1.3 ng m<sup>-3</sup> <sup>[6]</sup>. Data found in the literature show a great variability in TGM concentration near emission sources, depending on the type and proximity of the sources. For example, higher TGM concentrations are expected near chlor-alkali plants. DOMMERGUE<sup>[7]</sup> observed mean TGM concentrations of 3.4 ng m<sup>-3</sup>, with many peaks above 10.0 ng m<sup>-3</sup>, and a maximum of 45.9 ng m<sup>-3</sup>. EBINGHAUS AND KRÜGER<sup>[8]</sup>, in measurements also carried out at the perimeter of a chlor-alkali plant, found values that varied from 10 to 530 ng m<sup>-3</sup>. The analysis of seasonal data did not indicate any significant difference between wet and dry season at both sites. Diurnal variability showed higher TGM concentrations during daytime and lower concentrations during the night. This behavior was observed for both sites in both seasons. This behavior was also observed by EBINGHAUS AND KRÜGER<sup>[8]</sup>. In all these cases, this pattern was associated to sites close to TGM emission sources, since the TGM present in air masses from medium and long

**Table 1.** Summary of TGM data at Unicamp and Paulínia.

Site	Data	TGM (ng m <sup>-3</sup> )			
		Min. Conc.	Max Conc.	Mean	Median
UNICAMP	Dec. 2002	3.3	37.8	11 ± 9	7.2
	May 2003	0.8	11.9	5 ± 3	3.9
Paulínia	Jan. 2003	1.2	15.3	6 ± 3	5.2
	May 2003	0.3	90.8	7 ± 4	6.2

distances is dispersed. For these authors, the variations could be associated to factors like the increase of the anthropogenic emissions during the day, the removal of the Hg<sup>0</sup> by humidity of the air during the night and the differences of atmospheric turbulence between day and night.

The sampling of TPM was carried out in parallel to the sampling of TGM. The TPM concentration data for the sampling campaigns are shown in Table 2. The mean TPM concentration calculated for the total period of sampling was 465 ( $\pm$  225)  $\mu\text{g m}^{-3}$  at Unicamp and 332 ( $\pm$  319)  $\mu\text{g m}^{-3}$  at Paulinia, without any significant difference ( $p < 0.05$ ).

Data found in literature for urban/industrialized areas varied from 22  $\mu\text{g m}^{-3}$  to 1.984  $\text{ng m}^{-3}$ <sup>[9]</sup>. The highest TPM values were detected during the dry period at both sites (Unicamp: 778  $\mu\text{g m}^{-3}$ ; Paulinia: 1231  $\mu\text{g m}^{-3}$ ) and could be related with the pluvial index: 0 mm of rain for both sites during the dry period and

25.9 mm of rain (with 9.9 mm on the first day of sampling) at Unicamp and 53.0 mm of rain at Paulinia during the wet period. Rain drags the existing particulate material in air to the ground (wet deposition), contributing to the removal of mercury particulate from the atmosphere. No significant correlation was observed between TGM and TPM concentration.

The percentage of TPM in relation to total atmospheric mercury was calculated, assuming that total atmospheric mercury is given by the sum of total gaseous mercury and of total particulate mercury. The calculated percentage of TPM was: 4.5 % (wet) and 12.2 % (dry) for the measurements at Unicamp and 3.3 % (wet) and 4.9 % (dry) at Paulinia. These results agree with those expected for concentrations of TPM in industrialized regions, where TPM can constitute up to 40 % of total atmospheric mercury, while in more remote areas TPM contributes less than 1 % of the total atmospheric mercury<sup>[10]</sup>.

**Table 2.** TPM concentration data for the sampling campaigns.

		TPM ( $\mu\text{g m}^{-3}$ )		
		Min. Conc.	Max. Conc.	Mean
<b>UNICAMP</b>	Dec 2002	104	555	337 $\pm$ 219
	May 2003	298	778	593 $\pm$ 232
<b>PAULINIA</b>	Jan 2003	24	458	228 $\pm$ 165
	May 2003	67	1231	437 $\pm$ 473

## CONCLUSIONS

The TGM and TPM concentrations data at Unicamp and Paulinia clearly indicate the influence of anthropogenic emission sources of atmospheric mercury in this region, leading to some events with high concentrations. These results confirm those found by

FOSTIER<sup>[1]</sup> about Hg concentration in the rivers of this region, and by OLIVARES<sup>[11]</sup> about Hg emissions and are pointing out the necessity of more data about atmospheric Hg concentrations and the better control of the anthropogenic Hg sources in the Brazilian industrialized regions, as is probably true for many other developing countries.

## Acknowledgements

This work was supported by CNPq, FAPESP and CETESB.

## REFERENCES

- [1] FOSTIER, A. H. (2003): *Fontes naturais e antrópicas de mercúrio atmosférico no Brasil*. Proceeding of the II Encontro Nacional de Química Ambiental. Brasília. Brasília (DF). 17-19/03/2003. CD-Rom.
- [2] OLIVARES, I. R. B., GUIMARÃES, J. R., FOSTIER, A. H. (2004): *Assessment of anthropogenic mercury emissions from a highly industrialized Brazilian region (Paulínia, São Paulo State)*. 7<sup>th</sup> International Conference on Mercury as a Global Pollutant, Slovenia, 2004.
- [3] SOUZA, K. R. P. (2002): *Estudo sobre compostos orgânicos voláteis presentes no ar do município de Paulínia*. Ms Thesis. Campinas. State University of Campinas. 2002, 250 p.
- [4] US-EPA (1999): *Sampling and analysis for atmospheric mercury*. EPA/625/R-96/010a.
- [5] BLOOM, N. S., FITZGERALD, W. F. (1988): Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold vapor atomic fluorescence detection. *Analytica Chimica Acta* 209, pp. 151-161.
- [6] FADINI, P., JARDIM, W. F. (2001) Is the Negro River Basin, Amazon impacted by naturally occurring mercury?. *Science of the Total Environment*. 275 (1-3), pp. 71–82.
- [7] DOMMERGUE, A., FERRARI, C. P., PLANCHON, F. A. M., BOUTON, C. F. (2002): Influence of anthropogenic sources on total gaseous mercury variability in Grenoble suburban air (France). *Science of the Total Environment* 297, pp. 203 – 213.
- [8] EBINGHAUS, R., KRÜGER, O. (1996) Emission and local deposition estimates of atmospheric mercury in north-western and central Europe. In: *Global and Regional Mercury Cycles*, NATO Advanced Science Institute Serie (R. EBINGHAUS, W. BAYENS, O. VASILIEV, Eds.), Novosibirsk, Siberia. Kluwer, Dordrecht, Holland, pp.135-159.
- [9] FANG, F., WANG, Q., LIU, R., MA, Z., HAO, Q. (2001): Atmospheric particulate mercury in Changchun City, China. *Atmospheric Environment* 35, pp. 4265-4272.
- [10] MUNTHE, J., WÄNGBERG, I., PIRRONE, N., IYERFELDT, L., FERRARA, R., EBINGHAUS, R., FENG, X., GLRDFELDT, KEELER, G., LANZILLOTTA, LINDBERG, S. E., LU, J., MAMANE, Y., PRESTBO, E., SCHMOLKE S.; SCHROEDER W. H.; SOMMAR J.; SPROVIERI F.; STEVENS R. K.; STRATTON W.; TUNCEL, G., URBA, A. (2001): Intercomparison of methods for sampling and analysis of atmospheric mercury species. *Atmospheric Environment* 35, pp. 3007-3017.
- [11] OLIVARES, I. R. B. (2003): *Emissões antrópicas de mercúrio atmosférico na região de Paulínia (SP)*. Ms. Thesis, Campinas, Universidade Estadual de Campinas, 100 p.

# Mercury in Coal Ash and its Fate in the Indian Subcontinent

ARUN B. MUKHERJEE<sup>1</sup>, RON ZEVENHOVEN<sup>2</sup>

<sup>1</sup>Department of Biological and Environmental Sciences, P.O. Box 27, FIN-00014 University of Helsinki, Finland; E-mail: arun.mukherjee@helsinki.fi

<sup>2</sup>Energy Engineering and Environmental Protection, Helsinki University of Technology, P.O. Box 4400, FIN-02015 Espoo, Finland; E-mail: ron.zevenhoven@hut.fi

**Abstract:** In the Indian subcontinent power generation is mainly dependent upon the thermal power units and coal is burnt as a fuel for the production of heat and electricity. In India, bituminous and sub-bituminous coals are used which contain over 40 percent of ash. At present, 80-90 million tons of fly ash and bottom ash are generated from 85 existing coal based thermal power plants. Coal contains trace metals of which mercury is most toxic for humans and aquatic fauna. The problem of mercury in the society is not new, but in recent years the Indian subcontinent has gained the reputation of being “a dumping ground for mercury”. This study focuses on mercury in fly ash and its releases to the atmosphere and soils cross the country. The utilization of coal ash in India has also been addressed although it is still in its nascent stage. About 10 % of produced fly ashes are used in India whereas in Western countries its use is typically over 70 %.

**Key words:** Fly ash, uses, coal, mercury, India.

## INTRODUCTION

In the Indian subcontinent there are abundant reserves of coal, which have become India's most important source of primary energy. Global bituminous coal production in 2001 was 3,834 Mt (million metric tons) of which India shared 8.2 % (312.5 Mt). There are ~85 utility thermal power plants, which generate 80 % of India's thermal energy and the rest 20 % stems from diesel, wind, gas, hydro-electric power, renewable energy sources, nuclear industry and solar energy (CLARKE ET AL., 1998; SHARMA AND VISWANATH, 2001). These thermal plants use mostly bituminous or sub-bituminous coals containing 30-45 % ash, which yield large volume of fly ash containing mercury (Hg) and other trace elements. In recent years, the problem of Hg has received attention in the Indian subcontinent

as well as fly ash management remains an important national concern.

## RESULTS AND DISCUSSION

### Indian Fly Ash and its Mercury Concentration

Fly ash is an inorganic residue from combustion. Chemical composition of fly ash from coal is based on the coal quality and operating conditions of the power plant. In combustion plants and heat-producing units, the ash-forming matter undergoes complex changes due to physical processes, temperature, turbulence and conditions in gas cleaning equipment. MEIJ (1989) and many others classified trace elements in three groups and Hg belongs to group 3. Due to its

physiochemical properties, it passes into the atmosphere as a gaseous form and a part is condensed on smaller fly ash particles, which have large surface area to volume ratio (CLARKE AND SLOSS, 1992; PACYNA AND PACYNA, 2001). Hg content in different fuels and Indian coal are shown in Table 1. It is

noted that due to different quality of coal, Hg content varies significantly. Indian coal fly ash is quite alkaline (concentrations of Na<sub>2</sub>O and K<sub>2</sub>O in the order of 0.20-0.45 %wt and 0.50-1.10 %wt, respectively); typical trace element concentrations are listed in Table 2.

**Table 1.** Mercury content in different fuels (MEIJ ET AL., 1999) and Indian coals (RAJAGOPALAN, 2003) in mg kg<sup>-1</sup> (dry)

Indian coal	Typical coal	Oil	Petroleum coke	Paper sludge	Sewage sludge	Waste wood	Biomass
0.26-0.49	0.11	0.01	0.02	0.24	3.28	0.17	0.06

**Table 2.** Trace metals concentration (mg kg<sup>-1</sup>) in Indian Coal fly ash (SRIVASTAVA ET AL., 2001).

Cu	Ni	Co	Pb	Mn	Zn	Cd	Cr	Se	As	Hg
42.0	58.0	45.0	87.0	281.0	60.0	7.2	46.9	2.0	0.003	2.1*,0.244-0.812** 18-116***

\*Santhaldih Thermal Power Plant, West Bengal; \*\*Renusagar Thermal Power Plant, Hindalco; Singrauli Thermal Power Plant, Uttar Pradesh; Anpara Thermal Power Plant, Uttar Pradesh (RAJAGOPALAN, 2003); \*\*\* Singrauli power plants in Uttar Pradesh (SHARPE ET AL., 2001)

In recent years, 75 to 90 Mt of fly ash were generated each year from 250 Mt of coal for thermal power generation. Hg in fly ash varies from one corner of the subcontinent to another and Table 2 indicates different Hg values in fly ash from different power plants (Hg was measured in four thermal power plants with capacity 70-500 MW) whereas in coal, Hg concentration was 0.26 – 0.487 mg kg<sup>-1</sup> (Table 1).

In this study, the higher Hg values have been neglected. Based on the rest data (0.244-0.812 mg kg<sup>-1</sup>), the mean Hg in Indian fly ash can be been estimated at 0.528 mg kg<sup>-1</sup>. Other reported values of Hg in fly ash were 0.28 ± 0.13 mg kg<sup>-1</sup> (for the Netherlands, Meij et al. 2002) and 0.5 mg kg<sup>-1</sup> (for the US, Ladwig, 2001). Hence, the estimated total amounts of Hg in fly ash in different regions of India are given in Table 3.

**Table 3.** Detailed mercury in fly ash in five regions of India, 1997-98 (based on data from MOHAN KUMAR ET AL., 2001)

Regions	Installed capacity (MW)	Ash produced (Mt)	Estimated Hg in fly ash (t)*	Ash utilized (Mt)	Utilization (%)
Northern	13146.5	19.08	<b>10.07</b>	2.33	12.21
Western	17393	28.547	<b>15.07</b>	1.86	6.52
Southern	10632.5	18.37	<b>9.70</b>	0.791	4.30
Eastern	11735	11.943	<b>6.30</b>	3.42	28.64
North-East	240	0.037	<b>0.02</b>	0.03	81.08
Total	53147	77.98	<b>41.16</b>	8.430	10.81

Regions: Northern: Jambu & Kashmir, Himachal Pradesh, Haryana, Rajasthan, Delhi and Uttar Pradesh

Western: Gujarat, Maharashtra, Madha Pradesh, and Goa; Southern: Andhra P radesh, Karnataka, Tamil Nadu, and Kerala; Eastern: Bihar, West Bengal, and Orissa; North -East: Meghalaya, Manipur, Sikkim, and Mizoram

## FATE OF MERCURY IN FLY ASH

Still today the utilization of fly ash in India is very small compared to developed countries (where it can be > 70 %). Recent study suggested that fly ash consumption in India has increased from 0.762 Mt (4.47 %) in 1990-91 to 8.43 Mt (10.81 %) in 1997-98 (Table 4).

There is a scarcity of studies in India regarding the release of Hg from coal ash to the atmosphere. SRIVASTAVA ET AL. (2001) studied leaching of trace elements from coal ash

and confirmed that the leaching of As, Hg and Se was below their detection limit. Studies have been conducted in the United States, Finland, and the Netherlands which suggested volatilization and leaching of Hg from fly ash were minimal. In the Netherlands, leaching of Hg from fly ash was only 1.0 % (MEIJ ET AL., 1994). However, at large power plants, a wet disposal method is adopted to transport fly ash from the plant area to an ash pond. Due to the alkaline nature of the fly ash (pH 9.29) and pond ash (pH 8.86), the risk of Hg leaching from the ash pond may be low.

**Table 4.** Consumption pattern of fly ashes in India, 1997-98 (MOHAN KUMAR ET AL. 2001).

Agriculture	Cement	Landfill	Ash dykes	Road work	Mines	Brick
2 %	26 %	51 %	9 %	2 %	5 %	5 %

## CONCLUSIONS

Diffusion emissions of Hg from fly ash should be studied thoroughly to estimate total Hg release to the atmosphere and other ecosystems. Not all Indian thermal power plants do produce alkaline fly ash. Generally, Hg and other trace elements uptake by plants and their leaching possibilities are based on fly ash quality, pH and quality of soils. Hence, effects caused by Hg in fly ash to the terrestrial and aquatic species should

be evaluated. There is no lack of technology for using fly ash. Encouragement should be made among companies and rural people. Acidic fly ash can also be used as a mine filler after addition of alkali oxides.

## Acknowledgements

We would like to acknowledge the thoughtful comments made on the extended abstract by Dr. R. Meij, KEMA Netherlands B.V., Arnhem, The Netherlands.

## REFERENCES

- CLARKE, L. B. & SLOSS, L. L. (1992): Trace elements – emissions from coal combustion and gasification; *IEA Coal Research*, London, IEACR/49, 111 p.
- CLARKE, L. B., WALKER, S. & MONTFORT, O. (1998): Coal prospects in India; *IEA Coal Research*, Report No. IEAPER-37, London, UK, 71 p.
- LADWIG, K. (2001): *EPRI Perspectives on mercury in coal combustion byproducts*; Presented at the EPA Coal Combustion Residues Workshop, Research Triangle Park, NC, January 10-11, 2001.

- MEIJ, R. (1989): Tracking trace elements at a coal-fired power plant equipped with a wet-flue-gas desulphurization facility; *KEMA Scientific and Technical Reports*, Special issue 7(5): pp. 267-355.
- MEIJ, R., & SCHAFTENAAR, H. P. C. (1994): Hydrology and chemistry of pulverized fuel ash in a lysimeter or the translation of the results of the Dutch column leaching test into field conditions; In *Environmental aspects of construction with waste materials*; Proc. of the Int. Conf. WASCON '94 (GOMANS, J. J. J. M., VAN DER SLOOT, H. A., AALBERS, TH. G., Eds.), Maastricht, Netherlands, June 1994; Elsevier, Amsterdam, 491 p.
- MEIJ, R., TE WINKEL, B. H. & HAVINGA, H. (1999): *Emissions of micro- and trace elements from co-firing 10 % secondary fuels and biomass in pulverized coal – fired units in the Netherlands*; Report 99530162-KST/MAT 99-6579, KEMA, Arnhem, Netherlands, 49 p. (in Dutch).
- MEIJ, R., VREDENBREGT, L. H. J. & WINKEL, B. H. (2002): The fate of mercury in coal fired power plants; *J. Air & Waste Manag. Assoc.* 52, pp. 912-917.
- MOHAN KUMAR, RENGASWAMY, A. & CHANDRA, S. (2001): National scenario on PFA production and utilization; In *2<sup>nd</sup> Int Conf on Fly Ash Disposal and Utilisation*, Vol I(1-3) (VARMA, C. V. J., VIMAL KUMAR, KRISHNAMURTHY, R., Eds), 2-4 Feb 2000, New Delhi, India, pp. 21-28.
- PACZYNA, J. M., & PACZYNA, E. G. (2001): An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide; *Environ. Rev.* 9, pp. 269-298.
- RAJAGOPALAN, R. (2003): Monitoring and regulation the use of mercury: Government perspective; In *National Conference on Mercury Pollution in India*, 3<sup>rd</sup> November 2003, New Delhi, India.
- SHARMA, S. R. & VISWANATH, K. (2001): Fly ash utilization: India's state-of-art present scenario; In *2<sup>nd</sup> Int Conf on Fly Ash Disposal and Utilisation*, Vol I (I-14) (VARMA, C. V. J., VIMAL KUMAR, KRISHNAMURTHY, R., Eds.), 2-4 Feb 2000, New Delhi, India, pp. 93-100.
- SHARPE, M., DUBE, S. K., CREEMENS, D. L., GOLLAKOTA, S. & VERMA, S. (2001): Environmental considerations for the study of ash haul back to abandoned open cast coal mine in Singrauli region in conjunction with the financial aspects; Vol II (VII-1), *ibid*, pp.1-17.
- SRIVASTAVA, N. K., RAM, L. C. & SINGH, G. (2001): Prediction of leaching behaviour of TPP ash under simulated condition by column studies; Vol I (IV-3), *ibid*, pp.16-28.

## Emissions of Mercury from Coal Fired Power Plants in Russia

JOHN MUNTHE<sup>1</sup>, INGVAR WÄNGBERG<sup>1</sup>, ALLA N. CHUGAEVA<sup>2</sup>, NINEL V. KISELEVA<sup>2</sup>,  
IGOR N. SMIGOL<sup>2</sup>, OLGA N. BRAGINA<sup>2</sup>, SERGEY N. ANICHKOV<sup>2</sup>, ANATOLY G. TUMANOVSKY<sup>2</sup>

<sup>1</sup>IVL Swedish Environmental Research Institute, PO Box 47086, S- 402 58 Gothenburg, Sweden

<sup>2</sup>VTI All Russia Thermal Engineering Institute. 14/23, Avtozavodskava Str.,  
Moscow 115280 Russia.

**Abstract:** This report consists of a preliminary estimate of the emissions of mercury from Russian coal-fired power plants. The results presented in this report are based on information on coal consumption in Russian power plants along with analytical results of coal samples.

**Key words:** mercury, coal, emissions, power plants, Russia

### INTRODUCTION

The coal fired power plant sector is one of the main emission sources of mercury on a global scale. Within this sector, actual emissions are determined by concentrations of mercury in the coal used as well as efficiency of emission control installations. This study was initiated with the aim to develop a detailed emission inventory for mercury in the Russian coal fired power plant sector. Here we report preliminary results of total usage of coal, sources of this coal and a preliminary evaluation of the total emissions of mercury from this sector. A detailed assessment of mercury concentrations in coal and efficiency of emission control equipment is on-going.

### RESULTS AND DISCUSSION

Information on coal consumption in Russian power plants was collected and evaluated by VTI. Technical data for the 129 largest power plants in Russia have been collected. From this data set, information on coal consumption and origin of coal were used for this preliminary estimate of the emissions of mercury. A summary of this data is presented in Figure 1.

Information on mercury contents in coal was provided by VTI. For most coal sources, mercury concentrations are around or below 0.1 mg/kg although values up to 0.8 mg/kg were found in coal from some coal fields. If available, average and maximum concentration

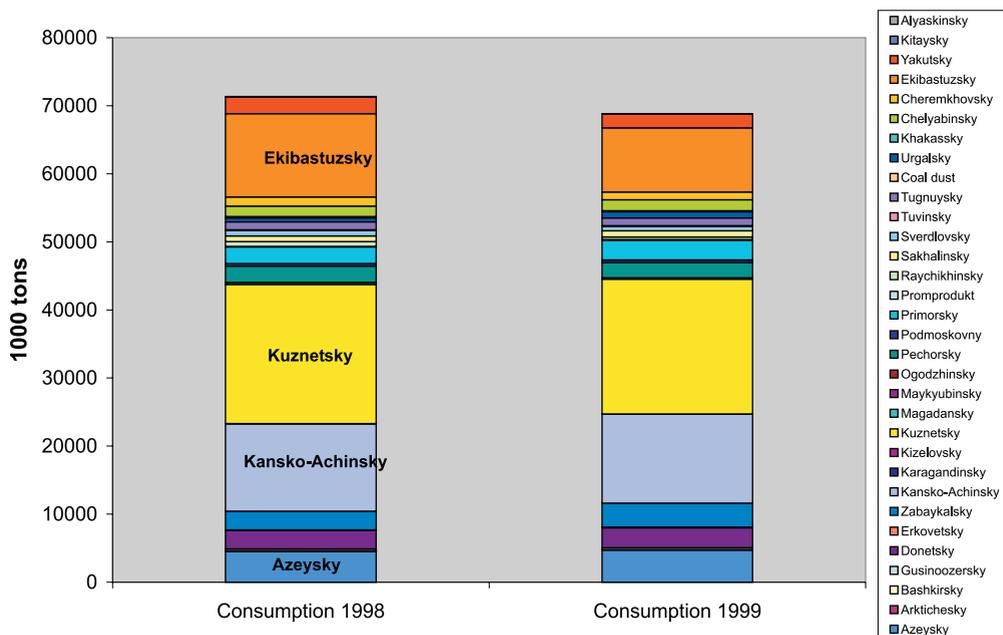


Figure 1. Origin of coal consumed in Russian power plants 1998 and 1999.

for each specific coal type were used to estimate overall emissions. For this preliminary emission estimate, no distinction between power plants using different control technology was made. All emissions were thus estimated from the coal consumption in year 2000, the contents of mercury in coal and an assumed removal efficiency of 20 %. This latter efficiency was based on a limited amount of stack gas measurements at a power plant in Russia.

With these assumptions, the emissions of mercury from coal fired power plants were

estimated to be in the range 5 to 7 tons per year. This number only represents the emissions from the main coal fired power plants investigated in this study. The total coal use in Russia is around a factor of 2 greater than that reported here indicating that the total emissions from coal usage in Russia is about twice that amount.

### Acknowledgements

This work was supported by the US EPA under contract No.: 1W-0007-NAFX and 1W-0088-NAFX.

# Large annual Hg emissions over Tallgrass prairie grasslands indicate vegetated terrestrial ecosystems to be sources of Hg to the atmosphere

DANIEL OBRIST<sup>1\*</sup>, MAE S. GUSTIN<sup>2</sup>, JOHN A. ARNONE III<sup>3</sup>, D. W. JOHNSON<sup>2</sup>,  
DAVID E. SCHORRAN<sup>3</sup>, PAUL S. J. VERBURG<sup>3</sup>

<sup>1</sup> University of Basel, Environmental Geosciences, Bernoullistrasse 30, 4056 Basel, Switzerland,

\*E-mail: daniel.obrist@unibas.ch

<sup>2</sup> University of Nevada, Reno, Desert Research Institute, Department of Environmental and Resource Sciences, Reno, NV 89557, USA

<sup>3</sup> Desert Research Institute, Division of Earth and Ecosystem Sciences, Reno, NV 89512, USA

**Abstract:** Here we present the first annual measurements of net Hg(0) exchange between a vegetated terrestrial ecosystem and the atmosphere. Annual net Hg(0) exchange between the atmosphere and four replicate intact Tallgrass prairie ecosystems (2.85 x 1.3 x 1.7 m, L x W x D) was  $61 \pm 25 \mu\text{g Hg m}^{-2} \text{ yr}^{-1}$  (mean  $\pm$  SE), indicating that the grassland ecosystems used in our study were clearly sources of Hg to the atmosphere. Hg exchange was positive (i.e., net Hg loss from the ecosystem to the atmosphere) during most of the year with the exception of the winter months when small rates of Hg deposition were observed. Throughout the year, ecosystem Hg fluxes showed pronounced dual patterns with higher daytime Hg fluxes compared to nighttime fluxes indicating that solar radiation, temperature, and evapotranspiration are important factors controlling Hg emissions. The magnitude of Hg emissions from this ecosystem was surprising in lieu of low soil Hg concentrations ( $7.4 \pm 1.3 \text{ ng Hg g}^{-1}$ ; mean across the top 170 cm). Measurement of Hg concentrations in irrigation and drainage water showed that  $2.5 \mu\text{g Hg m}^{-2} \text{ yr}^{-1}$  was added by irrigation and that drainage losses of Hg (at 1.7 m depth) were negligible. Our results indicate that terrestrial ecosystems might be large—yet still poorly quantified—sources of Hg to the atmosphere and that gaseous elemental Hg loss is an important pathway of Hg exchange for vegetated ecosystems exceeding other fluxes of Hg.

**Key words:** Elemental mercury emissions, tallgrass prairie, flux measurements, Ecologically Controlled Enclosed Lysimeter Laboratory (EcoCELLs)

## INTRODUCTION

Our understanding of the role of natural sources and sinks in the biogeochemical cycling of Hg is hindered by the dearth of direct exchange measurements of Hg between vegetated terrestrial ecosystems and the atmosphere (GRIGAL, 2002; SCHRODER, 1998;

LINDBERG, 1992). Initial measurements of elemental Hg exchange over temperate forest ecosystems during spring and summer months indicated that elemental Hg emissions from terrestrial ecosystems to the atmosphere could be up to three times higher than modeled estimates (LINDBERG, 1992; LINDBERG, 1998). Because Hg emissions to

the atmosphere are influenced by climatic conditions such as temperature and solar radiation (LINDBERG, 1998; ENGLE, 2001; LINDBERG, 2002), quantification of these emissions will require long-term measurements that cover different climatic conditions and vegetation development.

The objective of this study was to measure elemental Hg exchange between tallgrass prairie ecosystems and the atmosphere during one full year using the Ecologically Controlled Enclosed Lysimeter Laboratory (EcoCELLs) at the Desert Research Institute in Reno, NV, USA. The EcoCELLs are unique open flow gas exchange systems that allow for the measurement of whole-ecosystem gas fluxes from large soil-plant monoliths—excavated in the field in such ways as to minimize soil and vegetation disturbance—under precisely controlled environmental conditions (GRIFFIN, 1996). Within the EcoCELLs, monoliths were maintained under climatic conditions that tracked average annual conditions at the field site. We used tallgrass prairie monoliths in this study because grasslands are a major biome covering ~ 30 % of the earth's terrestrial surface area (DEFRIES, 1994; WILSON, 1995).

## RESULTS AND DISCUSSION

Cumulative annual exchange of elemental Hg for the four replicate EcoCELLs was  $60.4 \pm 27.1 \mu\text{g Hg m}^{-2}$ , demonstrating that substantial amounts of Hg were lost from all four ecosystems to the atmosphere. Hg exchange was positive (i.e., Hg emissions to the atmosphere) during most of the year with the exception of the winter months. The highest Hg emissions occurring during the warm

months and the low or even negative Hg fluxes (i.e., Hg deposition to the ecosystems) during the colder months indicate that temperature, solar radiation, and vegetation are the main factors affecting Hg exchange between terrestrial ecosystems and the atmosphere.

The gaseous losses of elemental Hg greatly exceeded all other Hg fluxes in and out of the ecosystems, with the result that the grasslands in our study were true net sources of Hg to the atmosphere during the one year of our study (Table 1). Total Hg concentrations of irrigation water ranged between 1.0 and 5.2 ng/L, and the 860 mm of irrigation water applied during the year yielded an Hg input of  $2.5 \mu\text{g Hg m}^{-2} \text{ yr}^{-1}$  to the ecosystem (i.e., wet deposition). Hg losses via drainage were very small ( $0.08 \pm 0.03 \mu\text{g m}^{-2}$ ) because only minimal amounts of water drained from the monoliths at 1.70 m depth. Finally, measurements of ionic Hg (i.e., reactive gaseous Hg: RGM) during a 1-week period in summer showed higher RGM concentrations at the EcoCELL's air outlet ( $86 \pm 34 \text{ pg m}^{-3}$ ) compared to concentrations measured at the air inlet ( $62 \pm 42 \text{ pg m}^{-3}$ ) indicating that RGM-fluxes could be an additional source of Hg to the atmosphere rather than a sink balancing elemental Hg emissions. Soil Hg concentrations were  $20.0 \pm 1.4 \text{ ng Hg g}^{-1}$  at 1 cm depth and much lower in deeper soils (e.g.,  $3.7 \pm 0.2 \text{ ng Hg g}^{-1}$  in 135 cm depth), and averaged  $7.4 \pm 1.3 \text{ ng Hg g}^{-1}$  across the whole soil profile of 170 cm depth. The measured gaseous Hg emissions, corrected by Hg inputs by wet deposition and Hg losses by drainage, would potentially deplete the soil Hg pools in only 250 years, indicating an imbalance of the Hg cycle in the four grassland ecosystems. This imbalance supports a

**Table 1.** Hg mass balance (1 full year) of the four tallgrass prairie grassland monoliths (in m m<sup>-2</sup>)

	EcoCELL 1	EcoCELL 2	EcoCELL 3	EcoCELL 4	Mean	SE
<b>Hg Inputs to ecosystem</b>						
Wet deposition (total Hg)	2.52	2.52	2.52	2.52	2.52	0.00
RGM dry deposition	?	?	?	?		
<b>Hg Outputs from ecosystem</b>						
Gaseous Hg loss (HgO)	39.79	48.00	14.82	139.04	60.41	27.14
Drainage (total Hg)	0.00	0.11	0.14	0.06	0.08	0.03
<b>Net Hg Loss (Inputs - Outputs)</b>	37.27	45.59	12.44	136.57	57.97	27.13
<b>Hg Stocks</b>						
Soil Hg Pool (0-170 cm)	15505.26	14740.75	14686.67	14965.10	14974.44	186.92

suggestion of LINDBERG (1998) that emissions of Hg from terrestrial ecosystems could be due to re-emission of the 200,000 tons of Hg that were mobilized during the last 150 years, of which 95 % is estimated to reside in surface soil pools (EXPERT PANEL, 1994).

## CONCLUSIONS

This first, year-long data set for elemental Hg exchange between a terrestrial ecosystem and the atmosphere indicates that elemental Hg emissions from vegetated terrestrial ecosystems might be large and that their role in the biogeochemical cycling of Hg is currently underestimated. We assume that

most of the Hg being emitted was previously deposited Hg and that re-emission of Hg from terrestrial ecosystems could be a major source of Hg to the atmosphere potentially maintaining high atmospheric Hg loads in spite of successful reductions of anthropogenic emissions.

## Acknowledgements

This work was supported the National Science Foundation with grants from the Atmospheric Sciences Division and the Integrated Research Challenges in Environmental Biology Program (IRCEB). We thank M. Markee, R. Bergin, L. Martindale, and H. Weatherly for laboratory analyses and daily tasks in the EcoCELLs.

## REFERENCES

- DEFRIES, R. S., TOWNSHEND, J. R. G. (1994): NDVI-derived land-cover classifications at a global scale; *Intern. J. Rem. Sens.*, Vol. 15, pp. 3567-3586.
- ENGLE, M. A., GUSTIN, M. S., ZHANG, H. (2001): Quantifying natural source mercury emissions from Ivnhoe Mining Destrict, north-central Nevada, USA; *Atmos. Environ.*, Vol. 35, pp. 3987-3997.
- Expert Panel on Mercury Atmospheric Processes (1994): *Mercury atmospheric processes: a synthesis report*; In Workshop Proceedings, EP6RI/TR-104214, Tampa, Florida, September 1994.
- GRIFFIN, K. L., ROSS, P. D., SIMS, D. A., LUO, Y., SEEMANN, J. R., FOX, C. A., BALL, J. T. (1996): EcoCELLs: tools for mesocosm scale measurements of gas exchange; *Plant Cell Environ.*, Vol. 19, pp. 1210-1221.
- GRIGAL, D. F. (2002): Inputs and outputs of mercury from terrestrial watersheds: a review; *Environ. Rev.*, Vol. 10, 1-39.
- LINDBERG, S. E., DONG, W., MEYERS, T. (2002): Transpiration of gaseous elemental mercury through vegetation in a subtropical wetland in Florida; *Atmos. Environ.*, Vol. 36, pp. 5207-5219.
- LINDBERG, S. E., HANSON, P. J., MEYERS, T. P., KIM, K. H. (1998): Air/surface exchange of mercury vapor over forests – the need for a reassessment of continental biogenic emissions; *Atmos. Environ.*, Vol. 32, pp. 895-908.
- LINDBERG, S. E., MEYERS, T. P., TAYLOR, G. E., TURNER, R. R., SCHROEDER, W. H. (1992): Atmosphere-surface exchange of mercury in a forests: results of modeling and gradient approaches; *J. Geophysic. Res. – Atmos.*; Vol. 97 (D2), pp. 2519-2528.
- SCHROEDER, W. H., MUNTHE, J. (1998): Atmospheric Mercury – An overview; *Atmos. Environ.*, Vol. 32, pp. 809-822.
- WILSON, M. F., HENDERSON-SELLERS, A. (1985): A global archive of land cover and soils data for use in general circulation models; *J. Climat.*, Vol. 5, pp. 119-143.

# Atmospheric Mercury Species near the Gulf of Trieste, N Adriatic

NIVES OGRINC, VESNA FAJON, MILENA HORVAT

Department of Environmental Sciences, Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia; E-mail: nives.ogrinc@ijs.si

**Abstract:** First measurement results of the atmospheric mercury species total gaseous elemental mercury, total particulate mercury and reactive gaseous mercury near the Gulf of Trieste, N. Adriatic are presented.

**Key words:** atmospheric mercury, TGM, TPM, RGM, the Gulf of Trieste

## INTRODUCTION

Mercury is an atmospheric pollutant with a complex biogeochemical cycle including different processes such as oxidation/reduction, deposition and re-emission from natural and anthropogenic sources (SCHROEDER AND MUNTHE, 1998; WÄNGBERG ET AL., 2003). Atmospheric mercury exists in three different forms: gaseous elemental mercury ( $\text{Hg}^0$ ), divalent reactive gaseous mercury (RGM) and that associated with particulate matter (TPM). RGM and TPM are more readily deposited on local to regional scales through wet and dry deposition mechanisms. This presentation is concerned with the results from two weeks measuring campaigns made in the Gulf of Trieste, N Adriatic in November 2003 and January 2004. The research was performed within the on-going EU-project MERCYMS (An integrated approach to assess the mercury cycling in the Mediterranean Basin) where part of the project is related to the investigation of atmospheric mercury species in different marine background locations near the Mediterranean Sea. The Gulf of Trieste is the most mercury contaminated area in the Medi-

terranean Sea due to high mercury inputs from the River Isonzo whose tributary the River Idrijca has been draining the mercury mining area of Idrijca for nearly 500 years. These are the first measurements of atmospheric mercury species in this area (Figure 1).

The results of this study should help to understand the complete process of mercury cycling in this environment, including the complex chemistry of mercury in the atmosphere.

## EXPERIMENTAL

Total gaseous mercury (TGM) refers to  $\text{Hg}^0$  and small contributions from other gaseous Hg species that may also be trapped by the sampler and detected as  $\text{Hg}^0$ . The concentration of TGM was determined using the manual method based on gold trap amalgamation and detection by CV AFS (BLOOM AND FITZGERALD, 1988). The airflow was normally  $> 0.5 \text{ L min}^{-1}$ . With a 24 h sampling time the detection limit was typically  $0.01 \text{ ng m}^{-3}$ . Manual annular denuder methodology was applied to provide ambient RGM measure-



Figure 1. Sampling location in the Gulf of Trieste, N Adriatic.

ments (LANDIS ET AL., 2002). RGM was collected onto KCl-coated quartz annular denuders and then thermally decomposed (500 °C) and quantified as  $Hg^0$  using the standard CV AFS procedure. TPM was determined with a new method based on the AES Minitrap developed by LU ET AL. (1998) which was later patented under the name

AESminiSampIR™ (LU ET AL., 2003). The sampling device serves as both particulate trap and pyrolyzer for airborne particulate mercury species. The air sampling flow rate was  $\sim 10 \text{ L min}^{-1}$  and the detection limit for a 24 h sample was  $< 2 \text{ pg m}^{-3}$  for both RGM and TPM. The precision of measurements was estimated to be  $\pm 10 \%$  calculated as 1 S.D.

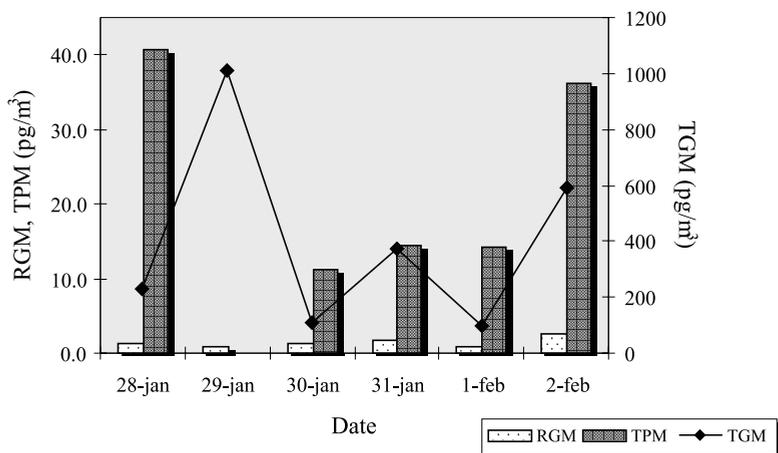


Figure 2. TGM, TPM and RGM concentrations during the sampling period in January, 2004.

## RESULTS AND DISCUSSION

The concentrations of RGM were low, ranging between 3.0 and 5.0 pg m<sup>-3</sup> in November 2003. Even lower RGM values were observed in January 2004 with an average value of 1.3 ± 0.6 pg m<sup>-3</sup>. The concentrations of TGM, TPM and RGM during the sampling period performed in January 2004 are shown graphically in Figure 2.

TGM concentrations were between 0.11 and 1.05 ng m<sup>-3</sup>, reflecting background conditions. TPM concentrations were in the range 11.7-42.7 pg m<sup>-3</sup> representing up to 17 % of the TGM. Fairly low RGM concentrations corresponding to about 1 % of the TGM in the atmosphere were found. These data are

comparable with the concentrations determined in other coastal sea locations near the Mediterranean and fall in the concentration range typical of ambient air in Europe (PIRRONE ET AL., 2001). However, on the basis of these first measurements no conclusions can be obtained and further investigation is needed to understand the observed concentration variations in atmospheric mercury species.

## Acknowledgments

Authors thank Dr. A. Byrne for linguistic corrections. This research was financially supported by the European Commission as a part of the MERCYMS project (Contr. No. EVK3-2002-00070).

## REFERENCES

- BLOOM, N. S. & FITZGERLAD, W. F. (1988): Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold vapor atomic fluorescence detection; *Anal. Chim. Acta* 209, 151-161.
- LANDIS, M. S., STEVENS, R. K., SCHAEDLICH, F. & PRESTBO, E. M. (2002): Development and Characterization of an Annular Denuder Methodology for the Measurement of Divalent Inorganic Reactive Gaseous Mercury in Ambient Air; *Environ. Sci. Technol.* 36, 3000-3009.
- LU, J. Y., SCHROEDER, W. H., BERG, T., MUNTHE, J., SCHNEEBERGER, D. & SCHAEDLICH, F. (1998): A Device for Sampling and Determination of Total Particulate Mercury in Ambient Air; *Anal. Chem.* 70, 2403-2408.
- LU, J. Y., SCHROEDER, W. H. & KEELER, G. (2003): Field intercomparison for evaluation and validation of the AESminiSampler™ technique for sampling and analysis of total particulate mercury in the atmosphere; *Sci. Total Environ.* 304, 115-125.
- PIRRONE, N., MUNTHE, J., BARREGÅRD, L., EHRLICH, H. C., PETERSON, G., FERNANDEZ, R., DOS SANTOS-ALVÉS, S. G., HANSEN, J. C., GRANDJEAN, P., HORVAT, M., STEINNES, E., AHRENS, R., PACYNA, J. M., BOROWIAK, A., BOFFETTA, P. & WICHMANN-FIEBIG, M. (2001): *Ambient air pollution by mercury (Hg)*; Position paper of European Communities, Luxembourg.
- SCHROEDER, W. H. & MUNTHE, J. (1998): Atmospheric mercury – an overview; *Atmos. Environ.* 29, 809-822.
- WÅNGBERG I., EDNER, H., FERRARA, R., LANZILLOTTA, E., MUNTHE, J., SOMMAR, J., SJÖHOLM, M., SVANBERG, S. & WEIBRING, P. (2003): Atmospheric mercury near a chlor-alkali plant in Sweden; *Sci. Total Environ.* 304, 29-41.

## Assessment of anthropogenic mercury emissions from a highly industrialised region of Brazil (Paulínia, São Paulo State)

IGOR R.B. OLIVARES <sup>1</sup>, JOSÉ R. GUIMARÃES <sup>1</sup>, ANNE H. FOSTIER <sup>2</sup>

<sup>1</sup>Faculty of Civil Engineering, UNICAMP, Brasil; E-mail: jorober@fec.unicamp.br

<sup>2</sup>Institute of Chemistry, UNICAMP, Brasil; E-mail: fostier@iqm.unicamp.br

**Abstract:** This work describes the study of anthropogenic mercury emissions in the city of Paulínia (São Paulo State, Brazil), where it was possible to identify at least twelve potential emission sources. Using international emission factors and information obtained for the potential emission sources, it was also possible to estimate the annual anthropogenic mercury emissions into the Paulínia atmosphere at approximately 147.2 kg per year (for the year 2000). The main emission sources were found to be oil and gas combustion (mainly in industrial boilers) and landfill sites (liberation of gases originating from garbage decomposition), which contributed with 32.34 % and 47.65 % respectively. Considering industrialisation as the main factor contributing to the increase of atmospheric mercury emissions and using the Paulínia industrialisation index in relation to Brazil, it was also possible to extrapolate the data obtained in the city to estimate the anthropogenic mercury emissions for the whole of Brazil. The estimated values were compared with values for other countries based on the average emission per person per year. Thus, it was possible to demonstrate that Paulínia presents an anthropogenic mercury emission into the atmosphere of approximately 2.87 g/person/year.

**Key words:** Mercury; Antropic Emissions; Brazil; Atmosphere; Emission Factor.

### INTRODUCTION

Apart from its high toxicity, the most important characteristic of mercury compared to other metals is its capacity to be emitted or re-emitted into the atmosphere, mainly in its elementary gaseous form ( $Hg^0$ ). This emission can originate directly from natural or anthropogenic sources. Due to its properties (low reactivity and low solubility in pure water),  $Hg^0$  presents a residence time in the atmosphere of around one year. This permits its distribution and deposition on a global scale. For this reason the concept “global pollutant” was developed for this element<sup>[1]</sup>.

According to MASON<sup>[2]</sup>, the mercury concentration in the atmosphere tripled over the course of the last century.

Different programs have been developed with the intention of evaluating mercury emissions into the atmosphere. Examples include the report “Mercury Study Report to Congress” in the United States<sup>[3]</sup>, the programs “Mediterranean Atmospheric Mercury Cycle System-MAMCS” and “Mercury over Europe - MOE” in the Mediterranean and North area of Europe<sup>[4]</sup>. More recently, decision 21/5 of the 21<sup>o</sup> (21<sup>st</sup>) session (February, 2001) of the United Nations Environment

Programme (UNEP) resolved to accomplish a global evaluation of mercury with participation of 57 governments, 9 inter-government organisations and 10 non-governmental organisations.

In the Southern Hemisphere, mining activities (gold and silver) were considered as the main mercury sources and data on other anthropogenic sources are scarce<sup>[5]</sup>. However, it should be considered that the productive capacity of several Southern Hemisphere countries has grown significantly over the last decade. Generally this occurs with the relocation of “heavy (dirty)” industries from the Northern Hemisphere, without necessarily being accompanied by regulations that limit emissions. Thus, obtaining and updating data related to anthropogenic mercury emissions into the atmosphere in the main industrial and economical centres of the Southern Hemisphere is indispensable on a regional and global scale in order to clarify the mercury cycle.

In Brazil, the most recent estimate was based on the production and consumption data for 1992 or previous years and some potentially significant sources, such as incineration of hospital residues were not considered<sup>[6]</sup>.

The Paulínia municipality, located in the Campinas Metropolitan Region (São Paulo State, Brazil) has a very expressive industrial area with potential Hg emission sources, such as the largest Brazilian petroleum refinery, petrochemical and chemical industries, oil derivation distributors, an Hg recycling industry, incinerators, etc. In 2000, the daily emissions of SO<sub>2</sub>, NO<sub>x</sub> and particulate matter were estimated to be 73.9 t, 15.8 t and 5.8 t, respectively. In the last decade the

population growth rate, in the Campinas Metropolitan Region was 2.2 % yr<sup>-1</sup>, a little higher than the rate of 1.9 % yr<sup>-1</sup> reported for the entire São Paulo State. During the same period, energy consumption by industrial activities increased 4.0 % yr<sup>-1</sup>, also faster than the 2.8 % observed for São Paulo State.

Among the problems faced due to this accelerated industrial development, was the necessity to compile an updated inventory of anthropogenic mercury emissions. The accelerated industrial development observed in Paulínia makes it an excellent area for the compiling of such an inventory.

## RESULTS AND DISCUSSION

The relationship of the anthropogenic mercury sources existent in Paulínia was obtained using the classification adopted by the U.S.EPA<sup>[3]</sup> in conjunction with information obtained from CETESB (Technology Company of Environmental Sanitation, which is responsible for environmental control in the city) and the city’s Environment and Industry office. With these entities it was possible to obtain information such as the number of industries in the district, pollutant sources, municipal landfills, incinerators and urban garbage destination.

After identifying the potential anthropogenic mercury sources existent in Paulínia, a meticulous study was performed in order to determine how these sources contribute to the atmospheric emission of Hg. This made it possible to decide which information would be necessary to calculate the amount of mercury emitted from these anthropogenic sources, e.g. the amount of mercury used di-

rectly, or the amount of raw material containing the metal used, in a specific process. To obtain this information, technical visits were realised, questionnaires were sent and data from the available literature was also used.

For the calculation of anthropogenic emission different mercury emission factors, for several anthropogenic sources, were applied. This varied for each source and as a function of several parameters. The emission factor used for each source was chosen with the aim of producing the best representation of the reality of the study area.

Of all potential sources of mercury emission identified, only 4 sources were not estimated due to lack of information. However, considering that in other countries these sources were shown to have little significance, it is considered that the non-inclusion of this data will not influence the reliability of results presented in this work.

The result of all anthropogenic mercury emissions into the atmosphere in Paulínia, divided into emission sources is showed in Table 1.

**Table 1.** Amount of mercury emitted into atmosphere in Paulínia for several sources (for the year 2000)

<b>Anthropogenic mercury sources in Paulínia</b>		<b>Amount emitted kg/year</b>	<b>Proportion (%)</b>
Diffuse Sources	F01-Breaking of electric lamps	0.14	0.10%
	F02-Laboratories	- <sup>(1)</sup>	-
	F03-Dental amalgams	0.11	0.08%
	F04-Landfills	70.14	47.65%
	F05-Paint	- <sup>(1)</sup>	-
	F06-Mobile sources (vehicles)	0.751	0.51%
	F07-Agricultural burning	- <sup>(1)</sup>	-
Point Sources	Combustion:		
	F08-Oil / gas	42.33 and 5.27	28.76% and 3.58%
	F09-Incineration of hospital residues	3.45	2.34%
	Industrial production:		
	F10-Eletro-electronic	0	0%
	F11-Recycling of residues with mercury	25	16.98%
	F12-Refineries	- <sup>(1)</sup>	-
Total:		147.2 kg/ano	<b>100%</b>

(1) No estimate due to the lack of information.

Considering that industrial development is the main contribution to atmospheric mercury emission, as the number of anthropogenic mercury sources increases the influence of these sources also increases, it is possible to extrapolate the values obtained for Paulínia to Brazil as a whole. For this calculation, initially the emission average

was calculated per inhabitant for Paulínia and after this (using the industrialisation index for Paulínia in relation to Brazil) it was possible to obtain the emission average per inhabitant in Brazil. These values were compared with the average values for other countries, as is demonstrated in Table 2.

**Table 2.** Average mercury emission for different countries

Place	Emission (g/person.year)
United States <sup>[3]</sup>	0.55 g
Germany <sup>[3]</sup>	0.75 g
Poland <sup>[3]</sup>	0.88 g
England <sup>[3]</sup>	0.90 g
Average in Europe <sup>[3]</sup>	1.2 g
Paulínia (This work)	2.87 g
Brazil (This work)	0.74 g

Finally, considering Brazil's population, it was possible to estimate the overall anthropogenic mercury emission into the atmosphere from industrial sources at approximately 125 tons per year, without considering the gold mining industry.

From the results presented, it was possible to observe that the sources which contribute most significantly to mercury emission are those where the mercury does not appear explicitly, as for instance emissions originating from landfills and oil and gas combustion. However, these sources do not present mercury in an explicit manner as a primary pollutant, but in small concentrations. For this reason a great difficulty exists in quantifying such sources due to the great variation in the mercury concentration. For example, the mercury concentration in petroleum and natural gas varies between 0.01 ppb and 10 ppm (m/m)<sup>[7]</sup> in different regions. This

highlights the well-known need to develop studies to determine in a precise way the contribution of mercury emission from different sources.

## CONCLUSIONS

In spite of being a small municipal district (with 51.290 inhabitants), due its accelerated industrial development, Paulínia behaves as a region with great potential to emit mercury into the atmosphere. The results of this work suggest that it is not only necessary to focus on mercury emission from activities that directly use this element, but also on sources present in great, industrialised centres. Such sources can contribute considerably to mercury emission and are not duly recognised and quantified in research concerning the cycle and transport of this element in the environment.

## REFERENCES

- [1] SCHROEDER, W. H. AND MUNTHE, J. (1998): Atmospheric mercury- an overview; *Atmospheric Environment* 32, pp. 809-822.
- [2] MASON, R. P., FITZGERALDO, W. F. (1994): The biogeochemical cycling of elemental mercury - Anthropogenic Influences; *Geochimica et Cosmochimica Acta* 58(15), pp. 3191-3198.
- [3] U.S. EPA (1997): *Mercury Study Report to Congress*. Volume II: An inventory of anthropogenic mercury emission in the United States; EPA-452/R-97-004.
- [4] PIRRONE, N. (2000): *Mercury research in Europe: towards the preparation of the New EU Air Quality Directive*; In: 11<sup>th</sup> Annual International Conference on Heavy Metals in the Environment (J. NRIAGU, Editor), University of Michigan, School of Public Health, Ann Arbor, MI, CD-ROM, Contribution #1010.
- [5] RAMEL, C. (1996): SCOPE Project: Evaluation of the role and distribution of mercury on ecosystem with special emphasis on tropical regions; In *Global and Regional Mercury Cycles*, NATO Advanced Science Institute Serie (R. EDINGHAUS, W. BAYENS AND O. VASILIEV, Eds.), Novosibersk, Siberia. Kluwer, Dordrecht, Holland, pp. 505-513.
- [6] LACERDA, L. D. AND MARINS, R. V. (1997): Anthropogenic mercury emissions to the atmosphere in Brazil: the impact of gold mining; *J. Geochem. Exploration* 58, pp. 223-229.
- [7] WILHELM, M., BLOOM, N. (2000): Mercury in petroleum; *Fuel Processing Technology* 63, pp. 1-27.

# Global Anthropogenic Sources and Emissions of Mercury in 2000

JOZEF M. PACYNA<sup>1</sup>, ELISABETH G. PACYNA<sup>1</sup>, FRITS STEENHUISEN<sup>2</sup> & SIMON WILSON<sup>3</sup>

<sup>1</sup>Norwegian Institute for Air Research (NILU), Kjeller, Norway

<sup>2</sup>Arctic Centre, University of Groningen, Groningen, Netherlands, The

<sup>3</sup>Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway

## 1. GOALS

- Present contributions from major source categories in different continents to the global mercury emission.
- Present emission maps for mercury and its major chemical species emitted from various sources.
- Compare mercury emissions in 2000 and 1990.

## 2. METHODOLOGY

Two approaches were used:

- collection of emission data from countries where such data were estimated by national emission experts, mostly in Europe and North America, and
- estimates of emission on the basis of emission factors and statistical data on the production of industrial goods and/or the consumption of raw materials. These estimates were carried out by the authors for the countries where national estimates were not available.

The data on emissions of total Hg and its three major chemical species from point and area sources were then spatially distributed within the grid system of 1° x 1°.

Details on methodology of emission estimates and mapping are available from PACYNA and PACYNA (2002) and PACYNA ET AL. (2003).

## 3. MAJOR CONCLUSIONS

- Three-quarters of the total 2000 Hg emissions were attributed to combustion of fossil fuels, in particular coal combustion in China, India, and South and North Korea.
- The Asian countries contributed about 53 % of the global Hg emissions to the atmosphere.
- The major chemical form of emitted Hg is gaseous elemental mercury (GEM), contributing about 53% of the total emissions, followed by gaseous divalent mercury with 37 %.
- An increase of Hg emissions in Asia between 1990 and 2003 can be related to the increasing demands for energy in this region. A decrease of Hg emissions in Europe and North America can be related to the continuous improvement of emission controls in these regions.

**REFERENCES**

- PACZYNA E.G., PACZYNA, J.M., 2002. Global emission of mercury from anthropogenic sources in 1995. *Water, Air and Soil Pollution*, 137,149-165.
- PACZYNA J.M., PACZYNA E.G., STEENHUISEN F., WILSON S., 2003. Mapping 1995 global anthropogenic emissions of mercury. *Atmospheric Environment*, 37, 109-117.

# Atmospheric transformation of elemental mercury upon hydroxyl radicals under near tropospheric conditions

BISWAJIT PAL AND PARISA A. ARIYA\*

Departments of Chemistry, and Atmospheric and Oceanic Sciences, McGill University, 801 Sherbrooke St. W., Montreal, PQ, H3A 2K6, Canada; \*E-mail: parisa.ariya@mcgill.ca

**Abstract:** Mercury is a trace element of special concern because of the toxicological and biogeochemical behaviour of its oxidised products, which undergoes deposition and can become subject to bioaccumulation. The oxidation by HO radicals is an important pathway for the removal of molecules in the atmosphere including  $\text{Hg}^0$ . In order to ascertain the environmental impact of the oxidation mercury and to provide further understanding of geochemical Hg cycling, we herein carried out kinetics and product studies under near atmospheric pressure ( $750 \pm 1$  Torr) in air diluents. Kinetics of the reactions with HO radicals was studied using a relative rate method by gas chromatography with mass spectroscopic detection (GC-MS). HO radicals were produced by photolysis ( $300 \leq \lambda \leq 400$  nm) of isopropyl nitrite. Products were analysed in the gas form, aerosols and deposits on the walls using direct MS.

**Key words:** Atmospheric reaction, Relative rate technique, Mercury, Hydroxyl radicals

## INTRODUCTION

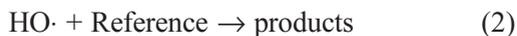
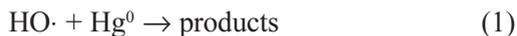
Mercury has been considered highly dangerous heavy metals present in the environment and is one of the major pollutants in the Arctic environment. The emission of mercury into the atmosphere from a variety of natural and anthropogenic sources, its long-range transport, and deposition followed by bioaccumulation in the food webs is a critical issue from a human health perspective<sup>[1, 2]</sup>. Rapid conversion of mercury to the reactive gaseous mercury and subsequent removal from the atmospheric boundary during spring has been observed in the high-Arctic region<sup>[3]</sup>, Arctic<sup>[4]</sup>, sub-Arctic<sup>[5]</sup> and is associated with surface snow and ice<sup>[6]</sup>. It is noted in the literature that the rapid transformation of elemental mercury ( $\text{Hg}^0$ ) to divalent mercury ( $\text{Hg}^{\text{II}}$ ) is due to high concentra-

tions of halogen species (e.g., Br, BrO)<sup>[7-10]</sup>. Very few kinetic data's are available in the literature for the reaction of various mercury species and free radicals (e.g., HO·,  $\text{HO}_2\cdot$  and  $\text{NO}_3\cdot$ )<sup>[11, 12]</sup> and it is suggested that further kinetic studies of the reaction of mercury and radicals are required to better describe the fate of atmospheric mercury. HO· is highly reactive species in the troposphere produced by a variety of photochemical processes and a major daytime oxidant for initiating oxidation of trace compounds in the atmosphere including  $\text{Hg}^0$ . Recently it has been proposed that HO radical is the dominant source of the sink of the tropospheric  $\text{Hg}^0$ <sup>[13, 14]</sup>. An attempt has therefore been made to investigate the oxidation of  $\text{Hg}^0$  by HO· and its possible impact on the global cycle of  $\text{Hg}^0$ . In this study we report the kinetics and product of gas phase reactions of  $\text{Hg}^0$  with HO·

under near atmospheric condition using relative rate technique by gas chromatography with mass spectroscopic detection (GC-MS).

## EXPERIMENTAL

The kinetic experiments on the reaction of HO radicals with Hg<sup>0</sup> were carried at 298 ± 1 K and 750 Torr of total pressure of synthetic air. We used the relative rate technique to perform kinetic studies, which is based on the measurement of disappearance of rate of mercury of interest and a reference molecule in the presence of HO·.



Provided that Hg<sup>0</sup> and the reference are removed solely by reaction with HO radicals, then

$$\ln\left\{\frac{[\text{Hg}]_0}{[\text{Hg}]_t}\right\} = k_1/k_2 \ln\left\{\frac{[\text{Reference}]_0}{[\text{Reference}]_t}\right\} \quad (3)$$

where [Hg]<sub>0</sub> and [Reference]<sub>0</sub> are the concentrations of Hg<sup>0</sup> and the reference compound, respectively at time 0; [Hg]<sub>t</sub> and [Reference]<sub>t</sub> are the corresponding concentration at time t; k<sub>1</sub> and k<sub>2</sub> are the rate coefficients for reactions (1) and (2), respectively.

The decay of mercury and reference upon photolysis of the reaction mixture were measured by MS (quadruple MSD HP5973) after a separation on gas chromatograph equipped with 0.25 mm ID x 30 m crossed linked phenyl-methyl-siloxane column using SIM mode. Experiments were carried out in a temperature controlled double-walled 3-1 Pyrex flask.

Hydroxyl radicals were generated by the photolysis (300 ≤ λ ≤ 400 nm) of isopropyl nitrite in presence of NO using synthetic air as diluent gas. Total irradiation times ranged from 15 to 30 min. The kinetic experiments were carried out relative to cyclohexane and n-butane. The approximate initial concentration of the reactants were as follows: Hg<sup>0</sup>, 0.5 ppm, reference, 5 ppm, isopropyl nitrite, 60 ppm, and NO, 10 ppm.

All chemicals used had a stated manufactured purity of >99 %. Isopropyl nitrite was prepared by the action of nitrous acid and isopropyl alcohol at 0 °C.

## RESULTS AND DISCUSSION

In order to avoid wall loss of the compounds, the reaction flask walls were coated with halocarbon wax before the kinetic run<sup>[15]</sup>. Preliminary experiments showed that there is no dark reaction between HO radical source, reference molecule, and Hg<sup>0</sup> of interest. As depicted in Figure 1, plots of the relative loss of Hg<sup>0</sup> and reference compound upon reaction led to straight lines with almost zero intercepts. An upper limit for the gas phase rate coefficient for reaction between elemental mercury and HO radicals was determined to be of the order of 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

The direct reaction between Hg<sup>0</sup> and HO· has been discounted as HgO and the H atom was produced with a very positive reaction enthalpy, 49.4 ± 7.9 kcal mol<sup>-1</sup> [16]. Many oxidation species are expected to react via multi step reaction mechanisms involving the formation of various intermediates that may be thermodynamically favorable even if for-

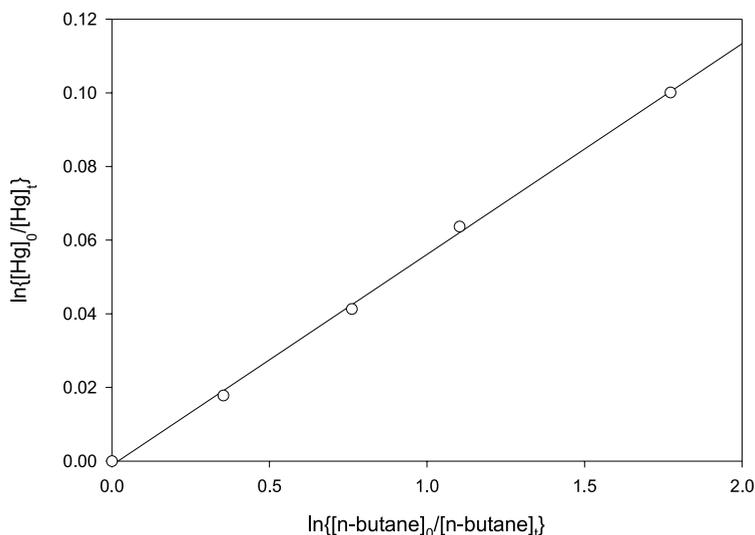
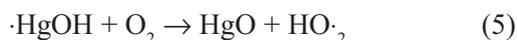


Figure 1. Typical relative rate plot for the reaction of  $Hg^0$  with  $HO\cdot$  at 298 K.

mation of products is unfavorable, leading to reasonably fast reaction rates. Using relativistic quantum chemical methods it has shown this reaction to produce the  $\times HgOH$  intermediate instead, with almost zero thermal effect ( $-1.4 \text{ kcal mol}^{-1}$ )<sup>[17]</sup>, which is then reacts with  $O_2$ .



Reaction products were collected by a flow of gas from a reaction flask through a Pyrex tube, which was inserted in liquid nitrogen. Condensed products were analyzed in chemical ionization ion source of a Kratos MS25RFA mass spectrometer. Under the

experimental condition we identified  $HgO$  as reaction product. The observed kinetic data provides evidence that the reactions of mercury with hydroxyl radicals are quite significant in the transformation of tropospheric mercury. Moreover, the identified product,  $HgO$  is more soluble than elemental mercury and, hence subject to bioaccumulation.

### Acknowledgements

We cordially thank to the Natural Science and Engineering Research Council of Canada (NSERC), the Fond pour la Formation de Chercheurs et l'Aide a la Recherche (FCAR), the Canadian Foundation for Innovation (CFI), the COMERN project, and Environment Canada for financial support.

## REFERENCES

- [1] LINDQVIST, O., RODHE, H. (1985): *Tellus*, Vol. 37B, pp.136-159.
- [2] GARDFELDT, K., SOMMAR, J., STROMBERG, D., FENG, X. (2001): *Atmos. Environ.*; Vol. 35, pp. 3039-3047.
- [3] SCHROEDER, W. H., ANLAUF, K. G., BARRIE, L. A., LU, J. Y., STEFFEN, A., SCHNEEBERGER, D. R., BERG, T. (1998): *Nature*, Vol. 394, pp. 331-332.
- [4] LINDBERG, S. E., BROOKS, S., LIN, C. J., SCOTT, K. J., LANDIS, M. S., STEVENS, R. K., GOODSITE, M., RICHTER, A. (2002): *Environ. Sci. Tech.*, Vol. 36, pp. 1245-1256.
- [5] POISSANT, L. (2001): personal communication.
- [6] LU, J. Y., SCHROEDER, W. H., BARRIE, L. A., STEFFEN, A., WELCH, H. E., MARTIN, K., LOCKHART, L., HUNT, R. V., BOILA, G., RICHTER, A. (2001): *Geophys. Res. Lett.*, Vol. 28, pp. 3219-3222.
- [7] BOTTENHEIM, J. W., FUENTES, J. D., TARASICK, D. W., ANLAUF, K. G. (2002) : *Atmos. Environ.*, Vol. 36, pp. 2535-2544.
- [8] SPICER, C. W., PLASTRIDGE, R. A., FOSTER, K. L., FINLAYSON-PITTS, J., BOTTENHEIM, J. W., GRANNAS, A. M., SHEPSON, P. B. (2002): *Atmos. Environ.*, Vol. 36, pp. 2721-2731.
- [9] ARIYA, P. A., KHALIZOV, A., GIDAS, A. (2002): *J. Phys. Chem.*, Vol. 106, pp. 7310-7320.
- [10] RAOFIE, F., ARIYA, P. A. (2003): *J. Phys. IV*, Vol. 107, pp. 1119-1121.
- [11] LIN, C. -J., PEHKONEN, S. O. (1997): *Atms. Environ.*, Vol. 31, pp. 4125-4137.
- [12] SOMMAR, J., HALLQUIST, M., LJUNGSTRÖM, E., LINDQVIST, O. (1997): *J. Atmos. Chem.*, Vol. 27, pp. 23-247.
- [13] SOMMAR, J., GARDFELDT, K., STROMBERG, D., FENG, X. (2001): *Atmos. Environ.*, Vol. 35, pp. 3049-3054.
- [14] BAUER, D., D'OTTONE, L., CAMPUZANO-JOST, P., HYNES, A. J. (2003): *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 157, pp. 247-256.
- [15] PAL, B., ARIYA, P. A. (2004): *Phys. Chem. Chem. Phys.*, Vol. 6, pp. 572-579.
- [16] YARWOOD, G., NIKI, H. (1990): A critical review of available information on transformation pathways for mercury species in the atmospheric environment; Centre for Atmospheric Chemistry and York University: Toronto 1990.
- [17] STROMBERG, D. (1990): Ph.D. Thesis, Goteborg University and Chalmrs University of Technology 1990.

# Mercury and Methyl Mercury in Precipitation Impacting the Venice Lagoon

JENNIFER L. PARKER<sup>1</sup>, NICOLAS S BLOOM<sup>1</sup>, AND LIGIA M. MORETTO<sup>2</sup>

<sup>1</sup>Frontier Geosciences, 414 Pontius North, Seattle, WA 98109 USA;

E-mail: jennp@frontiergeosciences.com

<sup>2</sup>Universita Ca'Foscari, Santa Marta, 2137 Venice (30123) Italy; E-mail: moretto@unive.it

**Abstract:** Atmospheric deposition of natural and anthropogenically derived mercury (Hg) is a significant source to most aquatic systems. In this study, precipitation samples were collected from a rooftop in Mestre, Italy over a 1-year period from May 2002 to June 2003. Samples were also collected from locations in Venice and Lido for approximately 3 months each during the autumn of 2002. Total Hg concentrations were randomly distributed throughout the year, with an average concentration ( $n = 46$  samples) of  $20.6 \pm 17.0$  ng L<sup>-1</sup> Hg, while monthly deposition was greatest in the spring and summer. Methyl Hg (CH<sub>3</sub>Hg) had a mean concentration of  $0.083 \pm 0.112$  ng L<sup>-1</sup> as Hg, and showed a strong seasonal pattern of highest concentrations and greatest deposition in the autumn and winter. The mean fraction of CH<sub>3</sub>Hg to total Hg in rainfall (0.54 %) was much lower than the percentage of CH<sub>3</sub>Hg found in three nearby rivers (2-14 %). Thus, it is likely that most of the CH<sub>3</sub>Hg in the rivers is produced *in situ*, with atmospheric deposition serving as an important source for methylation.

**Key words:** Rain, Speciation, Venice

## INTRODUCTION

Atmospheric deposition of natural and anthropogenically derived Hg is a significant source to most aquatic systems via direct deposition to the water surface or as watershed runoff (MASON ET AL., 1994). However, the long residence time of Hg in the atmosphere results in large-scale transport and redistribution (FITZGERALD ET AL., 1998; BULLOCK ET AL., 1998), making it difficult to discern the relationship between source and environmental effect. Because the consumption of aquatic biota is the dominant Hg exposure pathway to humans, and Hg concentrations in these organisms is directly linked to atmospheric deposition (ROLFUS ET AL.,

1995), measuring Hg concentrations in precipitation is an essential step in understanding Hg dynamics and forecasting Hg contamination. The objective of this study was to evaluate the atmospheric deposition of total and CH<sub>3</sub>Hg of the northern Venice Lagoon.

## RESULTS AND DISCUSSION

*Methodology.* Precipitation samples were collected from a rooftop in Mestre, Italy over a 1-year period from May 2002 to June 2003. Samples were also collected from locations in Venice and Lido for approximately 3 months each during the autumn of 2002.

Samples were collected as bulk deposition, using continuously open 10 cm diameter Teflon funnels, which drained directly to 250 mL HCl-preserved Teflon bottles. Sample bottles were changed approximately on a 0.5-2 week schedule, depending upon the amount of rainfall during the period, such that almost all precipitation during the study period was collected. Samples were shipped via express courier to the analytical laboratory in Seattle, where they were quantified for total Hg and CH<sub>3</sub>Hg (and other trace metals reported elsewhere) using cold vapour atomic fluorescence spectrometry (CVAFS). Total Hg was defined as the BrCl oxidizable Hg, which is released by SnCl<sub>2</sub> reduction and purging onto gold, while CH<sub>3</sub>Hg was extracted after distillation, by aqueous phase ethylation and isothermal GC separation prior to the CVAFS detection (BLOOM AND CRECELIUS, 1983; BLOOM AND FITZGERALD, 1988).

**Results.** The total amount of rainfall recorded for Venice (March 2002 - April 2003) was 0.98 m yr<sup>-1</sup>, and monthly data are shown in Figure 1. Hg concentrations were randomly distributed throughout the year, with an average concentration (n = 46 samples) of 20.6

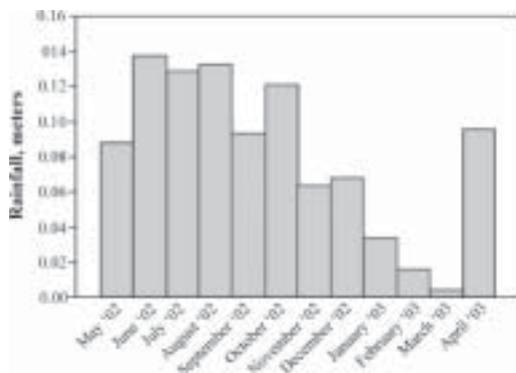


Figure 1. Monthly rainfall data for Venice from the Istituto Cavani (Osservatorio Meteorologico).

$\pm 17.0$  ng L<sup>-1</sup> Hg (Figure 2). CH<sub>3</sub>Hg, on the other hand, had a mean concentration of  $0.083 \pm 0.112$  ng L<sup>-1</sup> and showed a strong seasonal pattern of highest values in the autumn and winter, and very low concentrations during summer (Figure 2). No correlations were found between total Hg and CH<sub>3</sub>Hg concentrations.

Typically, most of the Hg in atmospheric deposition is ionic and less than 1 % of the total is CH<sub>3</sub>Hg (MASON ET AL., 1997; LAMBORG ET AL., 1999). In contrast, CH<sub>3</sub>Hg in rivers, lakes, and coastal waters generally represents a larger fraction of the total (BENOIT ET AL., 1998; MASON ET AL., 1999). Our data were consistent with the literature, as methyl Hg concentrations from all sites were on average 0.54 % of the total Hg concentration (Figure 4). Furthermore, the percentage of dissolved methyl Hg concentrations in nearby rivers (Dese = 2.0 %, Fusina = 8.7 %, and Porte Grandi = 14.3 %) represented a much greater fraction of total Hg than in rainfall.

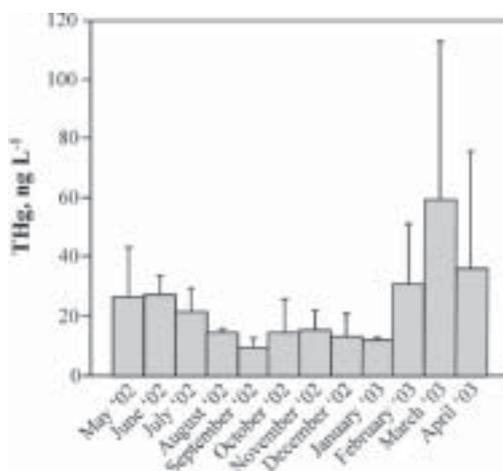
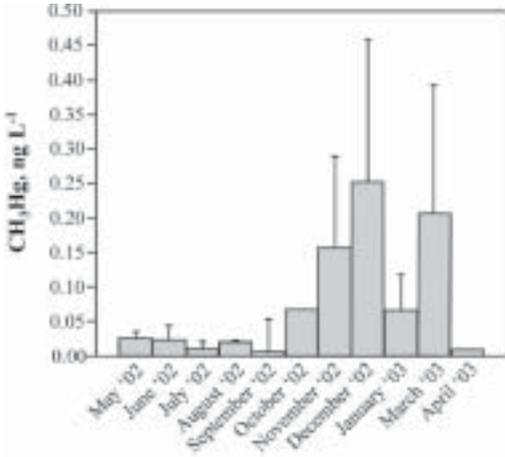
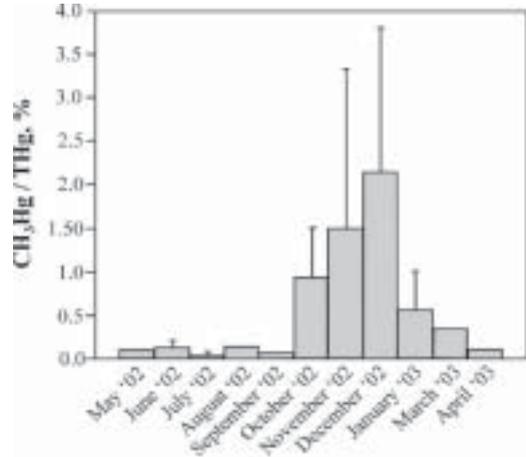


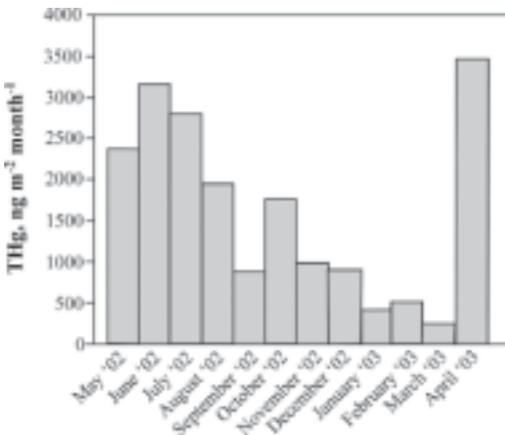
Figure 2. Mean total Hg concentrations in rainfall collected in northern Italy (Mestre, Venice, and Lido).



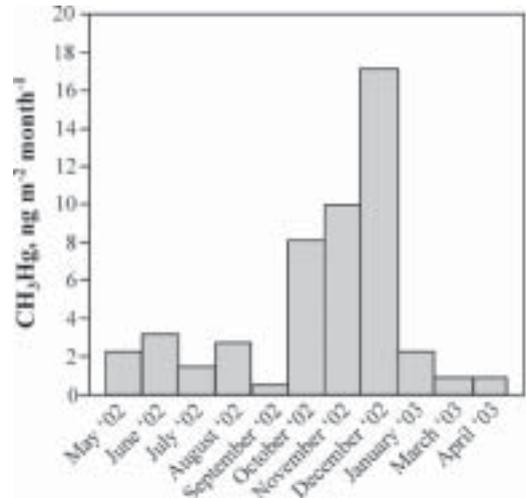
**Figure 3.** Mean CH<sub>3</sub>Hg concentrations in rainfall collected in northern Italy (Mestre, Venice, and Lido).



**Figure 4.** Mean fraction of CH<sub>3</sub>Hg to total Hg in rainfall collected in northern Italy (Mestre, Venice, and Lido).



**Figure 5.** Mean monthly total Hg deposition in the northern Venice Lagoon (2002-2003).



**Figure 6.** Mean monthly CH<sub>3</sub>Hg deposition in the northern Venice Lagoon (2002-2003).

In order to calculate monthly Hg deposition for the northern Lagoon, we used monthly rainfall depth measurements for Venice from the Istituto Cavanis (Osservatorio Meteorologico). Figure 5 shows that mean monthly total Hg deposition was greatest in the spring (2031 ng m<sup>-2</sup> month<sup>-1</sup>, March-May) and summer (2639 ng m<sup>-2</sup> month<sup>-1</sup>, June-August).

Interestingly, we found the opposite trend for CH<sub>3</sub>Hg deposition (Figure 6), with the greatest deposition in the autumn (6.20 ng m<sup>-2</sup> month<sup>-1</sup>, September-November) and winter (6.47 ng m<sup>-2</sup> month<sup>-1</sup>, December-February). These results warrant further investigation of the seasonal Hg deposition patterns in the Venice Lagoon.

## CONCLUSIONS

In general, total Hg concentrations were randomly distributed throughout the year, however, total Hg deposition was greatest in the spring and summer months. In contrast, CH<sub>3</sub>Hg showed a trend of higher concentrations and deposition in the fall and winter. Total Hg deposition was estimated to be 19.5 µg m<sup>-2</sup> yr<sup>-1</sup>, which is comparable to values (4-22 µg m<sup>-2</sup> yr<sup>-1</sup>) seen across the United States between 1995 and 2002. CH<sub>3</sub>Hg deposition was 0.049 µg m<sup>-2</sup> yr<sup>-1</sup>, lower than values found in the mid-western United States between 1995 and 2002 (0.41-1.11 µg m<sup>-2</sup> yr<sup>-1</sup>). On average, CH<sub>3</sub>Hg was 0.54 % of the total

Hg concentration in the northern Lagoon, and the percentage of dissolved CH<sub>3</sub>Hg in three nearby rivers ranged from 2-14 %. It is likely that most of the CH<sub>3</sub>Hg in these rivers is produced *in situ*, with atmospheric deposition serving as an important source for subsequent methylation. Over the period in which samples were collected at 3 sites on an east-west transect across the northern Lagoon, no significant differences were seen between the sites. This suggests both that deposition data from a single site is sufficient to characterize the Hg concentrations in precipitation to the northern Lagoon, and further, that there are not significant local sources of water soluble or particulate Hg to the regional atmosphere.

## REFERENCES

- BENOIT, J. M., FITZGERALD, W. F. AND DAMMAN, A. W. F. (1998): *Mercury Pollution Integration and Synthesis*; (WATRAS, C. J. AND HUCKABEE, J. W., Eds.), Lewis Publishers, Boca Raton, FL, USA, pp. 187-202.
- BLOOM, N. S AND CRECELIUS, E. A. (1983): *Mar. Chem.* Vol. 14, pp. 49-59.
- BLOOM, N. S AND FITZGERALD, W. F. (1988): *Anal. Chim. Acta.* Vol. 208, pp. 151-161.
- BULLOCK, R. O., BREHME, K. A. AND MAPP, G. R. (1998): *Sci. Tot. Environ.* Vol. 213, pp. 1-12.
- FITZGERALD, W. F., ENGSTROM, D. R., MASON, R. P. AND NATER, E. A. (1998): *Environ. Sci. Technol.* Vol. 32, No 1. pp. 1-7.
- LAMBORG, C. H., ROLFUS, K. R. AND FITZGERALD, W. F. (1999): *Deep-Sea Res. II.* Vol. 46, pp. 957-977.
- ROLFUS, K. R., FITZGERALD, W. F. (1995): *Water Air Soil Pollut.* Vol. 80, pp. 291-297.
- MASON, R. P., LAWSON, N. M., AND SULLIVAN, K. A. (1997): *Atm. Environ.* Vol. 31, pp. 3531-3550.
- MASON, R. P., LAWSON, N. M., LAWRENCE, A. L., LEE, J. G., LEANER, J. J., SHEU, G. R. (1999): *Marine Chem.*, Vol. 65, pp. 77-96.

# Investigating Mercury Re-Emission from Boreal Uplands and Wetlands: Latest Results from the Experimental Lakes Area, Canada

MARK PETERSON<sup>1</sup>, STEVE LINDBERG<sup>1</sup>, GEORGE SOUTHWORTH<sup>1</sup>,  
MARY ANNA BOGLE<sup>1</sup>, JENNY GRAYDON<sup>2</sup>

<sup>1</sup>Oak Ridge National Laboratory, USA; E-mail: petersonmj@ornl.gov

<sup>2</sup>University of Alberta, E-mail: jgraydon@ualberta.ca

**Abstract:** Mercury evasion over boreal upland and wetland surfaces was investigated over a three-year period (2001-2003) within the Experimental Lakes Area (ELA) of Canada. Our studies focused on understanding the magnitude and rate of mercury re-emission (i.e., the evasion of newly deposited mercury), the many factors that affect measured fluxes, and the role of re-emission in understanding the overall mass balance equation for the ecosystem.

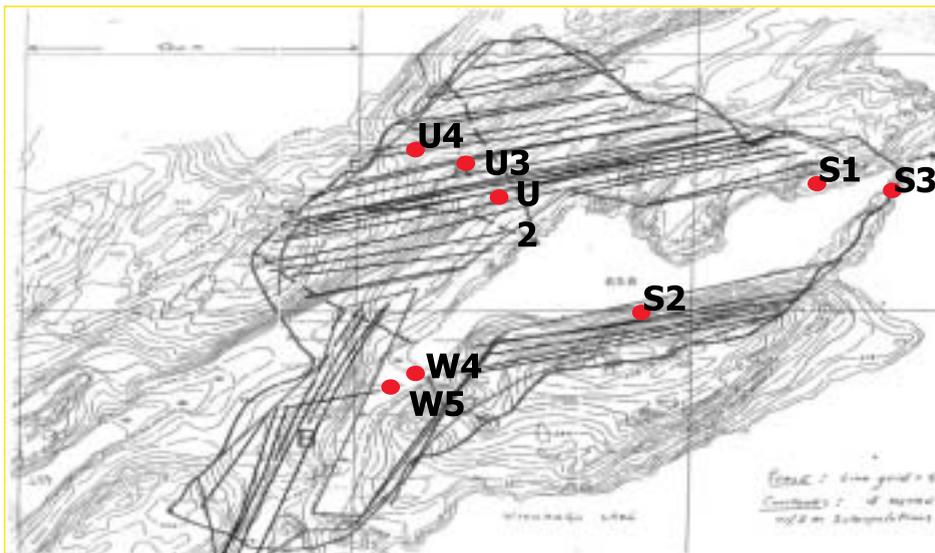
**Key words:** Mercury, Re-emission, Boreal uplands, Flux, Mass balance

## INTRODUCTION

The role of recent anthropogenic mercury emissions on mercury deposition and bioavailability, relative to the role of natural or “old” mercury, is a broad objective of METAALICUS (Mercury Experiment to Assess Atmospheric Loading in Canada and the U.S.), a multi-organizational, watershed-scale study being conducted within the Experimental Lakes Area of Canada. The METAALICUS studies will provide insight as to whether recent regulatory-driven reductions in industrial mercury emissions result in the desired reductions in ecosystem mercury levels. Our studies have focused on understanding the mercury re-emission part of the mass balance equation for the watershed.

Natural surfaces emit both natural Hg (geologic Hg) and Hg from recent atmospheric deposition. To differentiate recently deposited

mercury from the large pools of native mercury, three stable, non-radioactive isotopes of inorganic mercury (as Hg-II) were added experimentally to a small Boreal lake, its associated wetlands, and the surrounding uplands (202Hg, 198Hg, and 200Hg respectively). The uplands and/or wetlands were sprayed with isotope by plane (at ~ 12 to 25  $\mu\text{g}/\text{m}^2/\text{yr}$ ) during spring-time precipitation events from 2001-2003. To prevent drift, the upland lake margin was sprayed by hand. Dynamic flux chambers were used to measure mercury isotope re-emission from small trees (representing canopy evasion), and variable ground surfaces (rock, soil, water, and vegetation) at multiple upland and wetland locations during the growing season (Fig. 1). Flux measurements were focused on the period shortly after application (hours-days), when losses to the atmosphere were presumed to be greatest, but also included measures at 3-month, 6-month, and 1-year post-spray.

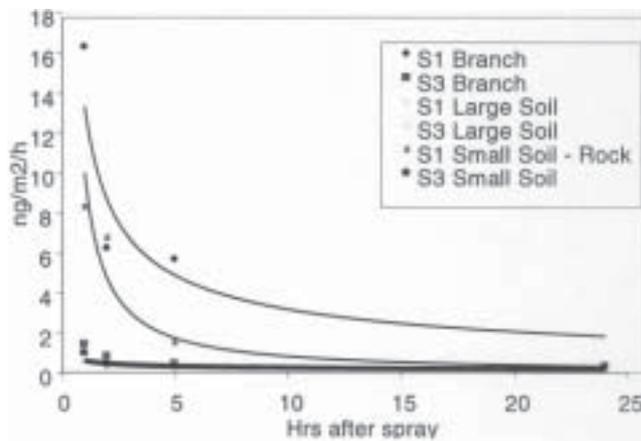


**Figure 1.** Monitoring locations for mercury flux measurements obtained in the 2001-2003 time period around Lake 658, Experimental Lakes Area, Canada. Site naming conventions “U”, “W”, and “S” indicate upland, wetland, and shoreline locations respectively. Lines show plane spray trajectories in 2002.

## RESULTS AND DISCUSSION

Photoreduction and re-emission of newly-deposited mercury occurred rapidly over both upland and wetland surfaces. Fluxes were highest within minutes of application

at all monitored sites, and decreased 5-10 fold within 1-2 days at rates well fit by a power curve ( $r^2 > 0.8$ ). For a one year application, fluxes were  $< 20 \text{ ng/m}^2/\text{hr}$  immediately after spray, and decreased dramatically within 2 days. Fluxes were proportional to

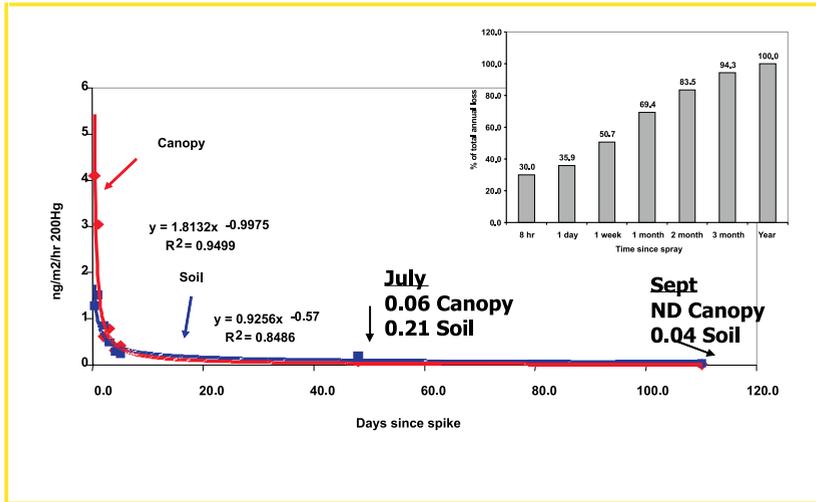


**Figure 2.** Measured fluxes over 24-hr period at sites receiving a 1-yr application rate in 2003, when fluxes were determined immediately after the spray ( $< 1 \text{ hr}$ ).

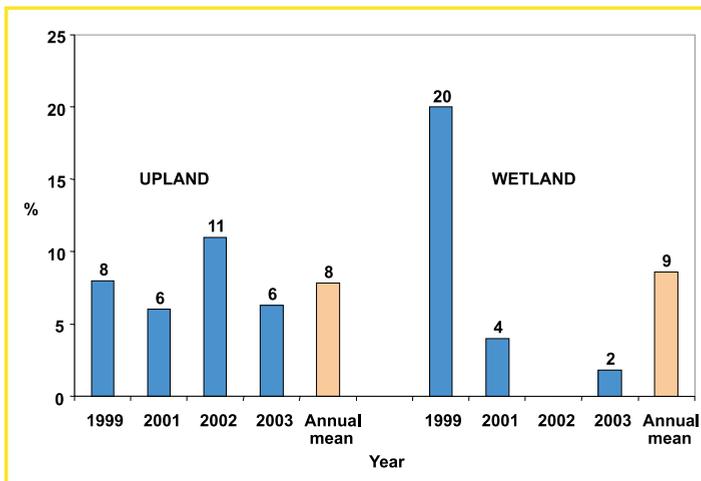
application rate, with fluxes near 90 ng/m<sup>2</sup>/hr measured at a site that receiving a 3X higher application.

Low fluxes were measured approximately one month post-spray, but re-emission was

marginally detectable at the end of the growing season (Fig. 3). At both a wetland and shoreline sampling site, measured fluxes were at or near the detection limit after one year. In general, when all site, year, and surface data (soil and canopy) are combined,



**Figure 3.** Hg-200 re-emission at the upland U3 site over the 2002 growing season. Soil chamber values for each sampling time were averaged. Inset shows the % of total annual loss for pre-designated time periods.



**Figure 4.** Estimate of percent annual re-emission of applied Hg-200 pool based on 100-day growing season. The 1999 data is from a preliminary ELA field experiment not part of the Lake 658 upland spray study.

approximately 1/3 of the total annual loss was lost during the first 8 hours, approximately 50 % by the first week, 75 % by the first month, and less than 25 % over the last 30-110 day period (Fig. 3 inset).

In general, measured fluxes were 1 – 3 X higher from the canopy than soil surfaces. Wetland fluxes were a factor of two higher than upland in preliminary 1999 studies, but recent comparisons suggest little difference. Mercury fluxes from bare rock, particularly for the first hours after application, were an order of magnitude higher than from nearby soil.

Using a simple mass balance, we estimate approximately 5-10 % of newly deposited mercury on uplands and wetlands was re-emitted (Fig. 4), with considerable site-specific and annual variation. If we assume the initial flux represents the “fresh deposition” re-emission rate, and the steady-state rate represents that of “older deposition,” this simple model suggests that ~40-60 % of the native Hg emission from upland surfaces at ELA consists of re-emitted deposition.

## CONCLUSIONS

Mercury evasion studies conducted at ELA over the last 5 years have provided useful information in understanding the magnitude and rate of re-emission of newly deposited mercury. Even when worst-case assumptions are used to scale up these data, the annual percent re-emission loss of the mercury pool was estimated below 20 %. Key additional findings include the importance of the first few hours/days immediately after a precipitation event, the type of soil or vegetation surface, and the solar intensity soon after deposition. Other potential factors like chamber type, flow rate, and wind speed were not deemed to be significant influences on measured fluxes in these studies.

## Acknowledgements

Appreciation is extended to the Department of Energy’s Office of Science who funded this research. Prepared by Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6285, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725.

## An Integrated Approach to Assess the Mercury Cycling in the Mediterranean Basin - The MERCYMS Project

NICOLA PIRRONE

CNR-Institute for Atmospheric Pollution, 87036 Rende, Italy  
E-mail: n.pirrone@cs.iiia.cnr.it

**Abstract:** The MERCYMS project is aimed to investigate dynamic patterns affecting the cycle of mercury within and between atmospheric and marine ecosystems of the Mediterranean basin. Within MERCYMS several on-shore and off-shore intensive measurement campaigns have already been performed and more are planned for the next two years. Meanwhile, ad-hoc atmospheric and water models have been developed and tested to assess the relative contributions of different patterns affecting the transport, transformations and transfer to and/or exchange fluxes of mercury compounds between the marine and atmospheric compartments. The integrated atmospheric-water modelling system is part of a policy tool where socio-economic models are used to analyse the effectiveness of current control policy and evaluate possible future strategies aimed to reduce the risk associated to mercury exposure.

**Key words:** mercury, modelling, socio-economic analysis, measurements, atmosphere, water

### INTRODUCTION

It is well known that mercury is released to the environment from a multitude of natural and anthropogenic sources (PIRRONE ET AL., 1996; PIRRONE ET AL., 2001). Once released to soil, water and atmospheric ecosystems it can be re-distributed in the environment through a complex combination of chemical, physical and biological processes that can act with different time scales (e.g., PIRRONE ET AL. 2000; SPROVIERI ET AL. 2003; HEDGECOCK ET AL. 2003). The relationship between the atmospheric input - the cycle in the marine environment and the re-emissions back to the atmosphere is not yet fully understood (FERRARA ET AL. 2000; MASON ET AL. 2003; PIRRONE ET AL. 2003; HEDGECOCK AND PIRRONE, 2004).

Recent surveys carried out by major international environmental and economic organisations (i.e., UNEP, World Bank, EEA) show that about 60 % of the world population lives within 60 kilometres of the coast-

INSTITUTIONS	RESPONSIBLE SCIENTISTS
CNR-IIA Rende, Italy	Nicola Pirrone Project Co-ordinator
IASA Athens, Greece	George Kallos
NILU Kjeller, Norway and NILU Polshe Ltd., Poland	Josef Pacyna
IVL, Sweden	John Munthe
Univ. Goteborg, Sweden	Oliver Lindqvist
IJS, Slovenia	Milena Horvat
TECHNION, Israel	Yaacov Mamane
IEIA, Poland	Janina Fudala
LCABIE, France	Olivier Donard
CNR-IB, Italy	Romano Ferrara
UOL, Slovenia	Rudi Rajar
European Commission	Hartmut Barth

line and more than 3 billion people rely in some manner on coastal and marine habitats for food, building sites, transportation, recreation and waste disposal. Nearly 30 % of the world's coastal regions are at high risk of degradation, particularly from land-based sources of pollution (i.e., industries, urban sewer systems, agricultural practices) and infrastructure development (i.e., dams, highways, ports). Population in the Mediterranean seaparian countries (primarily in the coastal zones) is projected to increase from 465 Mil. (2002) to as much as 550 Mil. (2025), this will lead to a sharp increase in environmental pressure as a result of socio-economic factors on the Mediterranean coastal zones. In fact, a recent survey by the European Environment Agency (EEA) and UNEP show that coastal zones in the Mediterranean basin are at high risk (~80 %), among the highest in the world. The overall goal of MERCYMS is to develop a methodological approach for assessing the relative contribution of all sources releasing mercury directly or/and indirectly to Mediterranean seawater where high levels of mercury have been measured in fish and food web. Therefore, based on the fact that mercury is a highly toxic element that can bioaccumulate in living species and cause serious health effects to the exposed population (PIRRONE ET AL., 2001), the social benefits of current and past research activities and outcomes depend on the capacity building that implies a correct implementation of advances achieved in research. Major benefits are related to the improvement of the quality of the environment in the Mediterranean Sea region through the implementation of strategies that would reduce the ecotoxicological risk associated with exposure to mercury as well as mercury levels in the food chain.

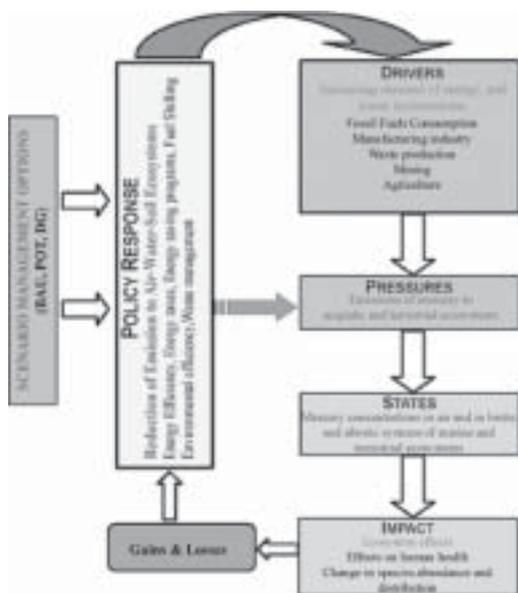
## AIMS

The research tasks carried out in MERCYMS are aimed to investigate the major patterns affecting the cycle of mercury within and between the atmospheric and marine ecosystems of the Mediterranean basin by integrating modelling and experimental tasks. The achievement of this overall goal implies: (1) to improve our capability to model the fate of Hg in the marine environment and specifically its translocation from one compartment to the other, (2) to assess the qualitative and quantitative relationship between atmospheric input - direct discharges to the sea and cycle of Hg in the marine environment and its re-emission back to the atmosphere, and (3) to develop an integrated modelling system (coupling atmospheric and water models) to be used as tool in the implementation, verification and revision of future EU Directives. In MERYCMS different environmental and socio-economic scenarios are being evaluated for identifying optimal emission reduction strategies and control policies. The research strategy developed and carried out within MERCYMS consortium (see table above) involves the following tasks:

- (a) Development of data bases which include (a) an Emission dBase for the releases of mercury and its compounds to the atmosphere and seawater from natural and anthropogenic sources, and (b) a socio-economic dBase. These dBases will be the core of the input data to both atmospheric and water modelling systems as well as to socio-economic analysis;



- (b) Development, validation and calibration of an Integrated Modelling System which includes a dynamic coupling of atmospheric and water modelling systems, it will provide information on key parameters affecting the fate of mercury and its compounds in the marine and atmospheric ecosystems and their interaction at the air-water interface (global cycling);
- (c) Intensive measurement campaigns at on-shore and off-shore sites where atmospheric and water measurements are carried out. Two-week 4 intensive campaigns are carried out (started in 2003) at five coastal sites (see figure). Off-shore measurement campaigns are carried out aboard the CNR-Research Vessel *Urania* where continuous atmospheric measurements have been coupled with surface and deep seawater measurements. The atmospheric and water measurements are aimed to assess temporal and spatial variations of ambient concentrations and air-water exchange fluxes of mercury and its compounds over the Mediterranean sea and major patterns affecting the cycle of mercury compounds between the atmosphere and seawater.
- (d) The atmospheric and water measurements are used to validate and calibrate the integrated modelling system. The results of the modelling simulations will represent the basis for the socio-economic analysis. Indeed the integration of the integrated modelling system with socio-economic analysis will focus on three specific scenarios including: the Business As Usual (BAU) scenario, the Policy Target (POT) scenario, and the Deep Green (DEG) scenario. These three scenarios will be based on the recommendations reported in the forthcoming EU Air Quality Directive on Mercury, EU Framework Water Directive (FWD), and international conventions on the protection of the European Seas, and on the needs of other working parties/stakeholders (i.e., fishery, WHO, UNEP). The outcome of these three scenarios will lead to the identification of the most cost-efficient strategy or/and policy to be adopted/considered at country and European levels in order to meet the targets of the above mentioned EU Directives and conventions.



## EXPECTED IMPACTS

MERCYMS consortium is developing a working tool (DPSIR framework – see below) for policy makers and environmental planners for a qualitative and quantitative assessment of the mercury cycle in the Mediterranean basin, and thus, elaborate, the most cost-efficient strategy(-ies) for reducing the impact of anthropogenic sources on the marine environment and human health. These methodologies are clearly needed (PIRRONE

AND WICHMANN, 2003) to achieve the targets of the (a) EU Directive on Mercury, and of (b) EU Framework Water Directive and support their implementation plans. It will help achieve the targets and goals of several international conventions and programmes on the protection of marine ecosystems and environment (i.e., MEDPOL, HELCOM, OSPARCOM) and will contribute to achieve the goals and fill the gaps as outlined in the EU Position Paper on Mercury (PIRRONE ET AL., 2001) and UNEP-GMA report (2003) and UNEP-Governing Council resolution (Decision 22/4 V on Mercury Pollution – February 2003).

## Acknowledgements

MERCYMS is a 3-year project funded by the European Commission (Contr. no. EVK3-2002-00070), major details can be found at: <http://www.cs.iiia.cnr.it/MERCYMS/project.htm>. I would like to acknowledge the contribution of all partners involved in the project as reported in the table above. Special thanks to all my co-workers including Francesca Sprovieri, Ian Hedgecock, Andrea Trunfio, Sergio Cinnirella and Franco Cofone for their effort in carrying out the project.

## REFERENCES

- FERRARA, R., MAZZOLAI, B., LANZILLOTTA, E., NUCARO, E., PIRRONE, N. (2000): Volcanoes as Emission Sources of Atmospheric Mercury in the Mediterranean Basin; *Sci. Tot. Environ.* 259, pp. 115-121.
- FERRARA, R., MAZZOLAI, B., LANZILLOTTA, E., NUCARO, E., PIRRONE, N. (2000): Temporal trends in gaseous mercury evasion from the Mediterranean Seawaters; *Sci. Tot. Environ.*, 259, pp. 183-190.
- HEDGECK, I. M., AND PIRRONE, N. (2004): Chasing Quicksilver: Modeling the Atmospheric Lifetime of  $Hg^0_{(g)}$  in the Marine Boundary Layer at Various Latitudes; *Environ. Sci. Technol.*, Vol. 38(1), pp. 69-76, DOI: 10.1021/es034623z
- HEDGECK, I., PIRRONE, N., SPROVIERI, F., PESENTI, E. (2003): Reactive Gaseous Mercury in the Marine Boundary Layer: Modeling and Experimental Evidence of its Formation in the Mediterranean; *Atmos. Environ.*, 37/S1, 41-50.

- HORVAT, M., KOTNIK, J., FAJON, V., LOGAR, M., ZVONARIC, T., PIRRONE, N. (2003): Speciation of Mercury in Surface and Deep Seawater in the Mediterranean Sea; *Atmos. Environ.* 37/S1, pp. 93-108.
- MASON, R. P., SHEU, G.-R. (2002): The role of the ocean in the global mercury cycle; *Global Biog. Cycles* 16(4), 1093. doi:10.1029/2001GB001440.
- PIRRONE, N., KEELER, G. J. AND NRIAGU, J. O. (1996): Regional Differences in Worldwide Emissions of Mercury to the Atmosphere; *Atmos. Environ.* 30, pp. 2981-2987.
- PIRRONE, N., HEDGECOCK, I. M., FORLANO, L. (2000): The role of the ambient aerosol in the atmospheric processing of semi-volatile contaminants: A parameterised numerical model (GASPAR); *Journal of Geophys. Res.* 105 (D8), 9773-9790.
- PIRRONE, N., AHRENS, R., BARREGLRD, L., BOFFETTA, P., BOROWIAK, A., EHRLICH, H.C., FERNANDEZ, R., GRANDJEAN, P., HANSEN, J. C., HORVAT, M., MUNTHER, J., PACYNA, J. M., PETERSEN, G., STEINNES, E. AND WICHMANN-FIEBIG, M. (2001): *EU Ambient Air Pollution by Mercury (Hg) - Position Paper on Mercury*; European Commission (Publisher), Office for Official Publications of the European Communities, Brussels, ISBN 92-894-2053-7.
- PIRRONE, N. AND WICHMANN, M. (2003): Some Recommendations on Mercury Measurements and Research Activities in the European Union; *Atmos. Environ.* 37/S1, pp. 3-8.
- PIRRONE, N., FERRARA, R., HEDGECOCK, I. M., KALLOS, G., MAMANE, Y., MUNTHER, J., PACYNA, J. M., PYTHAROULIS, I., SPROVIERI, F., VOUDOURI, A., WANGBERG, I. (2003): Dynamic Processes of Atmospheric Mercury Over the Mediterranean Region; *Atmos. Environ.*, 37/S1, pp. 21-40.
- SPROVIERI, F., PIRRONE, N., GARDFELDT, K., SOMMAR, J. (2003): Atmospheric Mercury Speciation in the Marine Boundary Layer along 6000 km Cruise path over the Mediterranean Sea; *Atmos. Environ.* 37/S1, pp. 63-72.

## Air- Water- Soil- Vegetation Mercury Gas Exchanges in the Baie Saint-François

LAURIER POISSANT<sup>1,2</sup>, HELEN HONG ZHANG<sup>3</sup>, DESSISLAVA GABROVSKA<sup>2</sup>, XIOAHONG XU<sup>3</sup>,  
MARTIN PILOTE<sup>1</sup> & CONRAD BEAUVAIS<sup>1</sup>

<sup>1</sup>Environment Canada, 105 McGill (7<sup>th</sup> floor), Montréal, Québec, H2Y 2E7

<sup>2</sup>Institut des sciences de l'environnement, UQAM

<sup>3</sup>Department of Environmental Engineering, Windsor University, Windsor, Ont.

**Abstract:** In order to evaluate and understand the mercury gas exchange processes in fluvial wetlands, related research was initiated in a St. Lawrence River wetland (Bay St. François, Québec, Canada). Mercury fluxes were measured using dynamic flux chamber, flux bag and micrometeorological techniques, coupled with automatic mercury vapor analyzers (namely Tekran, Model 2537A). Mercury speciation concentrations and deposition were measured with Tekran speciation units 1130 & 1135. Mercury concentrations were observed in various media such as plants, soils and water. This paper presents some information in regards to the mercury budget in the Baie St. François (Lake St. Pierre).

**Key words:** Mercury, wetlands, soil, air, plants, mercury speciation, budget

### INTRODUCTION

Mercury is among the most highly bioaccumulated trace metals in the food web and is very toxic for the whole ecosystem including human beings (IMURA ET AL., 1971). Aquatic and especially wetlands environments are key components in the mercury biogeochemical transformation and cycling (RUDD, 1995). Mercury air-surface gas exchange may be an important route of mercury transfer into or out of wetlands. Recent mercury air-surface exchange study in Florida wetlands (Everglades) has pointed out the predominant flux of Hg<sup>0</sup> over invasive cattail was emission (mean daytime fluxes over cattail ranged from ~20 (winter) to ~40 (summer) ng/m<sup>2</sup>/h). Emission from vegetation significantly exceeded evasion of Hg<sup>0</sup> from the underlying water surface (~1–2 ng/m<sup>2</sup>/h). (LINDBERG ET AL., 2002). The

latter rate is smaller, on average, than measurements at northern sites, for example, a mean evasion rate of 3.43 ng/m<sup>2</sup>/h at Burt Lake, MI (LINDBERG ET AL., 1999). The overall objective of this paper is to study the Air-Water- Soil- Vegetation exchanges of gaseous mercury in a wetland along the St. Lawrence River (Québec).

### RESULTS AND DISCUSSION

Soil-air, water-air and vegetation-air exchanges are important processes involved in cycling of mercury (Hg) in the biosphere. In order to assess the possible mechanisms/kinetics, environmental influences and better understand the biogeochemical processes/interactions with these three different com-

ponents in Hg atmosphere surface exchange, intensive field campaigns were achieved using dynamic flux chamber (DFC), dynamic flux bag (DFB) and micrometeorological systems in the Baie St- François (Québec, Canada) during Spring and Summer of 2003. Those intensive fields were achieved along Hg research monitoring part including water, air (Hg speciation), plants and soils survey. This study attempts to investigate and estimate the roles of three components in Hg cycling and compare the commons and dissimilarities. Dynamic flux chamber approach was used to measure Hg gas exchange fluxes over water and bare soil.

DFB was used for specific plant (e.g., *Scirpus fluviatilis*) air-vegetation gas exchanges whereas micrometeorological systems were applied over vegetation canopy.

Our data indicate that as a whole water and soil components acted primarily as sources of atmospheric mercury. Mercury evasion over these components exhibits a consis-

tently diurnal pattern with maximum evasion during the daytime and minimum during night-time.

The most significant parameters influencing surface air Hg fluxes in water were solar radiation, temperature and relative humidity. In generally, water-air exchange rate has the lowest rate. It is suggested that the main process for mercury vapour emission for the aquatic system is photochemical reduction of  $\text{Hg}^{2+}$  to  $\text{Hg}^0$ ; Hg evasion over a soil surface maybe controlled through thermodynamic processes.

Vegetation canopy is very active: Deposition and volatilisation are observed with diel profile. The average deposition velocity of the Hg speciation calculated from flux and concentration measurement were (GEM) < (PM) < (RGM). Although RGM should be rapidly depositing species, as predicted by its solubility, no significant RGM flux was observed at night. RGM fluxes are not driven by RGM solubility (in water) since the

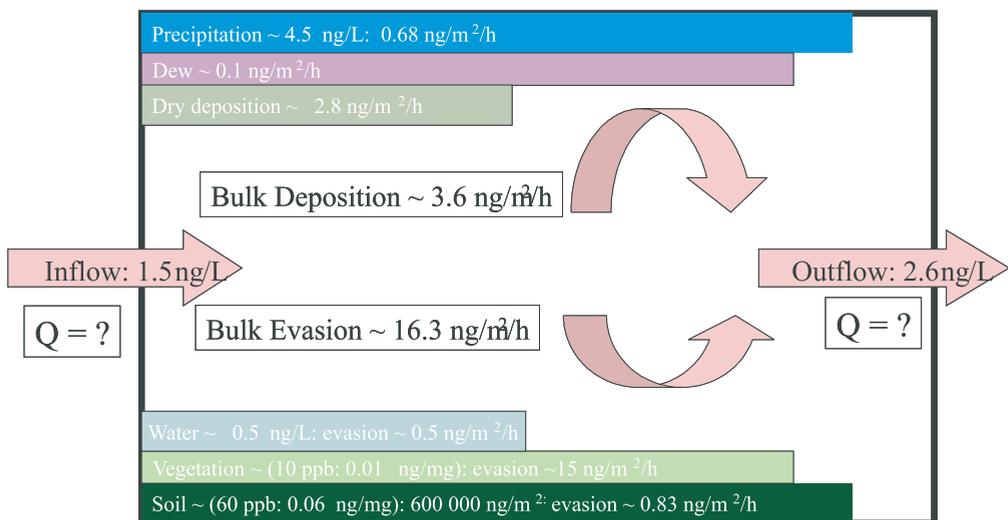


Figure 1. Mercury budget in the Baie St. François wetland

canopy was dry when larger RGM deposition periods were observed during daytime.

It is suggested that the vegetation might directly uptake RGM during daytime. While for GEM vegetation-air exchange, transpiration and diffusion through stomata are the proposed mechanisms.

Plants survey indicated that plants concentrated Hg in their various parts. However, the uptake processes are different through plant species. In example, *Mentha canadensis* will concentrate Hg at root level while *Scirpus fluviatilis* will concentrate mercury at leaves level.

Hence, those two plant species will have different exchange interactions and processes with the soil and the atmosphere. The *Scirpus* atmospheric gas uptake has been measured with the DFB system. Further attention will be given to those processes.

Finally, a first Hg budget is presented in the BSF wetlands (Figure 1): Dew deposition ( $\sim 0.1$  ng/m<sup>2</sup>/h) < Precipitation deposition ( $\sim 0.68$  ng/m<sup>2</sup>/h) < Dry deposition (2.8 ng/m<sup>2</sup>/h) for a total bulk deposition of

3.6 ng/m<sup>2</sup>/h. In an other hand, evasion from water (0.5 ng/m<sup>2</sup>/h) < evasion from soil (0.83 ng/m<sup>2</sup>/h) < evasion from plant canopy (15 ng/m<sup>2</sup>/h) for a total evasion term of  $\sim 16.3$  ng/m<sup>2</sup>/h. Bulk evasion is about 4.5 times larger than bulk deposition. The main Hg component is the soil/sediments reservoir. Water inflow and outflow are still to be evaluated. But mercury concentrations in inflow water are about 1.5 ng/L whereas outflow waters Hg concentrations are about 2.6 ng/L.

## CONCLUSION

Hg gas-exchange is very important in the Bay St. François wetland. However, many issues are still to be elucidated, namely the plants interactions within the fate of mercury.

## Acknowledgements

This study was funded by the St. Lawrence Action Plan (Vision 2000) (Environment Canada), the Toxic Substances Research Initiative (TSRI grant # 105) (Health Canada) and by NSERC-COMERN.

## REFERENCES

- IMURA, N., SUKAGAWA, E., PAN, S. K., NAGAO, K., KIM, J. Y., KWAN, T. AND UKITA, T. (1971): Chemical methylation of inorganic mercury with methylcobalamin, a Vitamin B12 analog; *Science* 172, pp. 1248–1249.
- LINDBERG, S. E., DONG, W. AND TILDEN MEYERS, T. (2002): Transpiration of gaseous elemental mercury through vegetation in a subtropical wetland in Florida; *Atmospheric Environment* 36, pp. 5207–5219.
- LINDBERG, S. E., ZHANG, H., MEYERS, T. P. (1999): *Application of field methods and models to quantify mercury emissions from wetlands at the Everglades nutrient removal project*; E-MASE, 155 p.
- RUDD, J. W. M. (1995): Sources of methylmercury to freshwater ecosystems: A review; *Water Air & Soil Pollut.* 80, pp. 697-713.

# Atmospheric Mercury & Ozone Depletion Events Observed at the Hudson Bay in Northern Québec along with BrO (DOAS) Measurements

LAURIER POISSANT<sup>1\*</sup> & GERD HOENNINGER<sup>2,3</sup>

<sup>1</sup> Meteorological Service of Canada, Atmospheric Toxic Processes Section, Environment Canada, 105 McGill, 7<sup>th</sup> floor (Youville), Montréal, QC H2Y 2E7, Québec, Canada; \*E-mail:

laurier.poissant@ec.gc.ca

<sup>2</sup> Institut fuer Umweltpophysik, University of Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

<sup>3</sup> now at Meteorological Service of Canada, 4905 Dufferin Street, Toronto, Ontario, M3H 5T4

**Abstract:** From April 15<sup>th</sup> to May 8<sup>th</sup> 2001, an intensive field campaign has been carried out in Kuujjuarapik/Whapmagoostui, Québec, Canada, to study boundary layer Ozone and Mercury Depletion Events (ODE and MDE) in the low Arctic region at the Hudson Bay. Mercury speciation concentrations (Total Gaseous Mercury (TGM), Total Particulate Mercury (TPM) & Reactive Gaseous Mercury (RGM)) using new mercury speciation units namely Tekran 1130 & 1135, were measured along with Ozone (Teco 49C), BrO mixing ratio (Differential Optical Absorption Spectroscopy, DOAS) and meteorological parameters (e.g., temperature, wind, etc.). Several episodes of low ozone and mercury concentrations related to elevated BrO mixing ratios have been captured.

**Key words:** Mercury depletion events, BrO, mercury speciation, Northern Québec

## INTRODUCTION

Atmospheric ozone and mercury depletion events were recently discovered in the high Arctic region during Polar Sunrise Experiments (e.g., BARRIE ET AL., 1988; SCHROEDER ET AL., 1998; LINDBERG ET AL., 2002) and the Antarctic (e.g., KREHER ET AL. 1997; EBINGHAUS ET AL., 2002). It is accepted that catalytic cycles involving Br/BrO are responsible for the majority of observed ozone losses, smaller contributions being proposed for cycles involving ClO and IO (BARRIE ET AL., 1988).

Recent theoretical and laboratory studies suggest that Br atoms are the major oxidant

for Hg<sup>0</sup> (KHALIZOV ET AL., 2003). A recent modelling study by Calvert and LINDBERG (2003) discusses several possible reaction pathways, however, missing kinetic and product data on the reaction BrO + Hg<sup>0</sup> as well as the lack of specific measurements of RGM species still leaves open questions.



and/or



BrO columns are observed over the Hudson Bay area and parts of the Canadian Arctic (RICHTER ET AL., 1998). Satellite observations from the Global Ozone Monitoring Experi-

ment (GOME) showed that tropospheric air masses enriched in BrO are always located close to sea ice and typically extend over areas of up to  $1.4 \times 10^7 \text{ km}^2$  (WAGNER AND PLATT, 1998). The BrO abundance remains enhanced for periods of 1 to 3 d, especially in late winter and springtime (RICHTER ET AL., 1998; WAGNER AND PLATT, 1998).

This paper presents the first field observations of mercury speciation concentrations along with ground-based DOAS measurements of BrO at high time resolution in a Low Arctic region and will discuss further the various results in regards to MDEs.

## RESULTS AND DISCUSSION

Mercury depletion events (MDEs) and ozone depletion events were observed in the low Arctic region of the Hudson Bay at Kuujjuarapik (POISSANT, 2001). Typically the MDEs are observed from mid-February to mid-May. Compared to the high Arctic (e.g., BOTTENHEIM ET AL., 1986; BARRIE ET AL., 1988; SCHROEDER ET AL., 1998) depletions occur more frequently but only rarely complete depletion of Hg or ozone is seen (Figure 1).

Our observations indicate that during the period from April 15, 2001 to May 8, 2001 enhanced BrO was observed during almost daily events associated with both depletions of TGM and ozone (Figure 2). Lost of TGM is concomitant with its transformation in RGM and TPM (Figure 3). The median concentrations along our observations were as follows: TGM ( $1.93 \text{ ng/m}^3$ ); TPM ( $183 \text{ pg/m}^3$ ); RGM ( $22 \text{ pg/m}^3$ );  $\text{O}_3$  ( $36.5 \text{ ppb}$ ) and BrO ( $0.35 \text{ ppt}$ ).

Enhanced BrO mixing ratios ( $>5 \text{ ppt}$ ) and RGM concentrations ( $>60 \text{ pg/m}^3$ ) were usually associated with cold ( $\sim < \text{minus } 8 \text{ }^\circ\text{C}$ ) Arctic air masses originating from higher latitudes. Furthermore, the BrO mixing ratio was anti-correlated with TGM ( $TGM = -0.05 \text{ BrO} + 1.99$ ;  $R^2 = 0.35$ ) and  $\text{O}_3$  ( $\text{O}_3 = -1.0 \text{ BrO} + 38.9$ ;  $R^2 = 0.33$ ) (Figure 2) whereas it was correlated with RGM ( $RGM = 4.6 \text{ BrO} + 21.3$ ;  $R^2 = 0.54$ ) but not with TPM (Figure 3).

One of the most important effects of temperature seemed to appear on TPM concentrations. Indeed, TPM correlated significantly with temperature ( $TPM = 8.8 \text{ T}(\text{ }^\circ\text{C}) + 245$ ;  $R^2 = 0.35$ ) but not significantly with others.

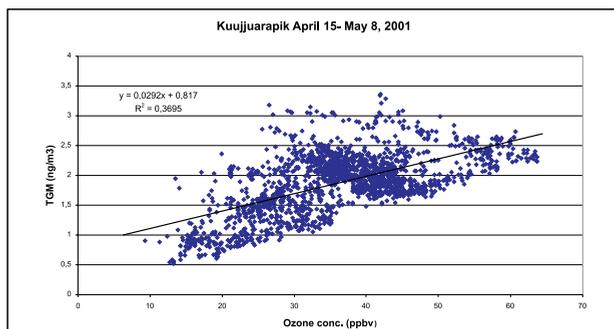


Figure 1. Relation between TGM and Ozone.

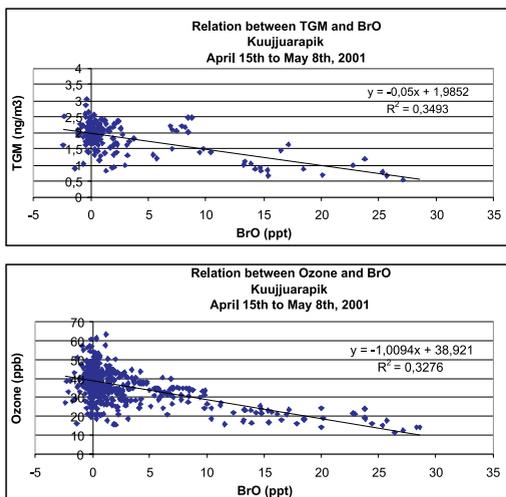


Figure 2. Relation between BrO and TGM and Ozone

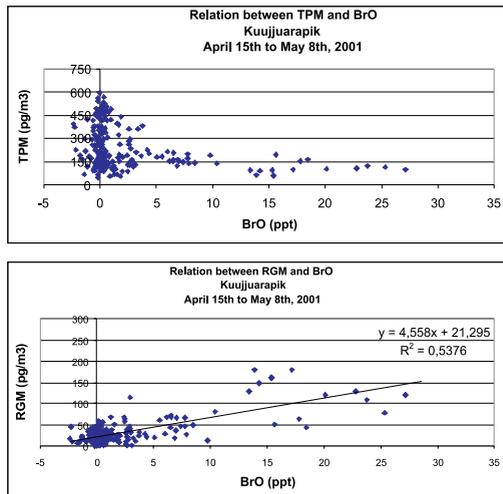


Figure 3. Relation between BrO and TPM and RGM

## CONCLUSION

Chemical conversion of  $\text{Hg}^{\circ}$  by Br species would yield particle-phase or reactive gaseous mercury species subject to dry deposition and might cause a large input of mercury into the fragile Arctic ecosystem. Further works have to be undertaken to better understand the mercury depletion event mechanisms.

## Acknowledgements

LP would like to thank the NCP for funding. Special thanks to Centre d'Étude Nordique of Université Laval for the laboratory facilities and C. Tremblay for his wonderful field support and Martin Pilote (MSC) for his research assistance. GH thanks H. Leser and O. Sebastián and U. Platt for making the DOAS work possible and the German Academic Exchange Service for support through a fellowship.

## REFERENCES

- BARRIE, L. ET AL. (1988): Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere; *Nature* 321, 138-141.
- BOTTENHEIM, J. W., GALLANT, A. G. AND BRICE, K. A. (1986): Measurements of NO<sub>y</sub> species and O<sub>3</sub> at 82°N latitude; *Geophys. Res. Lett.* 22, 599-602.
- CALVERT, J. G. AND LINDBERG, S. E. (2003): A modeling study of the mechanism of the halogen-ozone-mercury homogeneous reactions in the troposphere during the polar spring; *Atm. Env.* 37, 4467-4481.
- EBINGHAUS, R., KOCK, H., TEMME, C., EINAX, J., LÖWE, A., RICHTER, A., BURROWS, J. AND SCHROEDER, W. H. (2002): Antarctic springtime depletion of atmospheric mercury; *Environ. Sci. Technol.* 36, 1238-1244.
- KHALIZOV, A. F., VISWANATHAN, B., LARREGARAY, P. AND ARIYA, P. A. (2003): A Theoretical Study on the Reactions of Hg with Halogens: Atmospheric Implications; *J. Phys. Chem. A*, 107, 6360-6365.
- KREHER, K., JOHNSTON, P. V., WOOD, S. W. AND PLATT, U. (1997): Ground-based measurements of tropospheric and stratospheric BrO at Arrival Heights 78°S, Antarctica; *Geophys. Res. Lett.* 24, 3021-3024.
- LINDBERG, S. E., BROOKS, S., LIN, C.-J., SCOTT, K. J., LANDIS, M. S., STEVENS, R. K., GOODSITE, M. AND RICHTER, A. (2002): Dynamic Oxidation of Gaseous Mercury in the Arctic Troposphere at Polar Sunrise; *Environ. Sci. Technol.* 36, 1245-1256.
- POISSANT, L., AMYOT, M., KWAN, M. AND BÉGIN, Y. (2001): Atmospheric mercury transport, oxidation and fallout in northern Québec (Nunavik): an important potential route of contamination, Northern Contaminants Program, Vol. ISBN 0-662-30872-7, pp. 125-129, Indian and Northern Affairs Canada.
- RICHTER, A., WITTRICK, F., EISENGER, M. AND BURROWS, J. P. (1998): GOME Observation of tropospheric BrO in Northern hemispheric Spring and Summer 1997; *Geophys. Res. Lett.* 25, 2683-2686.
- SCHROEDER, W. H. ET AL. (1998): Arctic springtime depletion of mercury. *Nature*, 394, 331-332.
- WAGNER, T. AND PLATT, U. (1998): Satellite mapping of enhanced BrO concentrations in the troposphere; *Nature* 395, 486-490.

# Year Round Atmospheric Mercury Speciation Measurements in Southern Québec, Canada: Preliminary Results

LAURIER POISSANT\*, MARTIN PILOTE & CONRAD BEAUVAIS

Atmospheric Toxic Processes, Meteorological Service of Canada, Environment Canada, Quebec Region, 105 McGill street, 7<sup>th</sup> floor, Montreal, Quebec, H2Y 2E7, Canada;  
\*E-mail: Laurier.poissant@ec.gc.ca

**Abstract:** Atmospheric mercury speciation is very important in the determination of the mercury atmospheric residence time. From one side of the spectrum to another, elemental mercury can have a residence time of 1-2 years whereas that of Reactive Gaseous Mercury can be very short as a few hours. To further understand the fate of atmospheric mercury, atmospheric mercury speciation is measured since January 2003, in a rural site at St. Anicet, Southern Québec (Canada). The experiment is conducted using a Tekran® Model 2537A which is used together with a Model 1135 Particulate Mercury Unit and a Model 1130 Speciation Unit to simultaneously monitor gaseous elemental mercury ( $\text{Hg}^0$ ), particulate mercury (pHg: 0.1 - 2.5  $\mu\text{m}$ ), and reactive gaseous mercury (RGM) in ambient air. After a year round of mercury speciation measurements (number of measurements up to 3348), the mean concentrations were:  $\text{Hg}^0$  1.65  $\text{ng}/\text{m}^3$ , pHg 26  $\text{pg}/\text{m}^3$  and RGM 3  $\text{pg}/\text{m}^3$ . Important seasonal variations of mercury speciation were observed during this atmospheric mercury survey. RGM median concentrations were higher during wintertime whereas pHg median concentrations were maximal in springtime, more precisely in April and May. Ratio of pHg and RGM > 1 suggested mature air mass sources and faster RGM deposition velocity.

**Key words:** Total gaseous Mercury (TGM), Seasonal variability, Diurnal variability, mercury speciation

## INTRODUCTION

Mercury is among the most highly bioaccumulated trace metals in the food web and is very toxic for the whole ecosystem including human beings (IMURA ET AL., 1971). The dominant form of mercury in the atmosphere is gaseous elemental mercury (GEM) (>97 %). Because of the high volatility of elemental mercury, it is widely dispersed in the Earth's atmosphere (SLEMR ET AL., 1985). About 3 % of the atmospheric gaseous mercury is reactive gaseous mercury (RGM) including  $\text{HgCl}_2$ , particulate mercury (pHg)

and various organic mercury forms such as dimethylmercury (JOHNSON AND BRAMAN, 1974).

Atmospheric mercury speciation is very important in the determination of the mercury atmospheric residence time. From one side of the spectrum to another, elemental mercury can have a residence time of 1-2 years whereas that of RGM can be as short as a few hours.

To date, very few field studies have been conducted for atmospheric mercury specia-

tion measurements (e.g., JOHNSON AND BRAMAN, 1974; LINDBERG AND STRATTON, 1998; MALCOLM AND KEELER, 2002). None have been done year round for mercury a speciation survey. For this purpose, a field campaign was designed to measure and study automated high-time resolution mercury speciation of GEM, RGM and pHg in St. Anicet (Québec) using Tekran<sup>®</sup> mercury speciation units (model 1130 & 1135). This new information will enhance atmospheric mercury speciation knowledge, which is critical to address appropriate mercury modeling and regulation scenarios.

## RESULTS AND DISCUSSION

The mercury speciation measurement study was conducted under temperate climate in year 2003 as specific to St. Anicet site located in Southern Québec.

Average concentrations of GEM, RGM and pHg in 2003 were 1.65 (0.42) ng/m<sup>3</sup>, 3 (11) pg/m<sup>3</sup> and 26 (54) pg/m<sup>3</sup> respectively (Table 1). Larger standard deviations (terms in parentheses) for pHg and RGM indicate the larger reactivity and lower residence time of these latter mercury species. On an average the atmospheric mercury apportioned as following: GEM 98.4 %, RGM 0.2 %, and pHg 1.4 %.

Particulate Hg and RGM concentrations measured in St. Anicet were lower than the ones observed in the low Arctic region (POISSANT, 2001) and the high Arctic region (LINDBERG ET AL., 2002) during mercury depletion events. But they are very close to other values reported in various sites in Lake Superior and the Everglades (MALCOLM AND KEELER, 2002). LINDBERG AND STRATTON (1998) measured airborne concentration of RGM in the range of 50-200 pg/m<sup>3</sup> using a refluxing mist chamber (~ 1-h samples).

Figure 1 presents the year round time series of GEM, RGM and pHg in 2003. Large seasonality is observed. To better express this variability, Figure 3 shows the median monthly time series of each mercury species in term of GEM, RGM and pHg in respect to median air temperature. Largest GEM median concentrations were observed in winter and spring-time whereas the lowest were observed in summer and fall time. While the largest GEM concentration was in June and the lowest in September. pHg shows a sharp annual trend with maximum median concentration in April and May. This might be the result of pHg re-suspension due to soil erosion (e.g., ploughing). Some large pHg concentrations were present in winter-time due to house-heating or other combustion facilities. RGM monthly time series also has sharp

**Table 1.** Statistical Summary of mercury speciation measured in 2003 in St-Anicet (Québec)

	Hg <sup>o</sup> (ng/m <sup>3</sup> )	pHg (pg/m <sup>3</sup> )	RGM (pg/m <sup>3</sup> )
n	3348	3348	3348
median	1.61	9	1
mean	1.65	26	3
std	0.42	54	11

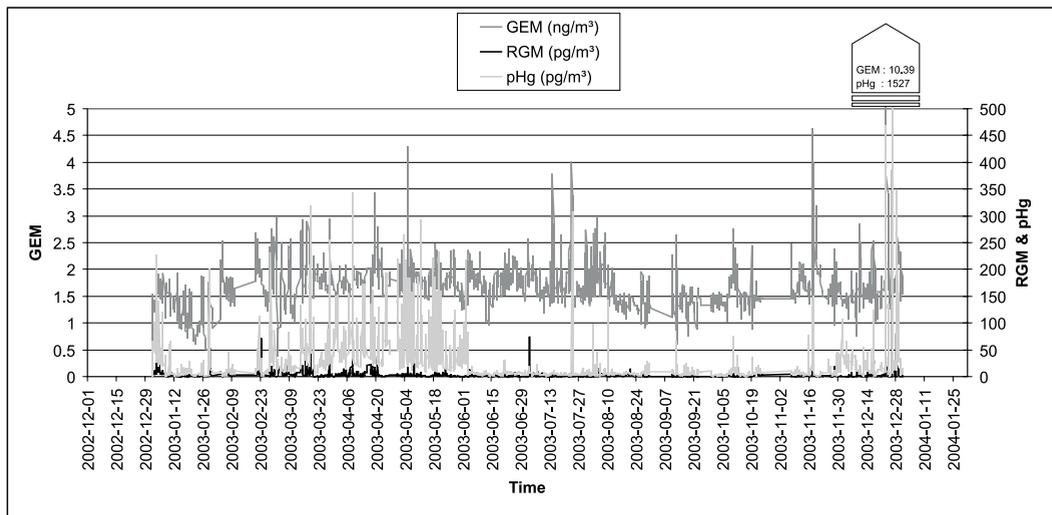


Figure 1. Mercury speciation time series in St. Anicet in 2003

annual trends with larger concentrations from February to April suggesting combustion sources. The highest summertime concentrations were detected in August along with the highest recorded temperature. On an average, the ratio of pHg and RGM  $> 1$  suggested mature air mass sources and faster RGM deposition velocity.

## CONCLUSIONS

This study presents one of the most extensive data sets regarding year round measurements of atmospheric mercury speciation,

namely GEM, RGM and pHg. The results showed large seasonality of GEM, RGM and pHg. As whole mercury speciation concentrations are larger in wintertime and lower in summertime. RGM and pHg showed sharp seasonal variation.

## Acknowledgements

The authors would like to thank the St. Lawrence Action Plan (SLAP) for their financial support as well as the MSC (Downsview). Special thanks to MSC-ARQM branch (Dr. M. Lusic) for funding.

## REFERENCES

- IMURA, N., SUKEGAWA, E., PAN, S. K., NAGAO, K., KIM, J. Y., KWAN, T. AND UKITA, T. (1971): Chemical methylation of inorganic mercury with methylcobalamin, a Vitamin B12 analog; *Science* 172, pp. 1248–1249.
- JOHNSON, D. L. AND BRAMAN, R. S. (1974): Distribution of atmospheric mercury species near the ground; *Environ. Sci. and Technol.* 8, pp. 1002-1009.
- LANDIS, M. S., STEVENS, R. K., SCHAEDLICH, F. AND PRESTBO, E. (2002): Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air; *Environ. Sci. Technol.* 36, pp. 3000-3009.
- LINDBERG, S. E., BROOKS, S., LIN, C.-J., SCOTT, K. J., LANDIS, M. S., STEVENS, R. K., GOODSITE, M. AND RICHTER, A. (2002): The Dynamic Oxidation of Gaseous Mercury in the Arctic Atmosphere at Polar Sunrise; *Environ. Sci. Technol.* 36, pp. 1245-1256.
- LINDBERG, S. E. AND STRATTON, W. J. (1998): Atmospheric speciation concentrations and behavior of reactive gaseous mercury in ambient air; *Environ. Sci. Technol.* 32, pp. 49-57.
- MALCOLM, E. G. AND KEELER, G. J. (2002): Measurements of Mercury in Dew: Atmospheric Removal of Mercury Species to a Wetted Surface; *Environ. Sci. Technol.* 36, pp. 2815-2821.
- POISSANT, L. (2001): *Atmospheric mercury transport, oxidation and fallout in northern Québec (Nunavik): an important potential route of contamination, Northern Contaminants Program; Synopsis of Research 2000-2001*, Indian and Northern Affairs Canada, ISBN 0-662-30872-7, pp 125-129.
- SLEMR, F., SEILER, W. AND SCHUSTER, G. (1985): Distribution, speciation and budget of atmospheric mercury; *J. Atmos. Chem.* 3, pp. 407-434.

## **Wet Deposition of Mercury in the U.S.A. and Canada, 1996-2002: Results from the NADP Mercury Deposition NETWORK (MDN)**

ERIC PRESTBO, ROBERT BRUNETTE & CLYDE SWEET

**Abstract:** The Mercury Deposition Network (MDN) is part of the National Atmospheric Deposition Program (NADP). MDN operates sites in the United States and Canada to monitor total mercury in wet deposition. Annual summaries from weekly data collected at 70 locations are reported for the years 1996-2002. The median mercury concentration for almost 10,000 samples collected during this period is 9.7 ng/L. Volume-weighted total mercury concentrations are lowest at remote sites in northern California and the Canadian maritime provinces (4 to 6 ng/L) and highest in Florida and Minnesota (10 to 16 ng/L). Wet deposition of mercury depends on both the concentration in the rain and the total rainfall amount. Wet deposition of mercury ranges from over 25 mg/m<sup>2</sup>/yr in south Florida to less than 3 mg/m<sup>2</sup>/yr in northern California. Mercury deposition is strongly seasonal in eastern North America. In the summer, the average mercury concentration in rain is about double that found in the winter. The average wet deposition of mercury is more than 3 times higher in summer than in winter. No statistically significant time trends have been measured. In addition, several MDN sites have been measuring monomethyl mercury wet-deposition. Monomethyl mercury concentrations, seasonal trends and comparison to total mercury deposition will be highlighted.

**Key words:** total mercury, methyl mercury, trends, wet-deposition, atmospheric cycling

# Measurement of Atmospheric Mercury Species via Manual Collection and Analysis Methods to Support the Calculation of Mercury Dry Deposition Rates in Indiana

ERIC PRESTBO, MARTIN RISCH<sup>1</sup> & LUCAS HAWKINS

<sup>1</sup>U.S. Geological Survey, 5957 Lakeside Boulevard, 46278, Indianapolis, IN, USA,  
e-mail: mrrisch@usgs.gov

**Abstract:** Starting in late 2000, an active 4-site Mercury Deposition Network (MDN) program has been operating to measure the wet-deposition rate of total and methyl mercury in Indiana. The U.S. Geological Survey (USGS) in cooperation with the Indiana Department of Environmental Management has since determined that the dry deposition rate of mercury is a critical data gap in the assessment of mercury inputs to sensitive aquatic ecosystems. Starting in the fall of 2003, a research campaign has been underway to determine the 3 key atmospheric mercury species, elemental (Hg<sup>0</sup>), reactive gaseous (RGM) and particulate-bound mercury (PHg), to support the calculation of mercury dry deposition rates at each of the 4 Indiana MDN sites. On-site meteorological data is combined with the mercury species concentration values to determine the dry deposition rate using a simple resistive model (indirect method). The atmospheric mercury species are sampled through a 2.5  $\mu\text{m}$  particulate impactor, KCl-annular denuder, quartz filter and gold trap to capture the individual species. Analysis in the laboratory is done by thermal desorption of each sample into a calibrated Tekran 2537A Cold Vapor Atomic Absorption Spectrometer. A single 12-hour sample is collected at each site at a frequency of once per week and then returned to the laboratory. In order to determine if there could be any bias in either the RGM or PHg results due to the transit time of several days, an initial holding time study was completed. For the holding time study, 8 or 4 samples were collected simultaneously on 4 separate occasions. Half of the simultaneously collected samples were analyzed immediately and the other half held in the dark at 20 °C for at least 120 hours and then analyzed. For RGM, the concentrations ranged from 1.1 to 10.5  $\text{pg}/\text{m}^3$  with a mean blank of  $1.0 \pm 0.7$  pg. For PHg the concentrations ranged from 0.54 to 14.6  $\text{pg}/\text{m}^3$  with a mean blank of  $5.1 \pm 5.0$  pg. The concentrations in short-holding time (less than 4 hours) and long-holding time (120 hours) were compared statistically and a significant difference was not demonstrated for RGM. The variance in RGM concentrations between short- and long-holding time samples ( $0.86 \text{ pg}/\text{m}^3$ ) was comparable to the variance among collocated duplicate samples ( $1.0 \text{ pg}/\text{m}^3$ ). A statistically significant difference was not demonstrated between short- and long-holding time samples for PHg. The variance in PHg concentrations between short- and long-holding time samples ( $0.61 \text{ pg}/\text{m}^3$ ) was comparable to the variance among collocated duplicate samples ( $1.07 \text{ pg}/\text{m}^3$ ). Based on this investigation, it was concluded that holding time did not have a significant effect on the concentration of RGM and PHg for the dry-deposition monitoring program in Indiana. Mercury species concentrations and dry deposition rates for the winter and spring periods in Indiana, USA will also be reported and compared to both current models and weekly wet-deposition values. In conclusion, the design, implementation and results of this initial mercury dry deposition campaign has provided a framework to fill a much needed measurement data gap.

**Key words:** dry deposition, speciation, atmospheric

## Interconversion of Emitted Atmospheric Mercury Species in Coal-Fired Power Plant Plumes

ERIC PRESTBO, LEONARD LEVIN<sup>1</sup>, JOHN JANSEN<sup>2</sup>, LARRY MONROE<sup>3</sup>, DENNIS LAUDAL<sup>4</sup>,  
RICHARD SCHULZ<sup>5</sup>, GRANT DUNHAM<sup>6</sup>, WILLIAM ALJOE<sup>7</sup>, RALPH J. VALENTE<sup>8</sup>,  
DAVID MICHAUD<sup>9</sup> & PHIL SWARTZENDRUBER

<sup>1</sup>EPRI, 3412 Hillview Avenue, 94303, Palo Alto, USA, e-mail: llevin@epri.com

<sup>2</sup>Southern Company, 600 N. 18th St. 14N-8195, 35203, Birmingham, USA,  
e-mail: jjjansen@southernco.com

<sup>3</sup>Southern Company, 600 N. 18th St. 14N-8195, 35203, Birmingham, USA,  
e-mail: lsmonroe@southernco.com

<sup>4</sup>Energy and Environmental Research Center, P.O. Box 9018, 58202, Grand Forks, USA,  
e-mail: dlaudal@undeerc.org

<sup>5</sup>Energy and Environmental Research Center, P.O. Box 9018, 58202, Grand Forks, USA,  
e-mail: rschulz@undeerc.org

<sup>6</sup>Energy and Environmental Research Center, P.O. Box 9018, 58202, Grand Forks, USA,  
e-mail: gdunham@undeerc.org

<sup>7</sup>U.S. Department of Energy, National Energy Technology Laboratory 626 Cochrans Mill Rd,  
15236, Pittsburgh, USA, e-mail: aljoe@netl.doe.gov

<sup>8</sup>Tennessee Valley Authority, Reservation Road CEB2A, 35662, Muscle Shoals, USA,  
e-mail: rvalente@tva.gov

<sup>9</sup>We-Energies, 231 W. Michigan, 53290, Milwaukee, USA,  
e-mail: dave.michaud@we-energies.com

**Abstract:** Starting in the fall of 2002, the emission plumes of two large coal-fired power plants have been the subject of extensive mercury speciation studies, using real-time stack measurements, two different types of on-stack dilution chambers and two aircraft platforms. The objective of the research campaigns is to help further characterize the presence, rates and end result of mercury chemical transformations that may occur in the emissions from elevated stacks of coal-fired electric power plants. This information is critical in determining the role of coal-fired plants in mercury deposition through modeling and then for developing cost-effective, environmentally sound policies and strategies for reducing mercury emissions. Recent research findings have indicated that the standard method for characterizing the mix of mercury species in emissions may misrepresent the forms dispersing into the ambient atmosphere from the emission plumes. Past research using on-stack dilution chambers to simulate plume conditions and mixing, found that at coal-fired power plants, there was evidence of a very rapid reduction of the Hg(II) to Hg(0), of the order of a 30 to 50 % conversion within a few minutes. Similarly, measurements at an ambient mercury sampling site in Georgia, south of a major coal-fired power plant, found a six-fold increase in the fraction of elemental mercury, and consequent decrease in divalent mercury, during traverse of the plant plume over the 25 km plant-to-sampler distance. In-stack mercury speciation (particulate-bound and gaseous elemental and divalent mercury) was determined using both the manual Sorbent Ontario Hydro Method and Continuous Emission Monitoring. The stack mer-

cury speciation values provided a baseline to which the plume mercury speciation is compared. The plume mercury speciation was characterized using a 0.5 m<sup>3</sup>, Teflon coated static plume dilution chamber (SPDC) and also a continuous flow, heated, Teflon lined dynamic plume dilution unit (DPD). Dilution ratios ranged from 120:1 to 400:1 with reaction times from 10 seconds to 150 seconds. In-situ plume mercury speciation was also measured using an instrumented Twin Otter airplane at both coal-fired power plants. A low dead-volume, fast-response nitrogen oxide detector was used to trigger the airplane mercury speciation sampling system and determine exact dilution ratios. The airplane measured plume mercury from 0.1 to 12 km downwind, reaction times of 20 seconds to ~60 minutes and dilution ratios from 400:1 to 25,000:1. Both the dilution chambers and the aircraft platform used the same methods for mercury speciation. Plume air is sampled through aerosol size-segregation inlet, KCl-annular denuder, quartz filter and then Tekran 2537A Cold Vapor Atomic Absorption Spectrometer to capture and determine the individual mercury species. Using an airplane flight track incorporating background measurements upwind of the plant and repeated crosswind traverses of the plume at fixed distances downwind, it was possible to accurately determine mercury speciation above that present in the ambient background. A mean conversion of Hg(II) to Hg<sup>0</sup> of 10 % and 14 % was observed for the first power plant campaign by the SPDC and airplane measurements, respectively. This mean conversion is on the low end of the range compared to previous observations with the SPDC only. For the second power plant campaign, completed in September 2003, more detailed analysis is currently underway and will be presented. Initial results for the SPDC and airplane measurements indicate a much wider range of Hg(II) to Hg<sup>0</sup> conversion factors.

**Key words:** mercury speciation, emissions, fate and transport, plume, coal-fired power plant

## Volcanic Emissions of Mercury to the Atmosphere: Uncertainties and Outstanding Issues

DAVID PYLE & TAMSIN MATHER

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge.  
CB2 3EQ, UK, e-mail: dmp11@cam.ac.uk

**Abstract:** Compiling a volcanic emissions inventory for mercury poses some considerable difficulties. While there is agreement that some volcanic emanations are enriched in mercury; and that volcanic mercury may be released as particulate Hg(p) and reactive Hg(II), as well as elemental Hg, the paucity of modern, and relevant, volcanic plume data means that there is still considerable uncertainty over the annual emission rate of mercury from volcanoes. Recent inventories still span three orders of magnitude (1–1000 Mg Hg/yr), or from <1% to ~50% of total natural Hg emissions.

Critical assessment of the literature reveals strong evidence for the important role of volcanoes in the global mercury cycle. Based on data from active volcanoes and natural ice-core and peat-bog archives, we have estimated that the time-averaged volcanic Hg emission rate is 700 Mg/yr, or 20–40% of total natural emissions. Year-on-year release of Hg from continuously erupting and degassing volcanoes is ~75 Mg/yr, or only about 10% of this time-averaged flux. 75% of volcanic Hg is released during ‘smaller’ sporadic eruptions (<10–100 Mg Hg/event). Several individual explosive eruptions per century will be large enough (>1000 Mg Hg) to overwhelm the total atmospheric burden, with subsequent deposition rates rivalling the anthropogenic maxima. Large eruptions account for about 15% of total volcanic Hg emissions, and it is the records of such past emissions that will be preserved as discrete ‘spikes’ in ice core and peat bog archives. Individual persistently active volcanoes (e.g. Etna, Sicily) may act as important local point sources of mercury emission to the atmosphere, and their contribution to regional emissions inventories should not be neglected.

Low global volcanic flux estimates (<50 Mg/yr) have tended to rely on the inappropriate extrapolation of data from low-temperature, fumarolic degassing at non-erupting volcanoes to the high-temperature emissions from active volcanoes. Considerable work remains to be done to define the Hg:S ratios in high temperature volcanic emissions; in particular during explosive eruptions. An understanding of the behaviour and fate of mercury species in the near-source volcanic environment is also essential to define how much volcanic mercury is exported to the far-field, or deposited locally. To address these issues, there is a need for new measurements of mercury both in volcanic rocks, and in the emissions from active volcanoes.

**Key words:** volcanic emissions, land-atmosphere exchange, biogeochemical cycles, emissions inventories

# Mercury Speciation upon BrO Initiated |Reactions of Elemental Mercury: Atmospheric Implications

FARHAD RAOFIE AND PARISA A. ARIYA\*

Departments of Chemistry and Atmospheric and Oceanic Sciences,  
McGill University, 801 Sherbrooke St. W., Montreal, PQ, CANADA, H3A 2K6

\*Corresponding author's E-mail: parisa.ariya@mcgill.ca

**Abstract:** Mercury is a toxic element and an important pollutant due to its accumulation in some aquatic organisms. Amongst the major atmospheric oxidants, BrO initiated oxidation of mercury has suggested to be a key player in the rapid mercury depletion events in the Arctic. We performed a product study of BrO initiated oxidation of mercury at near atmospheric pressure of c.a., 750 Torr and room temperature ( $T = 298 \pm 2$  K) in air and  $N_2$  diluents. Reaction products were analyzed in the gas phase from the suspended aerosols and from the well of reaction flask using chemical and electron impact ionization mass spectrometer, gas chromatograph mass spectrometer (GC-MS), cold vapor atomic fluorescence spectrometer (CVAFS), high resolution transmission electron microscopy coupled to energy dispersive spectrometry and MALDI-TOF mass spectrometer. We observed different oxidation forms of mercury in gas-aerosol mixture. Some results and their potential implications in the biogeochemical cycling of mercury are herein discussed.

**Key words:** mercury, BrO radicals, speciation, atmospheric implication

## INTRODUCTION

Mercury has been targeted for global concern as a highly toxic contaminant. The dominant form of mercury in the atmosphere is elemental mercury ( $Hg^0$ ) and is assumed to be long-lived ( $\sim 2$  years)<sup>[1]</sup>. This long lifetime permits long-range atmospheric transport of mercury to regions far from centers of anthropogenic activity, for example, the Atlantic and Pacific Oceans and the Arctic<sup>[2-6]</sup>. The speciation of mercury in open ocean surface waters is dominated by elemental mercury<sup>[7, 8]</sup>. Oceanic gas exchange is an important source of atmospheric Hg and is the primary mechanism controlling the residence of Hg in the surface Ocean. In addition to  $Hg^0$ , other species of mercury can be

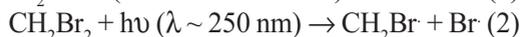
produced from reaction of mercury with oxidant (e.g., Br,  $O_3$ , HO·, BrO,  $NO_3$ )<sup>[9-13]</sup>

Reactions of mercury with halogen oxide radicals drew major attention in light of satellite "BrO" column measurement as well as simultaneous mercury and ozone depletion in the planetary boundary layer<sup>[14, 15]</sup>. It has become increasingly clear that mere physical processes such as adsorption and condensation of  $Hg^0_{(g)}$  on surfaces, including snow and ice-fog crystals, cannot elucidate the magnitude of  $Hg^0_{(g)}$  disappearance in the boundary layer<sup>[16]</sup>. Although the reactions of BrO have been suggested to be key processes driving mercury depletion events<sup>[17]</sup>, kinetic studies of BrO +  $Hg^0$  are very limited<sup>[11]</sup>. Furthermore, there have been

no previous product studies to identify the nature of the products of the BrO-initiated oxidation reaction of elemental mercury, and hence the extent of bioaccumulation of mercury in aquatic systems. In this study we report the products of gas phase reaction of  $\text{Hg}^0$  with BrO near atmospheric condition.

## EXPERIMENTAL

The product studies on the reaction of bromine oxide radicals with elemental mercury were carried out at room temperature ( $298 \pm 2$  K) and near atmospheric pressure ( $750 \pm 1$  Torr) in  $\text{N}_2$  and air. 2 and 3-L double-wall Pyrex flask equipped with magnetic stirrers were used as reaction chamber. BrO radicals were generated in-situ upon visible photolysis of bromine ( $400 \leq \lambda \leq 700$  nm) or UV photolysis ( $\lambda_{\text{max}} \cong 250$  nm) of dibromomethane, in the presence of ozone:

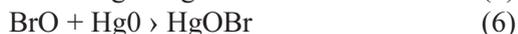


Ozone was produced using an ozone generator (Model OL 100 / DS, Ozone Services Inc.) by a silent discharge technique and was trapped on silica gel cooled to 200 K in a dry ice-Acetone mixture. Concentrations of mercury were monitored by MS detection (quadruple MSD HP 5973) after separation on a gas chromatograph (HP 6890) equipped with a 0.2 mm i.d.  $\times$  30 m cross-linked phenyl-methyl-siloxane column (Hp 5-MS). Speciation of mercury in gas phase, on suspended aerosols, and on wall deposits were done using direct mass (Kartos MS25RFA), GC-MS (HP6890, quadruple MSD HP 5973), Cold vapor atomic fluorescence spectrometer (Tekran 2600), Transmission elec-

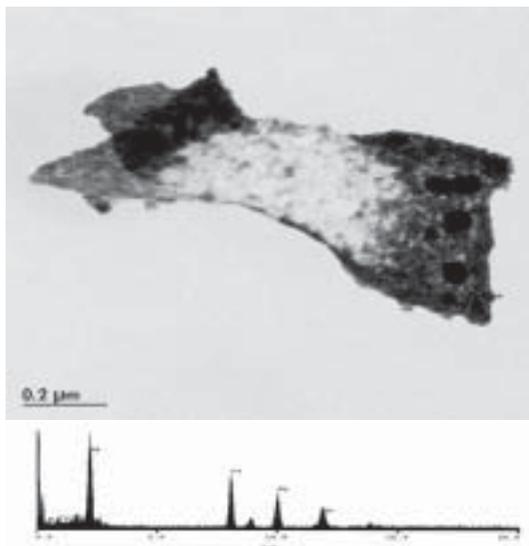
tron microscope with electron dispersive detector (JEOL 2000 FX TEM; EDS JEOL 2000), MALDI-TOF-MS (Kartos kompakt). All the chemicals used were of the highest possible purity.

## RESULT AND DISCUSSION

In order to prevent undesirable side reactions, the wall of the reaction flasks were coated with halocarbon wax (Supelco)<sup>[9]</sup>. The temperature was maintained at  $298 \pm 2$  K by circulating water through the outer jacket using a circulator (Neslab RTE 111). After completion the reaction condensed product were analysed with different methods (experimental section). Figure 1 depicts a typical result, which has been achieved from electronic microscope with EDS detector. The reaction products can be potentially formed via reactions (4) to (6).



Our experimental results indicate that there are several potential pathways for the formation of Hg(I) and Hg(II) upon the reaction of bromine oxide radicals with elemental mercury. The majority of mercury containing products was identified as deposits however a large portion of Hg containing aerosols were observed. Although, more detailed studies are required, the effect of deposition of oxidized mercury containing aerosols on the snow pack and in aquatic system and potential incorporation in the food chain should be considered.



**Figure 1.** HRTEM image of air-dried product of reaction elemental mercury with BrO radicals in presence of water collected from the gas-aerosol, dispersed onto carbon supported Cu grid (**top**); EDS spectrum showing the chemical composition of the product collected from the gas-aerosol (**bottom**).

## Acknowledgements

We cordially thank to the Natural Science and Engineering Research Council of Canada (NSERC), the Fond pour la Formation de

Chercheurs et l'Aide a la Recherche (FCAR), the Canadian Foundation for Innovation (CFI), the COMERN project, CFCAS and Environment Canada for financial support.

## REFERENCES

- [1] SCHROEDER, W. H., ANLAUF, K. G., BARRIE, L. A., LU, J. Y., STEFFEN, A., SCHNEEBERGER, D. R., BERG, T. (1998): *Nature (London)* 394, p. 331.
- [2] BOUTRON, C. F., VANDAL, G. M., FITZGERAD, W. F., FERRARI, C. P. (1988): *Geophys. Res. Lett.* 25, p. 3315.
- [3] MASON, R. P., FITZGERAD, W. F., VANDAL, G. M. (1992): *J. Atmos. Chem.* 14, p. 489.
- [4] SCHROEDER, W. H., KILLER, G., KOCK, H. H., ROUSSEL, P., SCHNEEBERGER, D. R., SHAEDLICH, F. (1995): *Water, Air and Soil. Pollut.* 80, p. 611.
- [5] EBINGHAUS, R., KOCK, H. H., JENNINGS, S. G., MCCARTIN, P., ORREN, M. J. (1995): *Atmos. Environ.* 29, p. 3333.
- [6] SCHROEDER, W. H., EBINGHAUS, R., SHOEIB, M., TIMOSCHENKO, K., BARRIER, L. A. (1995): *Water, Air and Soil. Pollut.* 80, p. 1227.
- [7] MASON, R. P., FITZGERAD, W. F. (1993): *Deep-Sea Res.* 40, p. 1897.
- [8] MASON, R. P., ROLFHUS, K. R., FITZGERAD, W. F. (1995): *Water, Air and Soil. Pollut.* 80, p. 665.
- [9] ARIYA, P. A., KHALIZOV, A., GIDAS, A. (2002): *J. Phys. Chem. A* 106, p. 7310.
- [10] PAUL, B., ARIYA, P. A. (2004): *Phys. Chem. Chem. Phys.* 6, p. 572.
- [11] RAOFIE, F., ARIYA, P. A. (2003): *J. Phys. IV* 107, p. 1119.

- [12] LIN, C- J., PEHKONEN, S. O. (1997): *Atms. Environ.* 31, p. 4125.
- [13] SOMMAR, J., GARDFELDT, K., STROMBERG, D., FENG, X. (2001): *Atmos. Environ.* 35, p. 3049.
- [14] RICHTER, A., WITTRICK, F., EISINGER, M., BURROWS, J. P. (1998): *Geophys. Res. Lett.* 25, p. 2683.
- [15] RICHTER, A., WITTRICK, F., LADSTÄTTER-WEIßENMAYER, A., BURROWS, J. P. (2002): *Adv. Space Res.* 29, p. 1667.
- [16] BARRIE, L. A., BOTTENHEIM, J. W., SCHNELL, R. C., CRUTZEN, P. J., RASMUSSEN, R. A. (1998): Ozone destruction and photo-chemical reactions at polar sunrise in the lower Arctic atmosphere: *Nature* 334, p. 138.
- [17] LU, J. Y., SCHROEDER, W. H., BARRIE, L. A., STEFFEN, A., WELCH, H. E., MARTIN, K., LOCKHART, L., HUNT, R. V., BOILA, G., RICHTER, A. (2001): *Geophys. Res. Lett.* 28, p. 3219.

## Performance of Atmospheric Long-range Transport Models for Mercury Species: Results from a Model Inter-comparison Study

ALEXEY RYABOSHAPKO<sup>1</sup>, RICHARD ARTZ<sup>2</sup>, RUSSELL BULLOCK<sup>3</sup>, JESPER CHRISTENSEN<sup>4</sup>, MARK COHEN<sup>2</sup>, ASHU DASTOOR<sup>5</sup>, DIDIER DAVIGNON<sup>5</sup>, ROLAND DRAXLER<sup>2</sup>, RALF EBINGHAUS<sup>6</sup>, ILIA ILYIN<sup>1</sup>, DAVID LEE<sup>7</sup>, JOHN MUNTHE<sup>8</sup>, JOZEF PACYNA<sup>9</sup>, GERHARD PETERSEN<sup>6</sup>, CHRISTIAN SEIGNEUR<sup>10</sup>, DIMITER SYRAKOV<sup>11</sup>, AND OLEG TRAVNIKOV<sup>1</sup>

<sup>1</sup>EMEP Meteorological Synthesizing Center "East", Russia, msce@msceast.org.

<sup>2</sup>NOAA ARL, USA, richard.artz, mark.cohen; roland.draxler@noaa.gov.

<sup>3</sup>Environment Protection Agency, USA, Bullock; Russell@epamail.epa.gov.

<sup>4</sup>National Environmental Research Institute, Denmark; jc@dmu.dk.

<sup>5</sup>Meteorological Service of Canada, Canada; ashu.dastoor@ec.gc.ca.

<sup>6</sup>GKSS - Research Centre, Germany, ralf.ebinghaus; gerhard.petersen@gkss.de.

<sup>7</sup>Centre for Aerospace Technology, UK; dslee@qinetiq.com.

<sup>8</sup>Swedish Environmental Research Institute, Sweden; john.munthe@ivl.se.

<sup>9</sup>Norwegian Institute for Air Research, Norway; jozef.pacyna@nilu.no.

<sup>10</sup>Atmospheric and Environmental Research, Inc., USA; cseigneur@aer.com.

<sup>11</sup>Institute of Meteorology and Hydrology, Bulgaria; dimiter.syrakov@meteo.bg.

**Abstract:** An inter-comparison study was organised to evaluate current atmospheric mercury models on national, continental and global levels. Nine models used in different countries participated in the study. The simulation results were compared between the models and against the observations. Performance of atmospheric chemical schemes, capabilities of the model to predict short-term variations of different Hg physico-chemical forms in air, and reliability of long-term pollution assessment were checked. All the chemical schemes included Hg<sup>0</sup> oxidation by ozone and Hg(II) reduction by sulphite. Some models included radical redox reactions. The models can reproduce variations of Hg<sup>0</sup> concentrations in air on regional and global levels with accuracy of 10 %. Simulated particulate Hg concentrations were within a factor of 2 of the measurements. Reliability of the models to simulate reactive gaseous mercury (RGM) is currently rather poor, as is the ability to measure RGM. In spite of known uncertainties and ongoing refinements, the results of the study suggest that current models of long-range atmospheric mercury transport can be used for assessment of mercury pollution levels and transboundary effects.

**Key words:** mercury, the atmosphere, concentration, deposition, numerical model, comparison

## INTRODUCTION

Numerical models are essential instruments for assessing atmospheric transport and deposition of heavy metals (HM) on regional and global scales. The models are widely used by national experts and on the international level by several different programs (AMAP, CEC, UNEP). Modelling is a critical component of the Protocol on Heavy Metals of the Transboundary Air Pollution Convention. The Protocol calls for model estimation of HM atmospheric transport between the countries of the Convention and of long-term trends of HM pollution. The Protocol considers Hg as one of the most dangerous HM for the environment and for human health.

## COMPARISON OBJECTIVE AND METHOD

Evaluation of the extent to which different models agree or disagree can provide unique insights regarding the simulation of atmospheric Hg cycling. Accordingly, the Meteorological Synthesizing Center “East” (MSC-E of EMEP) organised a Hg model inter-comparison study. The study involves comparison of each model’s results with available measurement data and with the results of other models. In the first stage of the project, modelling schemes of Hg chemical transformations in a cloud environment were compared. The second stage was focused on determination of capacities of the models for predicting short-term (hours-days) variations of airborne concentrations of the main Hg forms: gaseous elemental (GEM), reactive gaseous oxidised (RGM) and particulate oxidised (TPM). The last stage is focusing on capabilities of the models to reproduce the moni-

toring data obtained on a monthly basis as well as to estimate atmospheric Hg transboundary fluxes for individual countries. The primary task of the project was to assess acceptability of the MSC-E operational model for routine calculations of transboundary Hg transport within Europe. In addition, the comparison of the models allows Hg modelling approaches to be evaluated.

Nine models developed by leading expert groups from 7 countries of Europe and North America have participated in one or more phases of the study. They are: ADOM - Acid Deposition and Oxidants Model (Germany); CMAQ - Community Multi-Scale Air Quality model – EPA USA; GRAHM - Global/Regional Atmospheric Heavy Metals Model (Canada); HYSPLIT - Hybrid Single Particle Lagrangian Integrated Trajectory model (NOAA USA)\*; EMAP - Eulerian Model for Air Pollution (Bulgaria)\*; DEHM - Danish Eulerian Hemispheric Model (Denmark)\*; MCM – Mercury Chemistry Model (AER/EPRI USA)\*\*; CAM – Chemistry of Atmospheric Mercury model (Sweden); MSCE-HM (reg and hem) - EMEP MSC-E Heavy Metal model (regional and hemispheric versions). [\* Phases II and III only; \*\* Phase I only].

## RESULTS AND DISCUSSION

All of the models utilized chemical schemes, which included oxidation of Hg<sup>0</sup> in the gas phase and redox processes in the aqueous phase. It is universally recognised that a main oxidant both in gaseous and aqueous phases is ozone. However, some schemes included also oxidation by OH radical and chlorine. Common for all schemes was Hg reduction

in reactions of Hg-sulphite complex decomposition. In addition to this some schemes considered a possibility of reduction in reaction with HO<sub>2</sub> radical. All models included absorption of a portion of the aqueous-phase Hg compounds onto soot.

IN Phase I, initial conditions were characterised by occurrence in air of clean water droplets and of certain concentrations of the three Hg forms. Dynamics of Hg accumulation in the aqueous phase was simulated over the course of 48 hours. In the most realistic version of the initial conditions (corresponding to regional levels of atmospheric pollu-

tion) the following values were adopted: GEM=1.7 ng/m<sup>3</sup>, RGM=5 pg/m<sup>3</sup>, TPM=40 pg/m<sup>3</sup> and SOOT=0.5 ug/m<sup>3</sup>.

The models, which considered radical reactions, demonstrated a pronounced daily cycle of Hg concentration in water droplets. During night-time Hg accumulated in water while at daylight Hg reduction dominated and elemental Hg escaped to air. Ignoring the photochemical processes led to constant Hg accumulation in water droplets. Table 1 shows a range of variations of total Hg concentration in the aqueous phase during the second day of modelled period when the most realistic initial conditions were applied.

**Table 1.** Maximum and minimum aqueous Hg concentrations (ng/L) simulated during the second 24-h period.

Indian coal	Typical coal	Oil	Petroleum coke	Paper sludge	Sewage sludge	Waste wood	Biomass
0.26-0.49	0.11	0.01	0.02	0.24	3.28	0.17	0.06

The model differences leading to the largest Phase I simulation differences were determined. First, inclusion of HO<sub>2</sub> into a chemical scheme leads to dominating the daytime reduction over the oxidation. Second, assumption of total solubility of all Hg species results in completely reversible sorption process and in decreasing the total aqueous phase concentration. Third, inclusion of Cl<sub>2</sub> can increase overall oxidation rate by 30 %. Fourth, consideration of fast gaseous phase oxidation by OH radical can totally alter the picture of daily cycle – in this case maximum concentrations in water occur during daytime. Hg reduction via sulphite mechanism is strongly inhibited by relatively high chloride concentration in cloud water.

In the second stage of the modelling study, full atmospheric fate and transport models –

including chemistry schemes along with advection, dispersion, and deposition processes – were evaluated by comparing their results against observations carried out during two two-week campaigns at five EMEP monitoring stations in Europe. Two reference years – 1995 and 1999 – have been chosen. Temporal resolution for GEM was one hour while for RGM and TPM - one sample a day was taken. The models were different in their horizontal scales (5 regional, one hemispheric and one global), in their vertical extent (from 3.9 to 30 km height), in their spatial resolution (from 36\*36 km to 1\*1 degree), and in treatment of atmospheric transport and dispersion (Eulerian and Lagrangian approaches). In addition, all the models used different parameterisation of wet and dry deposition. At the same time the participating models used the same input information

(Hg emissions, relevant reactants) except for the meteorological data.

All models demonstrated some capability to simulate short-term variations of GEM. This was confirmed by rather high correlation coefficients for GEM prediction at the most polluted monitoring station in Germany (from 0.54 to 0.62). However, a systematic underprediction of the amplitudes of concentration peaks was generally found. A possible reason could be in the fact that only anthropogenic emissions were taken into account while natural emission and re-emission were ignored. One of concentration peaks of high amplitude (more than 3 ng/m<sup>3</sup>) was very probably connected with air mass transport from known pollution sources. In this case the models caught the peak and predicted its amplitude. Other potential reasons for the discrepancies include (a) errors in the emission inventory [an alternative inventory was found to produce improved results in some cases], and (b) the fact that the inventory was specified on a 50-km grid [the impact of sources within the grids containing monitoring sites could therefore not be accurately estimated].

The most challenging part of the second stage was an attempt to simulate RGM and TPM concentrations in air. Table 2 presents mean concentrations of RGM and TPM both measured and calculated by participating models. There is high scattering of the mean calculated RGM and TPM values. For RGM the results vary by an order of magnitude and can differ from the measured concentration up to 4 times. The most discouraging results were obtained for Mace Head station located in Ireland at the ocean shore far from known pollution sources. The HYSPLIT model, which demonstrated good agreement with observation included a chlorine oxidation reaction. Also, the HYSPLIT model assumed that dissolved Hg(II) in atmospheric droplets “counted” as RGM for the purposes of the comparison, and this may have been the reason for the improved results. The modeling results for TPM are better than for RGM. For practically all the samples the simulated concentrations differ from the observed ones at German stations by less than the factor of 2. Surprisingly, all models demonstrated very good results for Mace Head station.

**Table 2.** Mean observed and calculated concentrations of RGM and TPM, pg/m<sup>3</sup>.

Station Obs / Mod	Neuglobsow Germany		Zingst, Germany	Roervik, Sweden		Aspvreten, Sweden		Mace Head, Ireland	
	RGM	TPM	TPM	RGM	TPM	RGM	TPM	RGM	TPM
<b>Observ.</b>	<b>9</b>	<b>40</b>	<b>33</b>	<b>7</b>	<b>15</b>	<b>5</b>	<b>10</b>	<b>17</b>	<b>14</b>
CMAQ	32	73	61	11	45	6	46		
ADOM	24	31	19	2	15	1	12		
MSC-E-reg	20	32	34	6	14	4	11	3	13
GRAHM	36	62	43	5	40	3	52	0.2	14
DEHM	4	45	32	1	19	0.4	16	0.9	18
HYSPLIT	13	46	39	8	25	7	18	14	16
EMAP	9	32	26	8	15	6	10		

Finally, for international control of Hg pollution it is important to know the reliability of model-estimated transboundary fluxes. In the third stage the models are predicting mean monthly values of the Hg concentrations in air and precipitation at 10 monitoring stations. For these locations Hg wet and dry depositions were also calculated. In addition, transboundary budgets are being calculated for three countries – UK, Italy and Poland – as illustrative example. Modelling calculations were made for 1999. 8 models are participating in this stage, which is currently ongoing.

In preliminary results currently available for Phase III, the participating models are able to reproduce measured annual TGM concen-

trations to within  $\pm 10\%$ . At some sites the correlation for monthly mean values can reach 0.8. It should be kept in mind that quality of the TGM measurements is also on the level of  $\pm 10\%$ . Difference between measured and calculated wet deposition values can be considerably higher. Table 3 presents a preliminary comparison of wet deposition fluxes for February 1999. One can see that there are significant discrepancies for some stations. The models tend to overestimate wet deposition values. It should be mentioned that a significant contribution into the total uncertainty is given by both measured and evaluated precipitation amounts during individual months. On annual level, however, the models can reproduce the measured wet deposition fluxes within a factor of 2.

**Table 3.** Observed vs. modelled wet depositions of Hg at some monitoring sites in February 1999 ( $\text{g}/\text{km}^2/\text{month}$ ) [Results from GRAHM, HTSPLIT, DEHM and EMAP are not yet available].

Site Obs. / model	DE01 Germ	DE09 Germ	FI96 Finl	NL91 Neth	NO99 Norw	SE02 Swed	SE05 Swed	SE11 Swed	SE12 Swed
<b>Observation</b>	<b>0.67</b>	<b>0.31</b>	<b>0.05</b>	<b>0.47</b>	<b>0.93</b>	<b>0.52</b>	<b>0.12</b>	<b>0.73</b>	<b>0.14</b>
CMAQ	0.81	0.79	-	0.80	1.10	0.42	-	0.71	0.13
ADOM	0.18	0.14	0.05	0.13	0.05	0.06	0.05	0.08	0.07
MSC-E-reg	1.07	1.37	0.41	1.38	1.11	0.25	0.41	0.70	0.24
MSC-E-hem	0.62	1.01	0.47	0.84	0.78	0.50	0.60	0.68	0.63

Preliminary estimates of Hg atmospheric balances for individual countries (UK, Italy, Poland) showed that from 25 to 60 % of Hg emitted by a give country are deposited within that country. Direct transboundary contribution from European countries to Hg pollution is not so high (from 5 to 15 %), however, all sources outside the country can contribute up to 2/3 of total depositions to the country.

## CONCLUSIONS

Results to date suggest that current models of long-range atmospheric Hg transport can be used for assessment of Hg pollution levels and transboundary effects. In particular, the models can play an important role in the implementation of the International Protocol on Heavy metals, which came into effect in 2003. However, basic research should be continued to improve the ability of the models to simulate RGM and TPM since these forms of Hg are deposited from the atmosphere most efficiently.

## Dry Deposition of Mercury and Selected Trace Metals Measured with a Water Surface Sampler

MASAHIRO SAKATA & KOHJI MARUMOTO

Environmental Science Research Laboratory, Central Research Institute of Electric Power Industry (CRIEPI), Abiko 1646, Abiko, Chiba 270-1194, Japan; E-mail: sakata@criepi.denken.or.jp

**Abstract:** Dry deposition of mercury and selected trace metals (Cd, Cu, Mn, Pb, and Zn) in the Tokyo metropolitan area was measured using an improved water surface sampler. The dry deposition fluxes were compared to the wet deposition fluxes measured at the same site. Also, this paper evaluates the deposition of reactive gaseous mercury and particulate mercury individually.

**Key words:** mercury, trace metals, dry deposition, deposition velocity, dater surface sampler

### INTRODUCTION

The atmospheric deposition is an important source of various toxic substances to surface waters and terrestrial environments<sup>[1-3]</sup>. In recent years, there has been an increase in human health and environmental concerns related to the toxicity of methylmercury bioaccumulated in fish through the food chain. It is known that significant amounts

of methylmercury are produced by in situ methylation of inorganic mercury deposited into aquatic environments<sup>[3]</sup>. Atmospheric constituents are deposited through both wet and dry processes. Compared to the case for wet deposition, many uncertainties exist in the methods used to quantify dry deposition. In this study, an improved water surface sampler (Fig. 1)<sup>[4,5]</sup> was used to measure the dry deposition of mercury and selected trace

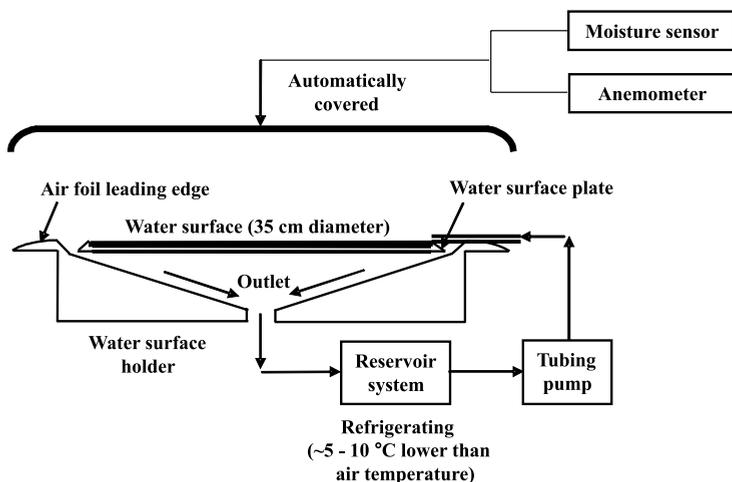


Figure 1. Schematic diagram of the improved water surface sampler

metals (Cd, Cu, Mn, Pb, and Zn). Mercury is deposited on the water surface in both gaseous (reactive gaseous mercury, RGM) and particulate (Hg(p)) forms. Observations were conducted at a study site in the Tokyo metropolitan area (Komae City). The dry deposition fluxes were compared to the wet deposition fluxes measured at the same site. Nine municipal solid waste (MSW) incinerators are located within 10 km of the study site. Previously, SAKATA ET AL.<sup>[6,7]</sup> reported that the MSW incinerators are the predominant sources of mercury and other trace metals as As, Cd, Pb, and Zn in the atmosphere.

#### DRY DEPOSITION AND ITS COMPARISON WITH WET DEPOSITION FLUX

Changes in dry deposition fluxes with time for trace metals are shown in Fig. 2. The Zn fluxes in May, July, and November 2002 were not obtained due to the contamination of the sampling solution by Zn, which originated from the additives in the PharMed tubing used. A Tygon tubing was used for sampling in December 2001 and September 2002. Fig. 2 shows that the dry deposition fluxes for trace metals increased according to  $Hg < Cd < Pb < Cu < Mn < Zn$  for almost all sampling periods. Also, there was no great difference in the deposition flux for each metal between periods. Thus, the seasonal changes were very small relative to those for wet deposition (Fig. 3). Next, the annual wet deposition fluxes from April 2002 to March 2003 were compared to the dry deposition fluxes during the same period. The dry deposition fluxes were estimated by multiplying the average deposition flux from five measurements (Fig. 2) by the hours of the dry period. As shown in Fig. 4, the dry deposi-

tion fluxes were 0.46 – 3.0 times larger than the wet deposition fluxes. Thus, dry deposition plays an important role in trace metal deposition in this urban area. In particular, the Cu, Zn, and Mn fluxes were about 3 times higher than the wet deposition fluxes. This is probably due to the fact that these metals are primarily associated with coarse particles<sup>[4,5]</sup>, which leads to their higher deposition velocities.

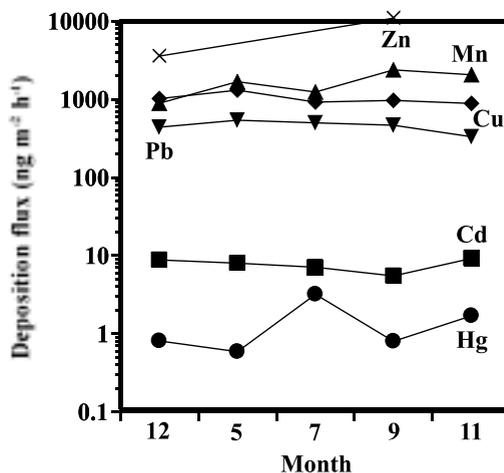


Figure 2. Change in dry deposition fluxes with time for trace metals (December 2001 to November 2002)

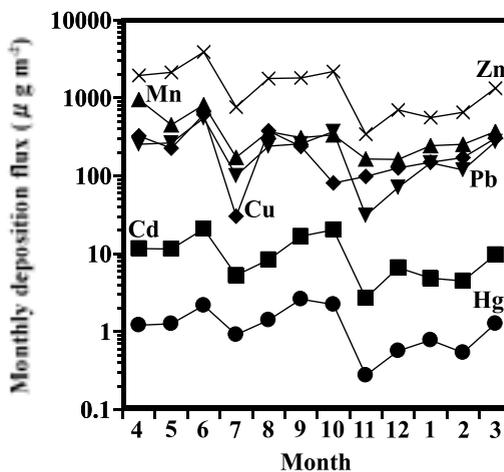


Figure 3. Monthly change in wet deposition fluxes for trace metals (April 2002 to March 2003)

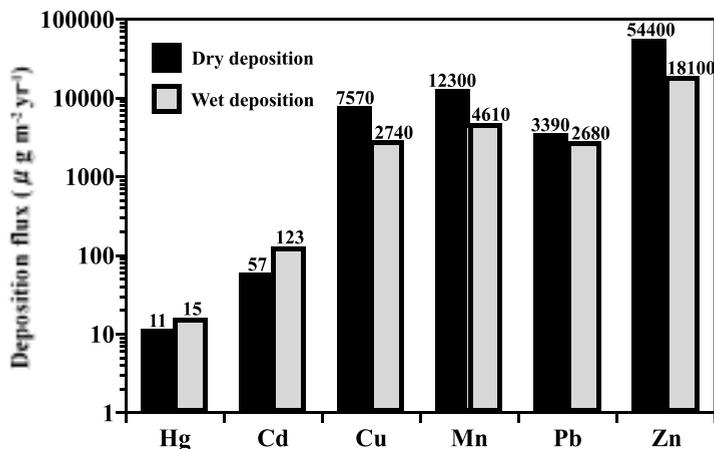


Figure 4. Comparison between dry deposition fluxes and wet deposition fluxes for trace metals (April 2002 to March 2003)

#### EVALUATION OF DRY DEPOSITION FOR Hg(P) AND RGM

The dry deposition flux of mercury,  $F_{Hg}$ , is given as the sum of the deposition fluxes of Hg(p),  $F_{Hg(p)}$ , and RGM,  $F_{RGM}$ :

$$F_{Hg} = F_{Hg(p)} + F_{RGM}$$

$$= v_{d,Hg(p)} C_{Hg(p)} + v_{d,RGM} C_{RGM},$$

where  $v_{d,Hg(p)}$  and  $v_{d,RGM}$  are dry deposition velocities for Hg(p) and RGM, and  $C_{Hg(p)}$  and  $C_{RGM}$  are atmospheric concentrations for Hg(p) and RGM, respectively. Our previous analysis suggested that the 84.13 % diameter is a more appropriate index for each deposited metal than the 50 % diameter in the assumed undersize log-normal distribution, because larger particles are responsible for the flux<sup>[5]</sup>. The deposition velocities for trace metals other than mercury increased exponentially with an increase in their 84.13 % diameters (Fig. 5). Using this regression equation, the deposition velocity for Hg(p)

was estimated from its 84.13 % diameter. The result gave  $v_{d,Hg(p)}$  values from 0.31 to 0.94 cm s<sup>-1</sup>. Next, the deposition fluxes for Hg(p) during the study periods were calculated from the estimated velocities and measured atmospheric concentrations. The ratio of the calculated flux for Hg(p) to the flux for Hg measured with the water surface sampler varied from 0.24 to 2.8, and significantly decreased in July. Essentially this ratio could not be higher than 1. The calculated fluxes are expected to have a large error on the basis of the 95 % confidence interval for the estimated  $v_d$  (Fig. 5). Thus, it is regarded that the calculated fluxes for Hg (p) are almost equal to the measured flux for Hg during the study periods except in July if the large error is taken into consideration. On the other hand, the ratio of the calculated Hg(p) flux to the measured Hg flux was very low in July. This suggests that the deposition flux for RGM increased abruptly in July. The reason seems to be that summer generally favors the formation of RGM due to higher air temperature, solar radiation intensity, and atmospheric ozone concentration<sup>[8]</sup>. However, the

uncertainty associated with a large error makes it difficult to estimate the deposition flux for RGM, although the RGM flux cor-

responds to the difference between the Hg flux measured with the water surface sampler and the estimated Hg(p) flux.

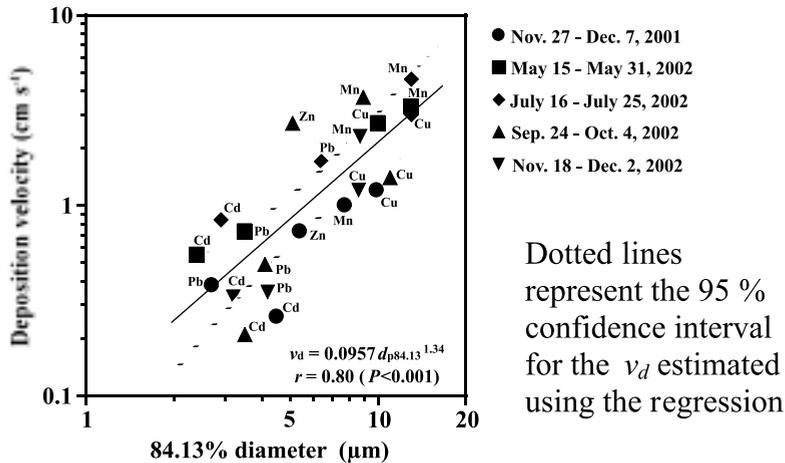


Figure 5. Relationship between dry deposition velocity and 84.13 % diameter for trace metals

## CONCLUSIONS

The results based on 1 yr observations found that dry deposition plays a significant if not dominant role in trace metal deposition in the Tokyo metropolitan area, contributing fluxes ranging from 0.46 to 3.0 times those of concurrent wet deposition fluxes. Also, the

limited results presented here tend to support the hypothesis that deposited mercury is mainly in particulate form except during summer, and that significant amounts of RGM are deposited during summer. However, further research is required to elucidate the relative importance of Hg(p) and RGM deposition more accurately and to consequently validate this hypothesis.

## REFERENCES

- [1] STRACHAN, W. M. J. & EISENREICH, S. J. (1988): *Mass Balance of Toxic Chemicals in the Great Lakes: The Role of Atmospheric Deposition*, International Joint Commission, Windsor, ON, Canada.
- [2] LANDIS, M. S. & KEELER, G. J. (2002): Atmospheric mercury deposition to Lake Michigan during the Lake Michigan Mass Balance Study. *Environ. Sci. Technol.* 36, 4518-4524.
- [3] ROLFUS, K. R., SAKAMOTO, H. E., CLECKNER, L. B., STOR, R. W., BABIARZ, C. L., BACK, R. C. MANOLOPOULOS, H. & HURLEY, J. P. (2003): Distribution and fluxes of total and methylmercury in Lake Superior; *Environ. Sci. Technol.* 37, 865-872.
- [4] SAKATA, M. & MARUMOTO, K. (2003): A new method for evaluating dry deposition of mercury using a water surface sampler; *J. Phys. IV France* 107, 1177-1180.

- <sup>[5]</sup> SAKATA, M. & MARUMOTO, K. (2003): Dry deposition fluxes and deposition velocities of trace metals in the Tokyo metropolitan area measured with a water surface sampler; *Environ. Sci. Technol.* (in press).
- <sup>[6]</sup> SAKATA, M., KURATA, M. & TANAKA, N. (2000): Estimating contribution from municipal solid waste incineration to trace metal concentrations in Japanese urban atmosphere using lead as a marker element; *Geochem. J.* 34, 23-32.
- <sup>[7]</sup> SAKATA, M. & MARUMOTO, K. (2002): Formation of atmospheric particulate mercury in the Tokyo metropolitan area; *Atmos. Environ.* 36, 237-244.
- <sup>[8]</sup> LINDBERG, S. E. & STRATTON, W. J. (1998): Atmospheric mercury speciation: concentrations and behavior of reactive gaseous mercury in ambient air; *Environ. Sci. Technol.* 32, 49-57.

# Comparison of Grid-based and Plume Modeling to Estimate the Local Impacts of Large Mercury Point Sources

CHRISTIAN SEIGNEUR<sup>1</sup>, KRISTEN LOHMAN<sup>1</sup>, KRISH VIJAYARAGHAVAN<sup>1</sup>,  
JOHN JANSEN<sup>2</sup> & LEONARD LEVIN<sup>3</sup>

<sup>1</sup>Atmospheric & Environmental Research, Inc., San Ramon, CA, USA;  
E-mail: seigneur@aer.com

<sup>2</sup>Southern Company, Birmingham, AL, USA

<sup>3</sup>EPRI, Palo Alto, CA, USA

**Abstract:** A grid-based model, TEAM, and a plume model, TRUE, are compared for atmospheric mercury deposition near the location of five coal-fired power plants. The grid-based model is shown to overestimate (compared to the plume model) mercury dry and wet deposition within the grid cell where the source is located. The causes of these overpredictions include enhanced vertical mixing of elevated plumes in the grid-based model and the fact that the grid-based model does not account for the exact location of the power plant. The grid-based model overestimates total mercury deposition within about 20 km from the source by a factor of 2 to 4 for the power plants considered here.

**Key words:** mercury deposition, power plants, grid-based model, plume model

## INTRODUCTION

Three-dimensional (3-D) grid-based models are used to calculate the atmospheric deposition of mercury (Hg) on global, continental and regional scales. Such models are appropriate to calculate Hg deposition at such scales but the 3-D grid structure is likely to lead to overestimates of mercury deposition at local scales, i.e., at scales commensurate with that of the grid resolution, when compared to a plume model. The reason for such overestimates is that the grid models do not resolve transport, dispersion and deposition processes at scales finer than the grid size. As a result, the emissions from major point sources such as power plants are instantaneously mixed within the grid cell volume where they are released. Such mixing can lead to overestimates of Hg deposition. To

address this issue, we compared Hg deposition fluxes calculated by a 3-D grid-based model, TEAM (SEIGNEUR ET AL., 2004) with those from a plume model, TRUE (CONSTANTINO AND SEIGNEUR, 1993), which provides a fine spatial resolution of the transport, dispersion and deposition of Hg emitted from point sources.

## GRID-BASED MODEL SIMULATION

The grid-based simulation was conducted with TEAM using 1998 meteorology and 1998/1999 emissions data. The boundary conditions were provided by a global model as described by SEIGNEUR ET AL. (2004). TEAM was applied over North America using a 100 km resolution and in a nested domain covering the central and eastern United States using a 20 km resolution (VIJAYARAG-

HAVAN ET AL., 2004). Next, simulations were conducted without Hg emissions from individual power plants. The difference between the base simulation and each sensitivity simulation represents the dry, wet and total deposition of Hg from an individual power plant. Five simulations were conducted to characterize the Hg deposition fluxes due to five power plants located in the southeastern United States.

### PLUME MODEL SIMULATIONS

Plume simulations were conducted for the five power plants using the atmospheric model of TRUE. This model is based on the Industrial Source Complex Long Term model (ISC-LT, Version 2). It includes the same chemical kinetic mechanism for Hg as TEAM. It also includes dry deposition and wet deposition of Hg(II) and Hg(p) using species-specific deposition characteristics (i.e., deposition velocities for dry deposition and scavenging coefficients for wet deposi-

tion). Meteorological variables are input as annual frequencies and the model calculates annual deposition fluxes at an array of receptor points distributed around the power plants. The same emissions of Hg species (i.e., Hg(0), Hg(II) and Hg(p)) were used for TRUE as for TEAM. These were based on EPRI analysis of the EPA utility Hg ICR stack flue gas data set; no changes in speciation were incorporated to account for potential in-plume redox reactions of Hg following stack emissions. The Hg deposition characteristics of TRUE were adapted to be consistent with those of TEAM.

### COMPARISON OF TEAM AND TRUE MERCURY DEPOSITION RATES

We compare in Table 1 the Hg deposition rates calculated with TEAM and TRUE in the grid cell where the power plant is located (hereafter referred to as the central grid cell). In the central grid cell, the ratio of the TEAM to the TRUE deposition rates ranges from

**Table 1.** Comparison of TEAM and TRUE mercury deposition rates (g/y) in the central grid cell<sup>a</sup> for the five power plants.

Power plant	Wet deposition			Dry deposition			Total deposition		
	TEAM	TRUE	Ratio	TEAM	TRUE	Ratio	TEAM	TRUE	Ratio
A	4291	1714	<b>2.5</b>	3170	156	<b>20</b>	7460	1871	<b>4.0</b>
B	2603	983	<b>2.6</b>	1156	74	<b>16</b>	3759	1056	<b>3.6</b>
C	1158	880	<b>1.3</b>	826	30	<b>28</b>	1984	910	<b>2.2</b>
D	704	220	<b>3.2</b>	280	55	<b>5.1</b>	984	275	<b>3.6</b>
E	385	240	<b>1.6</b>	180	16	<b>11</b>	565	257	<b>2.2</b>

a. the central grid cell is the grid cell where the power plant is located; the grid cell is 20 km x 20 km.

1.3 to 3.2 for wet deposition, from 5 to 28 for dry deposition and from 2.2 to 4 for total deposition. The differences between the TEAM and TRUE results are due to two major differences in the treatment of power plant Hg emissions.

First, in TEAM the emissions of the power plant are diluted instantaneously after plume rise in a grid cell enclosing the effective stack height of the plume and located above the central grid cell. This dilution occurs regardless of where the power plant is located within the central grid cell (i.e., whether it is at the center of the cell or near one of its boundaries). TRUE treats the plume rise, dispersion, transport and deposition of the power plant emissions explicitly with respect to the exact location of the power plant. If a power plant is located near the boundary of two grid cells, the power plant-emitted material will be distributed (according to the frequency of wind directions) by TRUE between those two grid cells. Therefore, different results will be obtained with TRUE if the power plant is located at the center of the grid cell or near one of the cell boundaries.

Second, the grid structure of TEAM favors dilution of the emissions from the power plant. Material released in a grid cell aloft will be distributed vertically via vertical mixing. On the other hand, the plume model, TRUE, tends to keep the plume material aloft except under very unstable atmospheric conditions that lead to fumigation and rapid mixing to the ground. Thus, vertical dilution in the grid model leads to greater ground-level concentrations near the source in TEAM than in TRUE. The difference in dry deposition between the grid model and the plume model is expected to be greater for cases of inter-

mediate effective stack height. For plumes that are released at very high elevations, vertical dilution in the grid model may bring only a negligible amount of plume material into the surface layer. For plumes that are released near the ground, both the grid model and the plume model will show plume material at ground level. Therefore, cases of plumes released at moderate elevations should show greater discrepancies, with the grid model predicting some plume material in the surface layer and the plume model predicting plume material mostly aloft.

The highest dry deposition with TEAM always occurs in the central grid cell because vertical mixing of emissions aloft leads to the highest ground-level concentrations in the central grid cell. On the other hand, the highest dry deposition with TRUE never occurs in that central grid cell because the plume remains aloft long enough that the highest ground-level concentrations occur farther downwind. For wet deposition, the highest deposition occurs in the central grid cell with both TEAM and TRUE because wet deposition removes Hg along a vertically integrated column and vertically-integrated concentrations are highest in the grid cell where the power plant is located for both models. Because wet deposition is more important than dry deposition in these case studies, the highest Hg deposition occurs in the central grid cell for both models.

## CONCLUSIONS

A comparison of grid-based and plume modeling of local (within about 20 km from the source) Hg deposition showed that the grid-based model overestimates Hg deposition

fluxes by a factor ranging from 2.2 to 4 for the power plants studied here. These results demonstrate that plume models are better suited for assessing local impacts. A sub-grid scale treatment of the plumes from large point sources is recommended for grid models.

## REFERENCES

- CONSTANTINO, E. & SEIGNEUR, C. (1993): A mathematical model for multimedia health risk assessment; *Environ. Software*, Vol. 8, pp. 231-246.
- SEIGNEUR, C., VIJAYARAGHAVAN, K., LOHMAN, K., KARAMCHANDANI, P. & SCOTT, C. (2004): Global source attribution for mercury deposition in the United States; *Environ. Sci. Technol.*, Vol. 38, pp. 555-569.
- VIJAYARAGHAVAN, K., SEIGNEUR, C., LOHMAN, K., KARAMCHADANI, P., LEVIN, L. & JANSEN, J. (2004): Modeling the impact of mercury speciation in power plant plumes on mercury deposition over the eastern U.S.; *7<sup>th</sup> Electric Utilities Environmental Conference – Air Quality, Global Climate Change and Renewable Energy*, 19-22 January, Tucson, AZ, USA.

## Acknowledgements

This work was supported by EPRI, Palo Alto, CA, under Contract EP-P11144/C5579.

## Dissolved Gaseous Mercury (DGM) Flux at the Water/Air Interface over The Negro River Basin, Amazon, Brazil.

GILMAR SILVÉRIO DA SILVA<sup>1</sup>, WILSON F. JARDIM<sup>2</sup> AND PEDRO SÉRGIO FADINI<sup>3</sup>.

<sup>1</sup> CEFET-PR/MD, Paraná, Brazil

<sup>2</sup> LQA-IQ, State University of Campinas (UNICAMP); <http://lqa.iqm.unicamp>

<sup>3</sup> PUC Campinas - ICBQ, Campinas, São Paulo, Brazil.

**Abstract:** The amount of dissolved gaseous mercury (DGM) released annually to the atmosphere by water bodies in each of the 18 major sub-basins of the Negro River tributaries has been estimated for the wet season. Using Remote Sensing (RS) and Geographic Information System (GIS), the total flooded area was estimated during the wet season period (May-July), being its maximum value around 10 % of the total basin area. DGM evasive fluxes values estimated in the last 4 scientific excursions varied between 0.45 and 7.9 pmol m<sup>-2</sup> h<sup>-1</sup>. Considering the flooded area of the Negro River Basin as 69,000 km<sup>2</sup>, the total amount of mercury emitted by all water bodies reaches nearly 0.26 ton y<sup>-1</sup>, what represents not more than 2 % of the total mercury found in the wet deposition in this same area.

**Key words:** geographic information system (GIS), remote sensing, dissolved gaseous mercury (DGM), Negro River, Amazon

### INTRODUCTION

Negro River basin spreads over an area of 690x10<sup>3</sup> km<sup>2</sup> of the Brazilian territory and is characterized by a predominance of black water bodies, showing amounts of dissolved organic matter, which can reach up to 20 mg C L<sup>-1</sup>, and low pH values, around 4. Recent studies have shown high concentration of mercury in fishes, soils, lakes and rivers, although anthropogenic point sources have not been identified in this region<sup>[1]</sup>. Another important aspect concerning the Negro River is the hydrological regime, with intense rains in the period of May-June, flooding a vast forest area called Igapós. In order to estimate the amount of mercury emitted at the water/

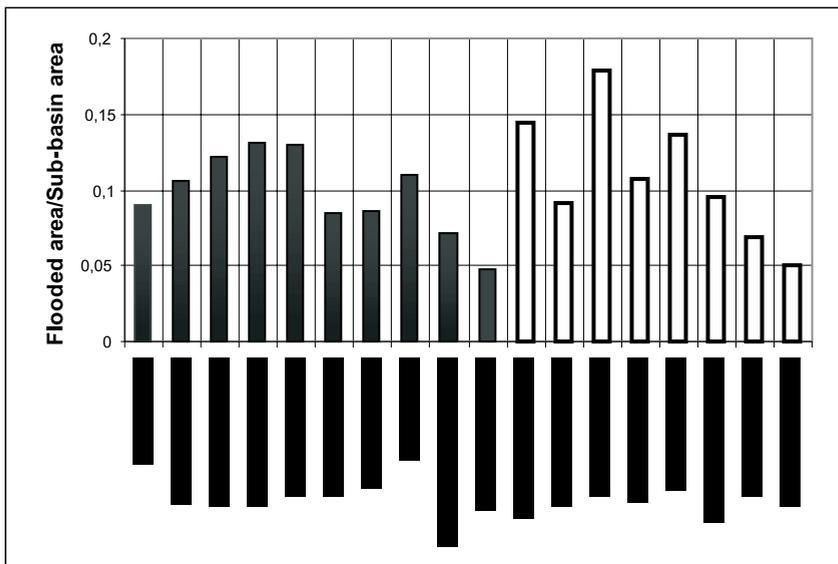
air interface from the major 18 sub-basins of the Negro River tributaries during wet season, DGM evasive fluxes were estimated in different lakes and rivers. Sub-basin areas and flooded areas were estimated with the help of remote sensing (RS) and geographic information system (GIS) tools. The GIS used in this work (SPRING 3.6) was developed by the INPE (National Institute of Spatial Research, Brazil). Satellite images from the Amazon region was generated by the Global Rain Forest Mapping Project South America, 1995-1996, Volume AM-1, obtained by the Japanese satellite JERS-1. The image allows to identify different types of soil coverage, such as rivers, rainforests and flooded areas.

## RESULTS AND DISCUSSION

Firstly, the areas of each 18 sub-basins of the Negro River tributaries were estimated (Table 1) for the Marauaiá, Tea, Uneiuxi, Aiuanã, Urubaxi, Cuini, Caurés, Unini, Jaú, Carabinani, Puduari, Jauaperi, Branco, Jufari, Demini, Aracá, Padaueri and Preto river. The largest tributary basin is from the Branco River, with 160,000 km<sup>2</sup>. In a second step, maximum flooded areas were estimated in respect to the total area for each sub-basin (Figure 1), with results varying from 0.05 up to 0.17, showing an average value of approximately 0.1. Adopting this value as representative for all the Negro River basin, it means that 10 % of total watershed will be flooded during wet season, which corresponds to 69,000 km<sup>2</sup>.

DGM evasive fluxes, estimated with the help of Fick's law, varied from 0.47 pmol m<sup>-2</sup> h<sup>-1</sup> up to 7.9 pmol m<sup>-2</sup> h<sup>-1</sup> measure over four different scientific excursion, with an average value of 2.2 pmol m<sup>-2</sup> h<sup>-1</sup> (n = 20). Combining this figure with the flooded area for each individual sub-basin, the amount of mercury emitted at water/air interface was calculated (Table 1). Another important information concerning the data presented in Table 1 is the total amount of mercury emitted by the whole flooded area of the Negro River basin, what has been estimated as 0.26 tons y<sup>-1</sup>.

It is worth comparing the total amount of mercury emitted from the Negro River basin with the total mercury input estimated from wet deposition<sup>[2]</sup>, whose value is 15.8 tons y<sup>-1</sup>. It can be seen that mercury wet deposition over this watershed is around 60 times higher than the mercury emitted from the water/air interface.



**Figure 1.** Flooded area/Sub-basin area ration to major Negro River tributaries. The black column represent right margin tributaries and white column represent left margin tributaries. Results obtained by using RS/GIS tools.

**Table 1.** Mercury emitted to the atmosphere associated to DGM evasive flux at the water/air interface in different tributaries flooded areas in the Negro River basin.

River	Sub-basin area (km <sup>2</sup> )	Flooded area (km <sup>2</sup> )	Mercury mass emitted from Flooded area (kg y <sup>-1</sup> )
Tea	5434	473	2.7
Uneixuí	9449	989	5.6
Aiuaná	3349	405	2.3
Urubaxi	6754	883	5.0
Cuiuni	12461	1456	8.3
Caurés	7079	426	2.4
Unini	32599	2678	15.2
Jaú	10898	948	5.4
Carabinani	8190	953	5.4
Puduari	3735	178	1.0
Jauaperi	31980	4237	24.1
Branco	161889	12314	70.1
Jufari	9095	1634	9.3
Demini	26552	2650	15.1
Araçá	18831	2391	13.6
Padaueri	7659	676	3.8
Preto	5852	345	1.6
Marauia	1919	95	0.4

## CONCLUSIONS

Considering the total flooded area of the Negro River Basin as 69,000 km<sup>2</sup>, the total amount of mercury emitted by all water bodies at water/air interface reaches 0.26 tons year<sup>-1</sup>. This figure represents around 2 % of the total mercury found in the wet deposition in this same area, e.g., 15.8 tons year<sup>-1</sup>. Among the 18 major tributaries sub-basin of the Negro River, the amount of mercury

emitted at the water/air interface varied from 0.4 up to 70.1 kg y<sup>-1</sup>. Therefore, the amount of mercury emitted from DGM evasive flux is very low compared to the mercury input from wet deposition.

## Acknowledgements

FAPESP, CAPES, CNPq, UNICAMP, PUC-Campinas and CEFET-PR/MD

## REFERENCES

- [1] FADINI, P. S. AND JARDIM, W. F. (2001): Is the Negro River Basin (Amazon) impacted by naturally occurring mercury?; *Sci. Tot. Environ.* 275(1-3), 71-82.
- [2] SILVA, G. S. AND JARDIM, W. F. (2003): Estimation of mercury wet deposition in the tributary sub-basins of the Negro River (Amazon-Brazil) using RS/GIS tools; *J. Phys. IV France* 107.

# Volatilization of Mercury from Soils in Response to Simulated Precipitation

XIAOXI SONG AND BILL VAN HEYST

School of Engineering, University of Guelph, Guelph, ON, Canada, N1G 2W1;  
E-mail: songx@uoguelph.ca, bvanheys@uoguelph.ca

**Abstract:** Increases in mercury volatilization from naturally enriched soils due to precipitation events have been observed in the field, leading to the need for further research on the exact mechanisms responsible for the increase in the observed fluxes. In this research, the effects of precipitation on fluxes are simulated in a controlled laboratory experiment using a dynamic flux chamber system with an internal precipitation generator. The experimental results indicate a sharp and rapid spike in the mercury flux, during and immediately following the precipitation event, which is partly due to physical displacement of mercury vapour in the surface soil interstitial air by incoming water, and partly due to the increase in soil moisture content. The magnitude of gaseous elemental mercury fluxes from the soil after the precipitation event is related to the soil moisture content both prior to and after the precipitation event.

**Key words:** gaseous elemental mercury, dynamic flux chamber, soil flux, precipitation effect

## INTRODUCTION

Mercury enriched soils are a major source to the global atmospheric mercury budget. In recent field studies, increases in mercury volatilization from soils in response to precipitation events have been observed (LINDBERG ET AL., 1999; POISSANT ET AL., 1999). The major suspected controlling processes are surface gaseous mercury displacement by water and aqueous divalent mercury redox reactions (ZHANG AND LINDBERG, 1999). However, there is no concrete evidence that these are the controlling processes due to the convolution of the field flux data with other environmental parameters.

To study the underlying mechanism of precipitation effects, the field-observed in-

creases in gaseous elemental mercury fluxes due to precipitation are simulated in a controlled laboratory experiment. In this manner, the specific effects that precipitation and the ensuing soil moisture have on the magnitude of mercury emissions can be isolated and studied. The experiments have been conducted using a dynamic flux chamber system with an internal precipitation generator and soil lysimeter containing soil that is naturally enriched with mercury. Mercury concentration at the inlet and outlet of the chamber was monitored during the experiment using a Tekran 2537A mercury vapour analyzer. Other measured environmental parameters include the inlet and outlet air temperatures and relative humidities, soil temperatures at two soil depths, and soil moistures at four soil depths.

The first set of experiments consisted of monitoring mercury emissions from a fairly dry soil (~5 %) and applying a 1L of deionized water to simulate a single precipitation event that lasted several hours. Mercury emissions as well as other environmental parameters were continuously monitored for an extended period after the precipitation event. As the soil dried back to approximately the same initial conditions, the experiment was repeated to verify the observed behaviour.

The second set of experiments consisted of monitoring mercury emissions from a fairly dry surface again, but the initial rain event was followed by a subsequent rain event of the same magnitude and duration on the next day. As with the first set of experiments, the mercury emissions and other environmental parameters were monitored and the soil was allowed to dry until it reached the same initial conditions, and then the experiment was repeated.

A third set of experiments was also conducted using a single precipitation event but with elevated soil moisture levels rather than the fairly dry initial conditions of the first two set of experiments.

## RESULTS AND DISCUSSION

The gaseous elemental mercury flux from a single precipitation event experiment is given in Figure 1 along with the soil moisture content at a depth of 1 cm and 5 cm. Figure 1 shows a rapid and sharp spike in the mercury flux during and immediately following the precipitation event. After the precipitation event, mercury fluxes remain elevated compared to those prior to the rain event, but decrease in an analogous manner to decreasing surface soil moisture, thus indicating a potential correlation between soil moisture and mercury flux. The initial spike appears to be the result of two processes: one related to the elevated soil moisture levels and one

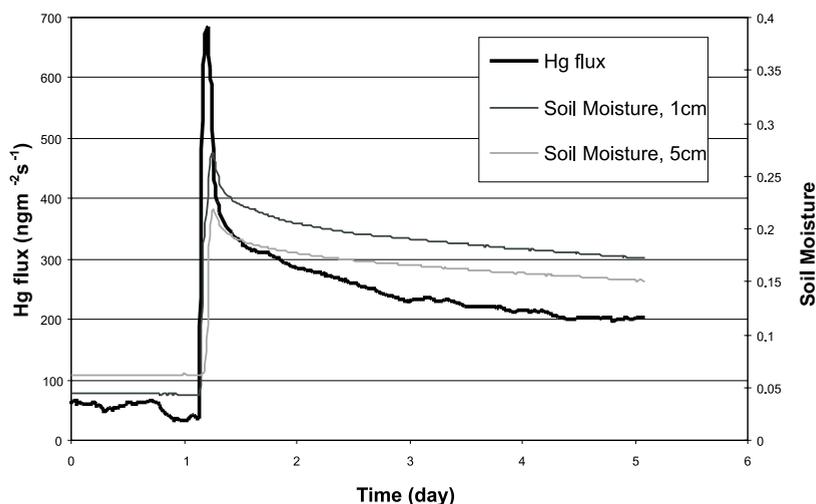


Figure 1. Mercury flux and soil moisture changes in single rain event

related to the physical displacement of gaseous elemental mercury in the surface soil interstitial air by the incoming water. Rough estimations of the surface soil air gaseous mercury concentration, at equilibrium with the soil substrate concentration, approximate the amount of mercury released in the initial

spike above that associated with the elevated soil moisture effects. Results from a repetition of the single precipitation event confirm the same behaviour, although the absolute peak values are somewhat different due to surface mercury depletion effects.

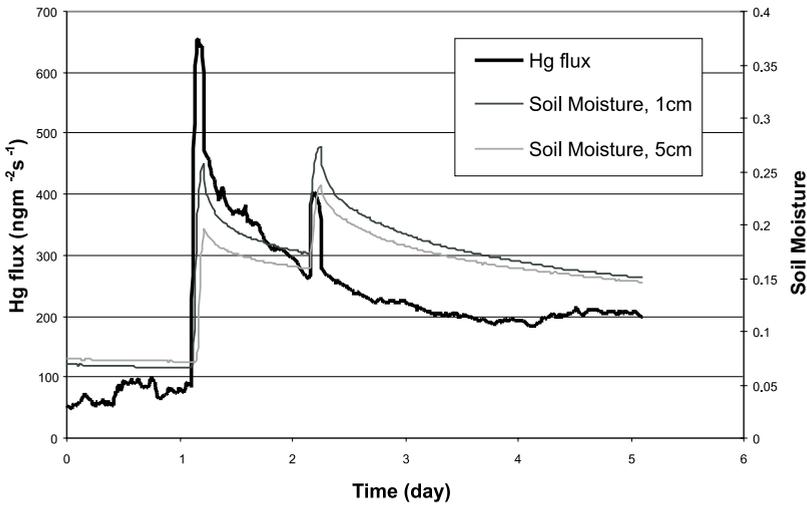


Figure 2. Mercury flux and soil moisture changes in double rain event

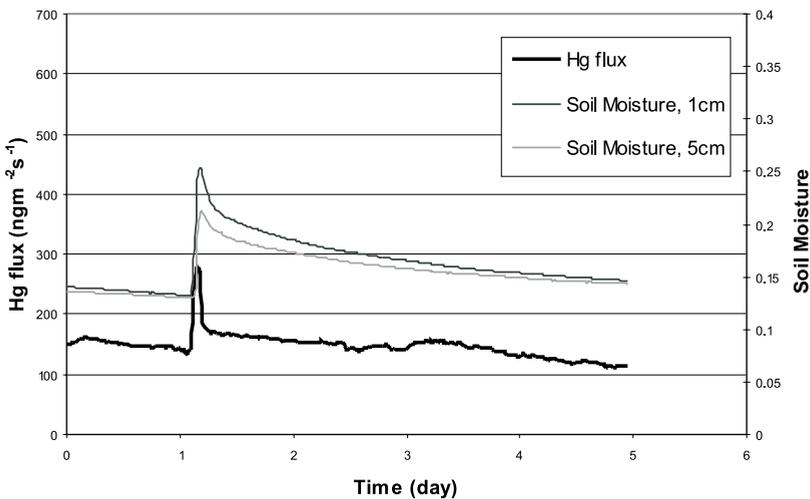


Figure 3. Mercury flux and soil moisture changes in the third rain event at higher initial soil moisture.

To gain further insight into the potential relationship between soil moisture and the gaseous elemental mercury flux, a double precipitation experiment was performed and repeated for the same initial conditions. The observed mercury fluxes and soil moisture levels for one of the experiments is given in Figure 2. As with the single precipitation experiments, the first application of water on the relatively dry soil results in a rapid and sharp spike in the mercury fluxes which tapers off after the end of the precipitation event. The application of water during the second precipitation event also produces a spike in the mercury flux, which is smaller in magnitude than the first, but still presumably the result of physical displacement of interstitial soil air by the incoming water. However, after the second precipitation event, instead of the mercury emissions remaining elevated relative to those before the precipitation event, the fluxes returned to nearly the same value and with a similar trend observed prior to the second rain event. This behaviour indicates that under moist soil conditions (~17%), further increases in soil moisture do not lead to prolonged increases in mercury fluxes as was the case with initially dry soils (~5%). Results from the repeated experiment using two precipitation events showed consistent behaviour.

Since the results from these tests indicated that the soil moisture level prior to the precipitation event has an effect on the mercury emissions following the event, a third precipitation event was conducted after the soil moisture content reached a value between the relatively dry soil (~5%) and relatively damp soil (~17%). Results are shown in Figure 3 and again show a spike, although smaller in magnitude, in the mercury emissions during the precipitation event. How-

ever, in this case, once the rain event was finished, the mercury fluxes remained at a somewhat elevated level over that of the fluxes prior to the rain event. This elevated level, however, was much smaller in magnitude than that observed for fairly dry soils following rain events.

## CONCLUSIONS

The field-observed increases in mercury fluxes due to precipitation have been simulated based on a laboratory experimental set-up. The immediate sharp spike in the gaseous elemental mercury flux during a precipitation event is the result of both the physical displacement of mercury vapour in the soil interstitial air by the incoming water, as well as by a process that is tied to the soil moisture content prior to the precipitation event. This second process also produces elevated mercury fluxes after the precipitation event, although the magnitude appears to be inversely related to the soil moisture content prior to the rain event. The exact mechanism behind this second process has yet to be identified, although the experimental behaviour is consistent with a hypothesis based on aqueous chemistry (either redox or sorption), in that once sufficient water content is reached, additional water will not produce enhanced reactions.

## Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canadian Foundation for Innovation (CFI), the Ontario Innovation Trust (OIT), and the School of Engineering, University of Guelph.

## REFERENCES

- LINDBERG, S. E., ZHANG, H., GUSTIN, M., VETTE, A., MARSIK, F., OWENS, J., CASIMIR, A., EBINGHAUS, R., EDWARDS, G., FITZGERALD, G., KEMP, J., KOCK, H. H., LONDON, J., MAJEWSKI, M., POISSANT, L., PILOTE, M., RASMUSSEN, P., SCHAEDELICH, F., SCHNEEBERGER, D., SOMMAR, J., TURNER, R., WALLSCHLAGER, D., XIAO, Z. (1999): Increases in mercury emissions from desert soils in response to rainfall and irrigation; *Journal of Geophysical Research*, Vol. 104, D17, pp. 21,879-21-888.
- POISSANT, L., PILOTE, M., CASIMIR, A. (1999): Mercury flux measurements in a naturally enriched area: Correlation with environmental conditions during the Nevada Study and Tests of the Release of Mercury From Soils (STORMS); *Journal of Geophysical Research*, Vol. 104, D17, pp. 21,845-21,857.
- ZHANG, H., LINDBERG, S. E. (1999): Processes influencing the emission of mercury from soils: A conceptual model; *Journal of Geophysical Research*, Vol. 104, D17, pp. 21,889-21,896.

## Atmospheric Mercury Species in Downtown Toronto

XINJIE SONG<sup>[1]</sup> & JULIA LU<sup>[2]</sup>

Department of Chemistry and Biology, Ryerson University, Toronto, Ontario, Canada M5B 2K3;  
<sup>[1]</sup>E-mail: xsong@ryerson.ca; <sup>[2]</sup>E-mail: julialu@ryerson.ca

**Abstract:** Atmospheric mercury speciation studies were conducted in downtown Toronto from December 20 2003. The concentrations of gaseous elemental mercury (GEM), gaseous oxidized inorganic mercury (GOIM, also called reactive gaseous mercury, RGM), and mercury associated with particulate matter <2.5  $\mu\text{m}$  (PM<2.5) were measured simultaneously using an automated mercury speciation unit. The results shown that in December 2003 the average [GEM] was  $5.56 \pm 2.07 \text{ ng/m}^3$  while [PM<2.5] and [GOIM] were  $7.48 \pm 10.26 \text{ pg/m}^3$  and  $12.77 \pm 1.38 \text{ pg/m}^3$ , respectively. In the first three months of 2004, the average [GEM] and [GOIM] fell to  $3.89 \pm 2.19 \text{ ng/m}^3$  and  $9.32 \pm 6.12 \text{ pg/m}^3$ , whereas [PM<2.5] increased to  $18.13 \pm 16.06 \text{ pg/m}^3$ . The concentrations of PM<2.5 were anti-correlated with the surface air temperatures.

**Key words:** gaseous elemental mercury (GEM), atmospheric mercury species, particulate mercury (PM), gaseous oxidized inorganic mercury (GOIM), reactive gaseous mercury (RGM)

### INTRODUCTION

Among many heavy metal pollutants, mercury is somewhat distinctive because of its bioaccumulation and long-term effects to the environment. Although the use of mercury and its emissions has been controlled by five decades of regulations, continuing increase of the amount of mercury in the environment has been reported recently. Marine mammals such as dolphins, seals and polar bears have continued to show increasing amounts of mercury in their bodies- with some increasing two- or threefold since 1970s<sup>[1]</sup>. The United States Food and Drug Administration (FDA) and Environmental Protection Agency (EPA)<sup>[1]</sup> have recently announced stringent warnings concerning mercury, which ensured the hazard to youngsters.

Both natural and man-made activities contribute to the mercury distribution in the environment and the long-range atmospheric circulation plays an important role in mercury deposition and re-emission around the world. Researches have been done and are being done to understand the transport, transformation and fate of mercury in the environment. It is verified that, under normal atmospheric conditions, gaseous elemental mercury (GEM) takes the major part of mercury in the atmosphere with a residence time of approximately 0.5-2 years while both particular mercury (PM) and gaseous oxidized inorganic mercury (GOIM), also called reactive gaseous mercury (RGM) are less than 2 %<sup>[2]</sup>. But in the polar region after polar sunrise, the distribution of mercury species may be reversed<sup>[3]</sup>, enhancing the depletion of GOIM and PM on the snow surface.

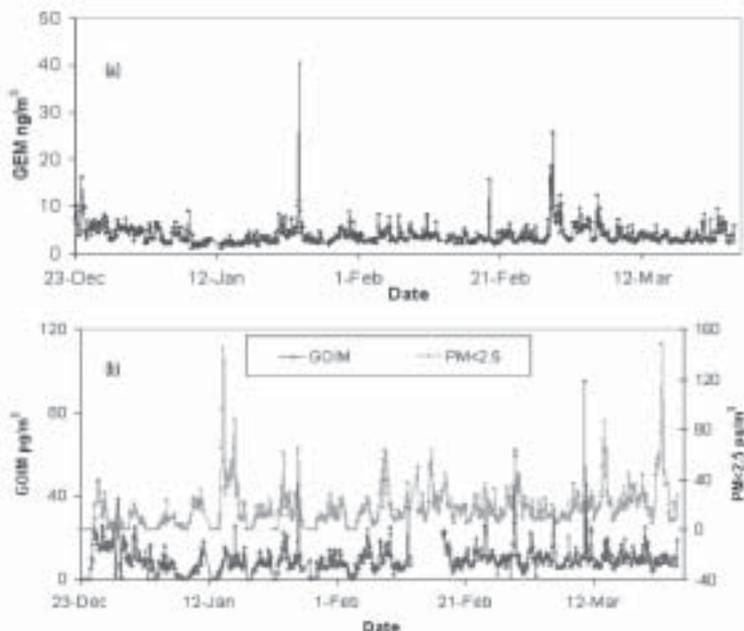
Mercury measurements in urban environment have been reported in New York (USA), Tokyo (Japan), Beijing (China), Seoul (Korea) and Guiyang (China)<sup>[4]</sup>. The Canadian Atmospheric Mercury Network (CAMNet) was established in 1996. It contains 11 rural and remote sites at various locations in Canada<sup>[5]</sup>. There is, however, no urban site in the network. CAMNet is currently monitoring GEM. New initiatives include measurement of GOIM and PM in the atmosphere. The objective of this work is to study mercury species in downtown Toronto, the largest city in Canada. The concentrations of gaseous elemental mercury (GEM), gaseous oxidized inorganic mercury (GOIM) and mercury associated with particulate matter < 2.5  $\mu\text{m}$  (PM<2.5) were measured simultaneously using an automated mercury speciation unit (Tekran, Model 1130/1135/2537A) on the

roof top of Science Building at Ryerson University, which is located in the core of city Toronto, from December 2003.

## RESULTS AND DISCUSSION

Figure 1 shows the trends of the three species respectively while Table 1 and Table 2 depict the overall statistical and monthly summary of the data from this time period.

Based on the average value, it is obvious that [GEM] comprises 99.36 % of all the mercury species, while [PM<2.5] accounts by 0.41 % and [GOIM] takes only 0.23 %. This is different from the results of mercury speciation in other studies conducted in rural areas<sup>[6]</sup>. [GOIM] is generally higher than [PM<2.5] in that study. The average value



**Figure 1.** Mercury species in downtown Toronto, Canada. (a) Gaseous Elemental Mercury (GEM) from Dec. 03-Mar. 2004; (b) gaseous oxidized inorganic mercury (GOIM) and particulate mercury (PM<2.5) from Dec. 03-Mar. 2004.

**Table 1.** Statistical summary of mercury species in downtown Toronto, Canada. December 2003 to March 2004, ng/m<sup>3</sup>, N/D: Not Detectable.

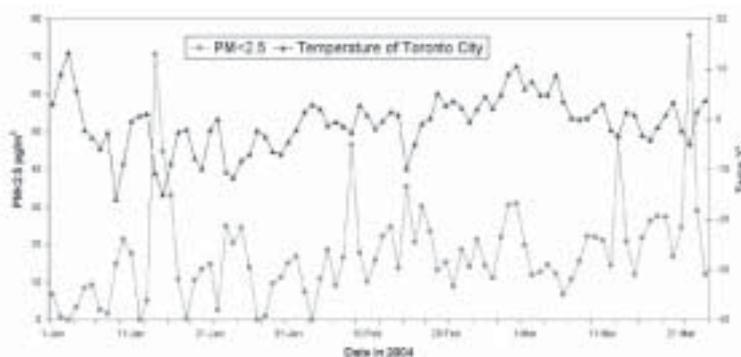
	N	Average	Standard Deviation	Median	Minimum	Maximum
<b>GEM</b>	1055	4.06	2.31	3.48	0.51	40.45
<b>PM&lt;2.5</b>	1049	$16.8 \times 10^{-3}$	$16.3 \times 10^{-3}$	$13.4 \times 10^{-3}$	N/D	$148 \times 10^{-3}$
<b>GOIM</b>	1005	$9.56 \times 10^{-3}$	$6.84 \times 10^{-3}$	$8.60 \times 10^{-3}$	N/D	$95.3 \times 10^{-3}$

**Table 2.** Monthly summary of mercury species in downtown Toronto, Canada, ng/m<sup>3</sup>

	December 2003	January 2004	February 2004	March 2004
<b>GEM</b>	$5.56 \pm 2.07$	$3.61 \pm 2.53$	$4.02 \pm 2.45$	$4.06 \pm 2.31$
<b>PM&lt;2.5</b>	$(7.50 \pm 10.2) \times 10^{-3}$	$(13.7 \pm 18.3) \times 10^{-3}$	$(18.5 \pm 12.3) \times 10^{-3}$	$(22.2 \pm 17.6) \times 10^{-3}$
<b>GOIM</b>	$(12.7 \pm 9.34) \times 10^{-3}$	$(6.89 \pm 5.22) \times 10^{-3}$	$(10.3 \pm 6.3) \times 10^{-3}$	$(10.8 \pm 6.9) \times 10^{-3}$

of GEM and its standard deviation obtained in this study ( $4.06 \pm 2.31$  ng/m<sup>3</sup>) are much higher than those from the CAMNet ([GEM] ranging from 1.33 to 1.90 with standard deviations ranging from 0.19 to 0.43 ng/m<sup>3</sup>)<sup>[5]</sup>. Several GEM spikes can be seen from Figure 1, which indicate the presence of some point anthropogenic sources.

Preliminary results revealed that meteorological conditions play some roles in mercury speciation. For example, an anti-correlation between the concentration of PM<2.5 and the surface temperature was observed during this period of experiment (Figure 2). This suggests that mercury condenses to the surface of the existing particles in the atmosphere when the air temperature drops, leading to the increase in the concentration of PM<2.5.

**Figure 2.** Time series of PM<2.5 and surface air temperature in downtown Toronto, Canada, January – March 2004.

## CONCLUSIONS

The concentrations of GEM, GOIM and PM<sub><2.5</sub> were monitored simultaneously during December 2003 to March 2004. Urban environment characteristics and the effect of human activities are reflected from (1) the high [GEM] values, (2) high levels of variation (standard deviations) on all the parameters measured; and (3) different distribution pattern between [GOIM] and [PM<sub><2.5</sub>]. Anti-correlation between the concentration

of PM<sub><2.5</sub> and the surface air temperature was observed in this study. The measurements are on-going.

## Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Foundation for Innovation (CFI), the Premier's Research Excellence Awards Program, and Ryerson University.

## REFERENCES

- [1] WITTNICH, C. AND BELANGER, M. (2004): *Environmental pollution: Long-term effects unknown*; Toronto Star, March 31, p. A19.
- [2] POISSANT, L. (2000): Total gaseous mercury in Quebec(Canada) in 1998; *Science of the Total Environment* 259(1-3), pp. 191-201.
- [3] LU, J. Y., SCHROEDER, W. H., BARRIE, L. A., STEFFEN, A., WELCH, H. E., MARTIN, K., LOCKHART, L., HUNT, R. V., BOILA, G. RICHTER, A. (2001): Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry; *Geophysical Research Letters* 28(17), pp. 3219-3222.
- [4] FENG, X. B., TANG, S. L., SHANG, L. H., YAN, H. Y., SOMMAR, J., LINDQVIST, O. (2003): Total gaseous mercury in the atmosphere of Guiyang, PR China. *Science of the Total Environment* 304(1-3), pp. 61-72.
- [5] KELLERHALS, M., BEAUCHAMP, S., BELZER, W., BLANCHARD, P., FROUDE, F., HARVEY, B., McDONALD, K., PILOTE, M., POISSANT, L., PUCKETT, K., SCHROEDER, B., STEFFEN, A., TORDON, R. (2003): Temporal and spatial variability of total gaseous mercury in Canada: results from the Canadian Atmospheric Mercury Measurement Network (CAMNet). *Atmospheric Environment* 37(7), pp. 1003-1011.
- [6] POISSANT, L. (2004): Atmospheric Mercury Speciation Measurements Workshop, Vallyfield, QC.

## Isotopic Tracer Studies of Volatilization of Mercury from a North Temperate

GEORGE SOUTHWORTH<sup>1</sup>, STEPHEN LINDBERG<sup>1</sup>, MARYANNA BOGLE<sup>1</sup>, MARC AMYOT<sup>2</sup>, ALEXANDRE POULAIN<sup>2</sup>, HOLGER HINTELMANN<sup>3</sup>, MARK OLSEN<sup>4</sup>, KEN SANDILANDS<sup>5</sup>

<sup>1</sup>Oak Ridge National Laboratory, USA; E-mail: southworthgr@ornl.gov.

<sup>2</sup>University of Montreal, Canada.

<sup>3</sup>Trent University, Canada.

<sup>4</sup>U.S. Geologic Survey, USA.

<sup>5</sup>Dept. of Fisheries and Oceans, Canada.

**Abstract:** Inputs of mercury to lakes from direct atmospheric deposition and runoff is counterbalanced to some extent by the photo-reduction of oxidized mercury species to gaseous elemental mercury and its subsequent volatilization from the lake surface back to the atmosphere. As part of the METAALICUS Project, we investigated the rate of return of Hg-202 to the atmosphere following bi-weekly additions of Hg-202 nitrate directly to the surface waters of a lake in northwest Ontario. The isotopic tracer was readily photoreduced and volatilized, returning roughly 2 % of the epilimnetic Hg to the atmosphere per day. The isotopic spike and native mercury in the lake behaved similarly with respect to susceptibility to reduction and volatilization. Simple physical descriptions of the volatilization process underestimated mercury fluxes under high sunlight, low wind conditions.

**Key words:** mercury, dissolved gaseous mercury, DGM, volatilization, METAALICUS, lakes, flux chamber

### INTRODUCTION

Inputs of mercury to lakes from direct atmospheric deposition and runoff is counterbalanced to some extent by the photo-reduction of oxidized mercury species to gaseous elemental mercury and its subsequent volatilization from the lake surface back to the atmosphere. As part of the METAALICUS Project, we investigated the rate of return of Hg-202 to the atmosphere following bi-weekly additions of Hg-202 nitrate directly to the surface waters of a low alkalinity, humic rich lake in northwest Ontario. Flux measurements were made using floating polycarbonate chambers, with dissolved gas-

eous mercury and inlet and outlet air sampled by metering flow through traps containing gold-coated sand. Concentrations of individual mercury isotopes were measured by inductively-coupled plasma/mass spectrometry after thermal desorption of mercury from the gold traps.

### RESULTS AND DISCUSSION

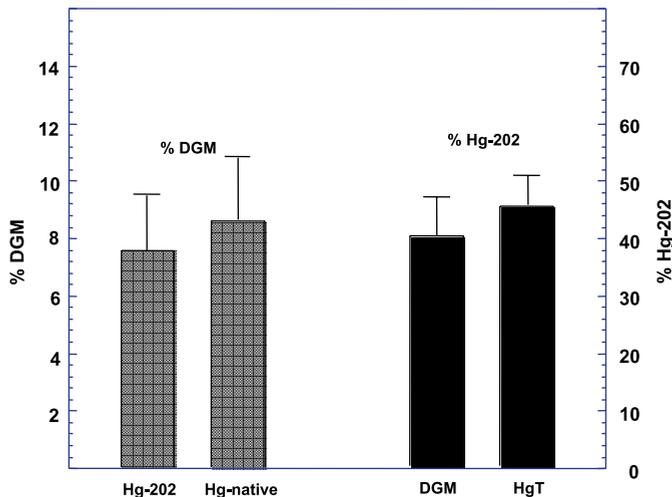
The Hg-202 added to the epilimnion of the lake in oxidized form (Hg (II)) was readily reduced to dissolved gaseous (elemental) Hg, or DGM, by photochemical processes (AMYOT ET AL., 1997). By midsummer and

beyond, DGM typically constituted slightly less than 10 % of the total dissolved mercury in the upper epilimnion (Fig. 1). Mercury-202 DGM concentrations were subject to short-term fluctuations, but generally ranged between 50 and 150 pg/L. Daily DGM concentrations would be expected to vary with changes in rate of production (related to sunlight intensity and duration, and transparency of the water column), and rate of removal (related to wind driven mixing of the water surface). The fraction of DGM and total dissolved Hg comprised by Hg-202 were similar (Fig. 1), providing evidence that the isotopic spike and native Hg in the lake behaved similarly with respect to reduction and volatilization processes.

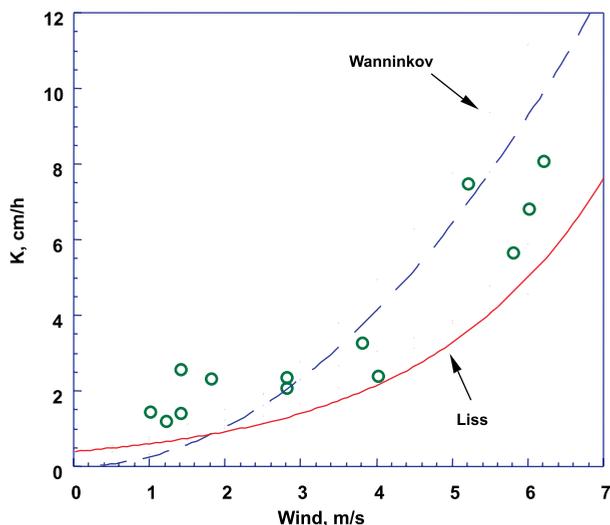
Gas exchange across the air:water interface has often been described by physical transport models that assume mass transfer rate is determined by fine scale concentration gradients on either side of the interface. For volatilization, such models operationally

express the process as a first order change in concentration of the gas in the bulk, or mixed phase of the water below the gradient, and thus use a simple mass transfer coefficient,  $k$ , acting on the concentration differential between the two mixed phases (air and water). Physical factors that act to affect the interfacial gradients (wind mixing, or current in flowing water) or the rate of diffusion of the gas (temperature) thus are primary determinants of the volatilization of gases from water.

In a one-week period in September 2002, the measured volatilization mass transfer coefficients for Hg-202 in Lake 658 varied with wind velocity in a manner similar to that predicted in other studies, although volatilization rates at low wind velocities generally exceeded modeled estimates (Fig. 2). Results from the following September were similar, but values of  $k$  observed in early and mid summer 2003 were substantially higher at mean wind speeds below 2 m/s. As a con-



**Figure 1.** Percent of total dissolved Hg (HgT, isotope spike and native) comprised by DGM (gray) and percent of DGM and HgT comprised by Hg-202 spike in epilimnion of lake 658, summer 2001/2002.



**Figure 2.** Variation with wind mass transfer coefficient ( $k$ ) for volatilization of Hg-202 from water in Lake 658, measured in September 2002. Dashed and solid lines are predicted values from published measurements of gas transfer versus wind.

sequence, the combined data sets failed to exhibit a striking variation in volatilization rate with wind velocity.

Multiple linear regression of Hg-202 volatilization versus wind, solar radiation intensity, and DGM using the combined data found all three variables to be significantly related to mercury flux. No single variable was found to be a good predictor of flux by itself. When flux was normalized for DGM (expressed as  $k$ ), the concentration of DGM remained a significant correlate. We hypothesize that under high illumination of mid-summer, especially under relatively calm conditions and high air temperatures, the generation of DGM immediately below the air:water interface leads to the generation of a 'reverse' gradient at the interface, in which DGM concentration increases (or decreases less than predicted by physical transport models) between the bulk aqueous phase and the interface. The lessening of resistance to

mass transfer in the liquid phase associated with a diminished interfacial concentration gradient between bulk solution concentration and the interface thus leads to the higher observed values for volatilization mass transfer coefficients. We suspect that the relationship between  $k$  and DGM is related to the effect of HgT precursor concentrations on DGM production and the reverse gradient effect, and will test this hypothesis when HgT-202 concentration data for 2003 are available.

## CONCLUSIONS

Isotopically enriched (Hg-202) mercury added to a small lake in northwest Ontario was readily photoreduced to dissolved gaseous elemental mercury, which was subject to volatilization loss to the atmosphere. Simple description of the volatilization process as a function of DGM concentration and

physical variables failed to adequately describe the process under conditions of low mixing and high sunlight, generating substantial underestimates of observed volatilization rates. The behavior of the isotopic tracer with respect to photoreduction and volatilization was similar to that of native mercury in the system. Overall, photoreduction and volatilization was an important transport process in determining the fate of Hg added to the lake. The observed volatilization rates in this summer correspond to loss rates of about 2 % per day of the total Hg inventory in a 2-meter deep water column in this lake.

### **Acknowledgements**

This work was funded in part by the U.S. Department of Energy Office of Science. Oak Ridge National Laboratory is managed by UT-Battelle LLC for the U.S. Department of Energy under contract DE-AC05-00OR22725.

### **REFERENCES**

- AMYOT, M., MIERLE, G., LEAN, D., MCQUEEN, D. J. (1997): Effect of solar radiation on the formation of dissolved gaseous mercury in temperate lakes; *Geochimica et Cosmochimica Acta* 61, pp. 975-987.

## Mercury Monitoring

ZDRAVKO SPIRIC & JOSIP VADJUNEC

**Abstract:** Air monitoring is frequently required at natural gas plant sites because of the potential for release of airborne contaminants and in response to regulatory compliance and/or community issues. An adequate monitoring, similar to the program designed and applied at INA-Naftaplin's process plant is essential for evaluation of working environment condition. It extends to the whole eco-system in order to scan and determine the extent of mercury influence, but also helps in organisation and preparation activities in the process itself. Namely, results of accurate monitoring serve as an early warning, showing possible functional or process damage that could have an adverse effect on instalation and/or equipment performance, resulting finally with hazard to working and living environment.

This paper deals with the results covering the measurement of low level mercury content in ambient air surrounding the operating process plant. During several years of continuous metering at INA-Naftaplin's natural gas field Molve (5 wells + Gas treatment Plant), under defined meteorological conditions, the profile and dynamics of distribution of ambient air mercury pollution during observed time were taken, i.e. the actual concentration at the investigated locations had been measured.

**Key words:** mercury, monitoring, ambient air

## Springtime Mercury Depletion Events Observed in the Norwegian High Arctic, Ny-Alesund, Spitsbergen

SPROVIERI, F.<sup>1</sup>, PIRRONI, N.<sup>1</sup>, COFONE, F.<sup>1</sup>, STEVENS, R.<sup>2</sup>, LANDIS, M.<sup>3</sup>

<sup>1</sup>CNR-Institute for Atmospheric Pollution, 87036 Rende, Italy; E-mail: f.sprovieri@cs.iaa.cnr.it

<sup>2</sup>Florida Dept. Environmental Protection, NERL, USEPA, Research Triangle Park, NC 27709

<sup>3</sup>NERL, USEPA, Research Triangle Park, NC 27709

**Abstract:** During an intensive mercury measurement campaign, carried in the Spring 2003 in Ny-Alesund, it was found that mercury concentrations in the lower atmosphere dropped in tandem with ozone levels. Hg<sup>0</sup>(g), Reactive Gaseous Mercury (RGM) and Hg (p) concentrations were continuously measured at both the Italian research station (about 9 m a.s.l.), and on Zeppelin mountain, (474m a.s.l.) using Tekran system (2537A-1130-1135). Hg<sup>0</sup> concentrations ranged between 2.6 ng m<sup>-3</sup> to below the detection limit during the Mercury Depletion Events (MDEs) and then returned to typical levels, with an average of 1.3 ng m<sup>-3</sup> ± 0.4 ng m<sup>-3</sup>. Our RGM data show an opposite trend during the study period with sharp increase in RGM concentrations up to 220 pg m<sup>-3</sup>, following the same trend as Hg<sup>0</sup>(g) depletion. The observations at Ny-Alesund suggest that the depletion of Hg<sup>0</sup> in the lower atmosphere observed after polar sunrise, is photochemically driven by oxidation of boundary-layer Hg<sup>0</sup> probably by reactive halogens and that the springtime phenomenon creates a rapidly depositing species of oxidized gaseous mercury in the remote Arctic air at concentrations up to more than 220 pg m<sup>-3</sup>.

**Keywords:** mercury, Arctic, depletion, atmosphere, measurements

### INTRODUCTION

Mercury exists in ambient air predominantly in the zero oxidation state as gaseous elemental Hg (Hg<sup>0</sup>) and comprises 97-99 % of the total mercury found in the atmosphere with an estimated mean global tropospheric residence time on the order of 1 year<sup>1,2</sup> allowing sufficient time for long-range atmospheric transport. Hg<sup>0</sup> is, therefore, globally distributed by air mass circulation including remote environments such as the Arctic and the Antarctic. It has been found that during the polar spring elemental mercury may be converted to a reactive form that accumulates in the biota in the Arctic and Antarctic envi-

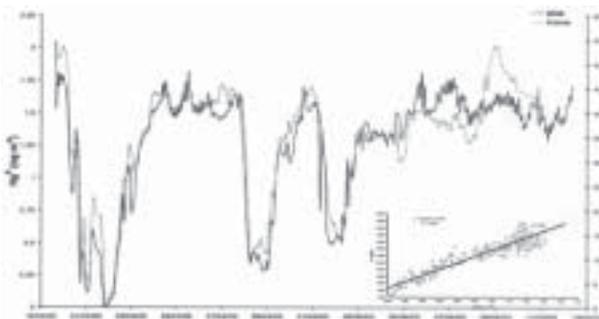
ronment. These unusual springtime phenomena, called mercury depletion events (MDEs), is an important removal pathway for atmospheric mercury, therefore, a better understanding of them could lead to an improved description of global mercury-cycling. Hg depletion events have been observed annually at maritime circumpolar stations in both the Arctic: Alert, Ellesmere Island (SCHROEDER ET AL., 1998; LU ET AL., 2001) Barrow, Alaska (LINDBERG ET AL., 2002), and in Antarctica, Terra Nova Bay, Victoria Land (SPROVIERI ET AL., 2002) after polar sunrise contemporaneously with tropospheric ozone depletion suggesting that both species were removed by similar un-

known homogeneous and/or heterogeneous oxidation reactions. Episodic depletions of  $\text{Hg}^0$ , closely resembling ozone depletions in Arctic surface level air, were frequently observed during an intensive atmospheric mercury campaign performed at Ny-Alesund, in the Norwegian high arctic (Svalbard Islands, Spitzbergen) from April 18<sup>th</sup> to May 12<sup>th</sup> 2003, during the arctic springtime.  $\text{Hg}^0$  concentrations dropped from around  $1.7\text{ngm}^{-3}$  to undetectable levels ( $< 0.1\text{ ng m}^{-3}$ ) and were strongly correlated with surface ozone ( $\text{O}_3$ ) depletion. The aim of this study was to present and discuss the results obtained during the Arctic spring campaign 2003 proposing a possible oxidative transformation process which converts  $\text{Hg}^0$  vapour into one or more much less volatile  $\text{Hg}^{(II)}$  species.

## METHODS

Springtime highly time-resolved measurements of atmospheric mercury species have been performed at Ny-Alesund, Svalbard Islands ( $78^\circ 54' \text{N}$ ,  $11^\circ 53' \text{E}$ ) from 18<sup>th</sup> of April to 12<sup>th</sup> of May 2003 in the presence of 24-h daylight. Mercury measurements were conducted at the Norwegian monitoring station on Zeppelin mountain ( $78^\circ 54' 42'' \text{N}$ ,  $11^\circ 55' 30'' \text{E}$ ), 474 m above sea level.  $\text{Hg}^0$ , RGM, and  $\text{Hg}(\text{p})$  concentrations were automatically measured with 5 minutes and 2 hours time resolution respectively; in addition, 5-minutes time resolution ozone levels were also collected. Mercury species were simultaneously quantified by an automatic integrated system (a Tekran automated unit, Model 1130 and a Tekran 1135 particulate unit, coupled to an automated gas-phase mercury

analyser, Tekran 2537A) which has the ability to concurrently monitor both elemental (GEM), reactive gaseous mercury (RGM) species and  $\text{Hg}(\text{p})$  in ambient air at the picograms per cubic meter level (Landis et al., 2002). While the RGM is collecting on a quartz KCl-coated annular denuder warmed at a temperature of  $50^\circ \text{C}$ ,  $\text{Hg}^0$  passes through at a flow rate of 1.5 L/min, with laminar flow and is collected at 5 minute intervals on a pair of gold traps in the Tekran 2537 analyser. While one trap is collecting the  $\text{Hg}^0$ , the second trap is heated at  $500^\circ \text{C}$  and the mercury released is analysed by Cold Vapour Atomic Fluorescence Spectrometry (CVAFS) (MUNTHE ET AL., 2001). The RGM collected on the KCl-annular denuders is thermally desorbed at  $500^\circ \text{C}$  to decompose and reduce RGM to the elemental form for the analysis step by the Tekran 2537A CVAFS downstream of the denuders. The Tekran 1135 particulate pyrolysis unit was used to determine  $\text{Hg}(\text{p})$  levels by a quartz regenerable filter after the passing of the sample through the impactor downstream the denuders to eliminate coarse particles and pyrolyzer for airborne particulate mercury species. The quartz filter was desorbed at  $800^\circ \text{C}$ . During the filter heating step, the pyrolyzer was maintained at  $800^\circ \text{C}$  to ensure complete decomposition of all  $\text{Hg}(\text{p})$  compounds evolved during the filter temperature ramp-

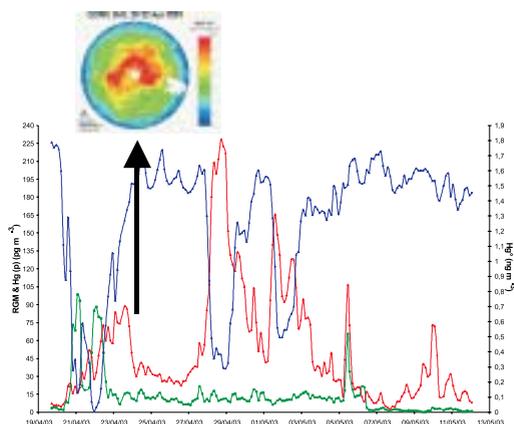


up to  $\text{Hg}^0$ . The total flow rate was 10 L.p.m. and the detection limit under the operating conditions used was  $< 2 \text{ pg m}^{-3}$ .

## RESULTS AND DISCUSSION

Three GEM depletion events are clearly recorded during the springtime campaign as shown in Figure 1, which shows the temporal trend of both GEM and  $\text{O}_3$  levels.  $\text{O}_3$  depletion is synchronized with  $\text{Hg}^0$  depletion.  $\text{Hg}^0$  concentrations ranged from background levels to undetectable values ( $< 0.1 \text{ ng m}^{-3}$ ) in connection with the MDEs and then returned to typical levels, sometime exceeding global background. In particular, during the first major depletion event, depicted from 21<sup>th</sup> to 22<sup>th</sup> of April, GEM levels dropped very fast within 24 hours and the concentrations changed from about  $1.7 \text{ ng m}^{-3}$  to below  $0.006 \text{ ng m}^{-3}$ , while in the following two minor depletion episodes GEM dropped below 0.25 and  $0.5 \text{ ng m}^{-3}$  respectively. It is noteworthy that MDEs coincide with polar sunrise ozone depletion events (ODEs) in the polar troposphere where ozone is destroyed by a photochemically reactions between ozone and reactive gaseous halogen species (especially bromine). These events cannot, in fact, be explained by changing meteorological parameters alone but coincide prevalently with the “bromine explosion” phenomena occurring especially close to abundant frozen and sea-ice surfaces. Bromine and chlorine radicals, in fact, are produced auto-catalytically from a heterogeneous photochemical mechanism involving sea-salt aerosol (PIRRONE ET AL., 2003; HEDGECOCK ET AL., 2003; SPROVIERI ET AL., 2003). During the ODEs,  $\text{Hg}^0$  exhibits a strong correlation with  $\text{O}_3$  ( $r^2 = 0.8$ ) (see

Fig.1) suggesting a possible link with the chemical reactions which destroy tropospheric ozone, as first suggested by SCHROEDER ET AL. (1998). Dramatically increased levels of  $\text{Hg}(\text{p})$  and RGM were measured as  $\text{Hg}^0$  concentrations dropped to undetectable levels during the 2003 experiment. It seems reasonable to suppose that Br-compounds or another halogen-containing radical or compound formed in the period around polar sunrise, is responsible for a sudden increase in oxidation of  $\text{Hg}^0(\text{g})$  and the formation of less volatile  $\text{Hg}(\text{II})$  compounds, which are either dry deposited to the underlying surface or condense onto pre-existing particulate matter (LU ET AL., 2001; LINDBERG ET AL., 2002). The data obtained (see Fig. 2) indicate that RGM is clearly the primary species formed during the MDE period and differently from  $\text{Hg}(\text{p})$ . In particular, from April 19<sup>th</sup> to April 23<sup>rd</sup> (the period covering the first major MDEs), particulate  $\text{Hg}$  and RGM showed a different trend with  $\text{Hg}(\text{p})$  peaking on the 21<sup>st</sup> and on the 22<sup>nd</sup> when  $\text{Hg}^0$  was at its minimum concentration, but decreasing rapidly when the  $\text{Hg}^0$  concentrations again increased. The 2003 findings from Zeppelin Station suggested that different reaction pathways or reactants may be, probably, responsible for creating  $\text{Hg}(\text{p})$  as com-



pared to RGM during the first and major MDE. In contrast, RGM concentrations progressively increased within the first major depletion event, showing an opposite trend to  $\text{Hg}^0$  during the whole time-series concentrations. In order to analyse and interpret the mercury behaviour recorded during the experiment, daily averaged BrO Vertical Column Densities observed from the GOME satellite were used. GOME BrO distributions revealed incidence of elevated BrO column densities simultaneously with the period of low  $\text{Hg}^0$  and  $\text{O}_3$  surface levels and elevated RGM levels coincided with a period characterized by increased levels of BrO. The preliminary analysis suggests that  $\text{Hg}^0$  destruction and simultaneous RGM production, is driven by an action of atmospheric halogen chemistry in the air at Ny-Alesund involving reactive Br-compounds. In order to evaluate the role played by the transport on the surface depletions recorded during the arctic experiment and, in particular, to test whether the low  $\text{Hg}^0$  concentrations observed might be a result of transport of air masses already depleted in mercury, detailed back trajectory analyses have been carried out and compared with daily average BrO vertical column density maps from the GOME satellite. The results from this investigation regarding the first and the second depletion events clearly show that the air masses arriving at Ny-Alesund on the 22<sup>nd</sup>, which is the day with maximum depletion, arrived from north-north-east and east-north-east. The trajectories originate from the Eastern High Arctic Sea. The comparison between the back-trajectories with the GOME BrO map thus suggests that the first strong MDEs occurring at Ny-Alesund coincide with the

arrival of air masses that resided most of the time over the ocean, covered with more than 40 % sea ice, before reaching Zeppelin Station. The trajectory thus stated in regions with strongly elevated Br-compounds. The air masses around 400, 500 and 600 meters above sea level pass through the arctic Sea inside the boundary layer until Ny-Alesund. These findings support the theory that the air mass with depleted mercury originated far from Ny-Alesund, before the measurement location. To examine potential influences of the meteorological factors on atmospheric reaction occurred during MDEs,  $\text{Hg}^0$  concentration-time series together with selected additional meteorological and chemical parameters were evaluated. Results obtained give clear evidence that the first depletion is associated with falling temperature and rising wind speed ( $T$  °C about  $-24$  °C and  $w_s$  about 10  $\text{ms}^{-1}$  for a few hours) and a rapid shift in wind direction to N-NW confirming the intrusion of an Arctic air mass. The 2003 measurements thus suggest that the MDEs occurred at Ny-Alesund were caused by transport of air masses depleted in  $\text{Hg}^0$  rather than solely the result of atmospheric mercury chemistry in the air at Ny-Alesund. It is however clear that more research is needed to improve our understanding of different aspects on the mercury cycle in the polar atmosphere.

### Acknowledgements

This work was funded by the United States Environmental Protection Agency (USEPA) and by the Italian National Research Council (CNR) under the cooperative agreement X4-83097301-0.

## REFERENCES

- HEDGECOCK, I. M., PIRRONE, N., SPROVIERI, F., PESENTI, E. (2003): *Atmospheric Environment*, Vol. 37, pp. 41-49.
- LANDIS, M. S., STEVENS, R. K., SCHAEDLICH, F., PRESTBO, E. M. (2002): *Environ. Sci. Technol.*, Vol. 36, No. 13, pp. 3000-3009.
- LINDBERG, S. E., BROOKS, S., LIN, C.-J., SCOTT, K. J., LANDIS, M. S., STEVENS, R. K., GOODSITE, M., RICHTER A. (2002): *Environ. Sci. Technol.*, Vol. 36, pp. 1245-1256.
- LU, J. Y., SCHROEDER, W. H., BARRIE, L. A., STEFFEN, A., WELCH, H. E., MARTIN, K., LOCKHART, W. L., HUNT, R. V., BOILA, G., RICHTER, A. (2001): *Geophys. Res. Lett.*, Vol. 28, pp. 3219-3222.
- MUNTHE, J., WANGBERG, I., PIRRONE, N., IVERFELD, A., FERRARA, R., EBINGHAUS, R., FENG, R., GERDFELT, K., KEELER, G.J., LANZILLOTTA, E., LINDBERG, S.E., LU, J., MAMANE, Y., PRESTBO, E., SCHMOLKE, S., SCHRODER, W.H., SOMMAR, J., SPROVIERI, F., STEVENS, R.K., STRATTON, W., TUNCEL, G., URBA, A. (2001): *Atmos. Environ.*, Vol. 35, pp. 3007-3017.
- SCHROEDER, W. H., ANLAUF, K. G., BARRIE, L. A., LU, J. Y., STEFFEN, A., SCHNEEBERGER, D. R., BERG, T. (1998): *Nature* 394, pp. 331-332.
- SPROVIERI, F., PIRRONE, N., HEDGECOCK, I. M., LANDIS, M. S., STEVENS, R. K. (2002): *Journal of Geophysical Research*; Vol. 107, (D23), 4722.
- SPROVIERI, F., PIRRONE, N., GERDFELT, K., SOMMAR, J. (2003): *Atmos. Environ.*, Vol. 37, pp. 63-71.
- PIRRONE, N., FERRARA, R., HEDGECOCK, I. M., KALLOS, G., MAMANE, Y., MUNTE, J., PACYNA, J.M., PYTHAROULIS, I., SPROVIERI, F., VOUDOURI, A., WANGBERG, I. (2003): *Atmos. Environ.*, Vol. 37, pp. 21-39.

## Mercury Species in Ambient Air During Two Intensive Campaigns in Southern Italy

SPROVIERI, F., PIRRONE, N., COFONE, F., ORRICO, F., GUARASCIO, A., BENCARDINO, M.

CNR-Institute for Atmospheric Pollution, 87036 Rende, Italy; E-mail: f.sprovieri@cs.iiia.cnr.it

**Abstract:** Intensive measurements of atmospheric mercury species were performed in order to improve our understanding of those mechanisms influencing the dynamics of mercury in the Mediterranean Region. The potentially important mechanisms including atmospheric transport pathways, and the chemical and physical transformations of  $\text{Hg}^0$  and its compounds in the atmosphere with changing meteorological conditions. Two seasonal campaigns were performed (from 20<sup>th</sup> October to 4<sup>th</sup> November 2003 and from 19<sup>th</sup> January to 2<sup>nd</sup> February 2004) at a coastal site (Fuscaldo) in Southern Italy. The study focused on different chemical species of mercury in the atmosphere including elemental mercury,  $\text{Hg}^0_{(g)}$ , gaseous divalent mercury,  $\text{Hg}^{\text{II}}_{(g)}$ , and particulate mercury,  $\text{Hg}^{\text{P}}$ . These species were monitored automatically and analysed using an integrated mercury speciation system (Tekran 2537A mercury analyser coupled to both a Tekran 1130 mercury denuder module and a Tekran 1135 particulate mercury unit). The time resolution for  $\text{Hg}^0$  was 5 minutes, and 2 hours for RGM and  $\text{Hg}^{\text{P}}$ . The results obtained were compared with changes in meteorological conditions.

**Key words:** mercury, Mediterranean, measurement, speciation, atmosphere

### INTRODUCTION

Several modelling studies and sensitivity analyses regarding the transport and removal of atmospheric mercury have highlighted the need to understand mercury speciation in the atmosphere. Knowledge of atmospheric mercury speciation is, in fact, critical in order to model its fate once released from emission sources. Mercury is emitted into the atmosphere from a variety of anthropogenic sources, such as cement production installations, waste incineration plants, power generation facilities and smelters, (PIRRONE ET AL., 1996; PIRRONE ET AL., 2001). It is also emitted from natural sources, such as volcanoes, crustal degassing, and from oceans. Natural emissions are generally assumed to

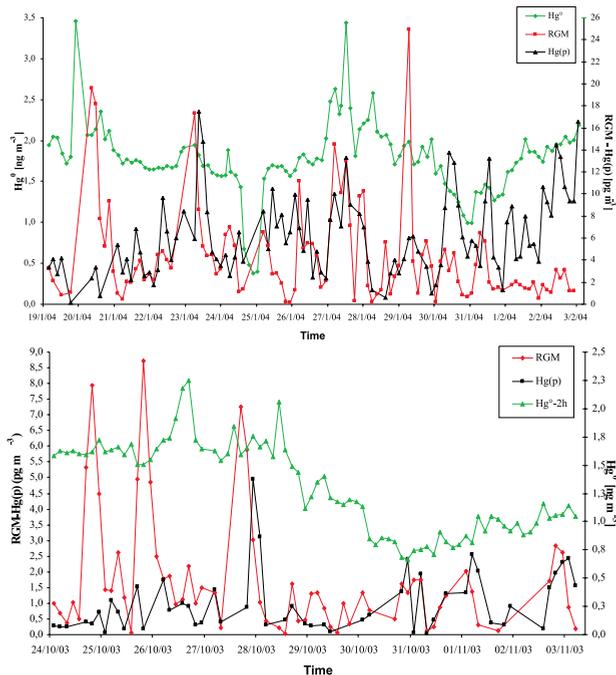
be  $\text{Hg}^0_{(g)}$ , whereas anthropogenic emissions may have different chemical and physical forms (PACYNA ET AL., 2001). Mercury cycling between different environmental compartments depends on the rate of different chemical and physical processes (i.e., dry deposition, wet scavenging) and meteorological conditions which affect its fate in the global environment. Synchronized seasonal field campaigns performed during the MAMCS and MOE projects around the Mediterranean Basin and in Northern Europe have highlighted that TPM and RGM concentrations were generally higher in the Mediterranean area than over northern Europe in spite of the higher density of industrial installations and urban centres (and consequently higher  $\text{Hg}^0_{(g)}$  concentrations) in

northern compared to southern Europe (WANGBERG ET AL., 2001; MUNTHE ET AL., 2003; PIRRONE ET AL., 2003). The most probable interpretation, which comes to mind, is more active atmospheric transformation processes in the Mediterranean Basin due to higher insolation and higher temperatures, as well as lower rates of wet deposition due to more sporadic and generally lower rainfall. It has been suggested that photochemical processes in the MBL lead to enhanced oxidation of elemental mercury vapour (HEDGECOCK ET AL., 2003; SPROVIERI ET AL., 2003) which would lead to increased concentrations of RGM and TPM via gas-particle interactions. In the framework of the MERCYMS project the results of simultaneous measurements of  $\text{Hg}^0_{(g)}$ , RGM and  $\text{Hg}^p$ , performed in the boundary layer on the Tyrrhenian coast (Fuscaldo, Calabria- Southern Italy) are presented. The aim of this paper is to discuss the mercury species

behaviour observed during two seasonal measurement campaigns with changing meteorological conditions and wind direction, in order to understand the most probable mechanisms involved in RGM and  $\text{Hg}^p$  production in the Mediterranean region.

## EXPERIMENTAL

High time resolution measurements of atmospheric mercury species have been performed at Fuscaldo Marina in southern Italy. Fuscaldo is a small village located on the west coast of Calabria (lat  $39^\circ$  - long  $16^\circ$ ). The measurement site was approximately 10 m a.s.l. and  $\text{Hg}^0$ , RGM and  $\text{Hg}^p$  concentrations were measured during two two-week campaigns, (from the 20<sup>th</sup> of October to the 4<sup>th</sup> of November 2003 and from the 19<sup>th</sup> of January to the 2<sup>nd</sup> of February 2004), using an automatic integrated measurement sys-



tem: a Tekran automated denuder unit, Model 1130, and a Tekran 1135 particulate unit, both coupled to an automated gas-phase mercury analyser, Tekran 2537A. While the RGM is being collected on a quartz KCl-coated annular denuder maintained at 50 °C, (sampling flow rate 1.5 L/min),  $\text{Hg}^0_{(g)}$  passes through the denuder with laminar flow and is collected at 5 minute intervals on a pair of gold traps in the Tekran 2537 analyser; while one trap collects  $\text{Hg}^0_{(g)}$ , the second trap is heated to 500 °C and the mercury collected during the previous 5 minutes is analysed by Cold Vapour Atomic Fluorescence Spectrometry (CVAFS) (LANDIS ET AL., 2002; MUNTHE ET AL., 2001). Every two hours the RGM was thermally desorbed from the denuder at 500 °C and then analysed by the Tekran 2537A CVAFS downstream of the denuder. The Tekran 1135 particulate pyrolysis unit was used to determine  $\text{Hg}^p$  levels using a quartz regenerable filter thermally desorbed at 800 °C. The flow rate used was 10 L/min and the detection limit of  $\text{Hg}^p$  under the operating conditions used was  $< 2 \text{ pg m}^{-3}$ .

## RESULTS AND DISCUSSION

Figures 1 and 2 show the temporal variability of  $\text{Hg}^0_{(g)}$ , RGM and  $\text{Hg}^p$  concentrations sampled during the two measurement campaigns. The average  $\text{Hg}^0$  concentrations show no significant seasonal variations (see Table 1). The relatively uniform distribution found is reasonable and similar to the northern hemisphere background concentration and only occasionally shows higher values due to the influence from major sources. Concerning RGM and  $\text{Hg}^p$ , there seems to be a more pronounced difference between the two seasons. In particular, higher RGM and  $\text{Hg}^p$  concentrations were recorded during the winter season in contrast to those obtained during the first campaign (see Table 1). The mercury species results were compared with meteorological conditions and an air mass back trajectory study in order to examine the potential influences of these factors on the mercury species behaviour. The discussion on the data recorded and in particular, on the most probable mechanism involved in the RGM and  $\text{Hg}^p$  production in

<b>Fall Campaign</b>			
	$\text{Hg}^0$ [ng m <sup>-3</sup> ]	RGM [pg m <sup>-3</sup> ]	$\text{Hg}(p)$ [pg m <sup>-3</sup> ]
Average	1.31	1.12	1.00
Std. Dev.	0.42	0.60	0.84
Min	0.10	0.19	0.03
Max	2.48	2.37	3.42
<b>Winter Campaign</b>			
	$\text{Hg}^0$ [ng m <sup>-3</sup> ]	RGM [pg m <sup>-3</sup> ]	$\text{Hg}(p)$ [pg m <sup>-3</sup> ]
Average	1.78	4.22	6,03
Std. Dev.	0.44	3.36	3,43
Min	0.11	0.57	0,14
Max	4.76	16.83	16,58

the Mediterranean region is presented in SPROVIERI ET AL. (2004, this volume). The results from the MERCYMS measurement campaigns constitute a new set of environmental data that combined with the data obtained during the two Med-Oceanor campaigns carried out on board the R.V. Urania and covering the western and eastern areas of the Mediterranean Basin, will be used in

the validation of models to describe the biogeochemical cycle of mercury in the Mediterranean area.

### Acknowledgements

This work is part of the MERCYMS (<http://www.cs.iiia.cnr.it/MERCYMS/project.htm/>) funded by the European Commission (Contr. No. EVK3-2002-00070).

### REFERENCES

- HEDGEcock, I. M., PIRRONE, N., SPROVIERI, F., PESENTI, E. (2003): Reactive gaseous mercury in the marine boundary layer: modelling and experimental evidence of its formation in the Mediterranean region; *Atmospheric Environment*, Vol. 37, pp. 41-49.
- MUNTHE, J., WÄNGBERG, I., PIRRONE, N., IVERFELD, A., FERRARA, R., EBINGHAUS, R., FENG, R., GERDFELT, K., KEELER, G. J., LANZILLOTTA, E., LINDBERG, S. E., LU, J., MAMANE, Y., PRESTBO, E., SCHMOLKE, S., SCHRODER, W. H., SOMMAR, J., SPROVIERI, F., STEVENS, R. K., STRATTON, W., TUNCEL, G., URBA, A. (2001): Intercomparison of Methods for Sampling and Analysis of Atmospheric Mercury Species; *Atmos. Environ.*, Vol. 35, pp. 3007-3017.
- MUNTHE, J., WÄNGBERG, I., IVERFELDT, Å., LINQVIST, O., STROMBERG, D., SOMMAR, J., GÄRDFELDT, K., PETERSEN, G., EBINGHAUS, R., PRESTBO, E., LARJAVA, K., SIEMENS, V. (2003): Distribution of atmospheric mercury species in Northern Europe: final results from the MOE project; *Atmos. Environ.*, Vol. 37, pp. 9-20.
- PACZYNA, E. G., PACZYNA, J. M., PIRRONE, N. (2001): European emissions of atmospheric mercury from anthropogenic sources in 1995; *Atmos. Environ.*, Vol. 35, pp. 2987-2996.
- PIRRONE, N., KEELER, G. J., NRIAGU, J. (1996): Regional differences in worldwide emissions of mercury to the atmosphere; *Atmos. Environ.*, Vol. 17, pp. 2981-2987.
- PIRRONE, N., COSTA, P., PACZYNA, J. M., FERRARA, R. (2001): Mercury emissions to the atmosphere from natural and anthropogenic sources in the Mediterranean region; *Atmos. Environ.*, Vol. 35, pp. 2997-3006.
- PIRRONE, N., FERRARA, R., HEDGEcock, I. M., KALLOS, G., MAMANE, Y., MUNTHE, J., PACZYNA, J.M., PYTHAROULIS, I., SPROVIERI, F., VOUDOURI, A., WÄNGBERG, I. (2003): Dynamic processes of mercury over the Mediterranean region: results from the Mediterranean Atmospheric Mercury Cycle System (MAMCS) project; *Atmos. Environ.*, Vol. 37, pp. 21-39.
- SPROVIERI, F., PIRRONE, N., GERDFELT, K., SOMMAR, J. (2003): Mercury speciation in the marine boundary layer along a 6000Km cruise path around the Mediterranean Sea; *Atmos. Environ.*, Vol. 37, pp. 63-71.
- WÄNGBERG, I., MUNTHE, J., PIRRONE, N., IVERFELDT, Å., BAHLMAN, E., COSTA, P., EBINGHAUS, R., FENG, X., FERRARA, R., GÄRDFELDT, K., KOCK, H., LANZILLOTTA, E., MAMANE, Y., MAS, F., MELAMED, E., OSNAT, Y., PRESTBO, E., SOMMAR, J., SCHMOLKE, S., SPAIN, G., SPROVIERI, F., TUNCEL, G. (2001): Atmospheric Mercury Distributions in North Europe and in the Mediterranean Region; *Atmospheric Environment*. Vol. 35, pp. 3019-3025.

## Intercomparison of Manual and Automated Methods for Determining Ambient Concentrations of Gas-Phase Divalent Mercury

SPROVIERI, F., PIRRONE, N., GUARASCIO, A., BENCARDINO, M., ORRICO, F., COFONE, F.

CNR-Institute for Atmospheric Pollution, 87036 Rende, Italy; E-mail: [f.sprovieri@cs.iaa.cnr.it](mailto:f.sprovieri@cs.iaa.cnr.it)

**Abstract:** The results from two intensive field seasonal campaigns performed within the MERCYMS Project are presented in this paper. Measurements were performed at a Tyrrhenian coastal site in the southern Italy (Calabria, Fuscaldo lat 39° - long 16°) from 20<sup>th</sup> of October to 4<sup>th</sup> of November 2003 and 19<sup>th</sup> of January to 2<sup>nd</sup> of February, 2004 respectively. Reactive Gaseous Mercury (RGM) concentrations were collected by both manual and automated KCl-quartz annular denuders and a field intercomparison between both sampling and analysis techniques was employed to test if these methods give comparable results. Manual sampling was performed with 12 hours time resolution at a flow rate of 10 L pm. The denuders, heated at 500 °C during the sampling time, have been analysed by a Tekran 2537A mercury analyser. RGM data obtained by the automated mercury system, comprising an integrated mercury speciation system (Tekran 2537A mercury vapour analyser coupled to Tekran 1130 and Tekran 1135 Units) with a time resolution of 2 hours and a flow rate of 10 Lpm. The results obtained were compared with changing of meteorological conditions determined in addition to the mercury measurements, during the sampling period.. Experimental details and results are presented and discussed.

**Key words:** annular denuder, reactive gaseous mercury, speciation

### INTRODUCTION

Mercury exists in the environment in a number of different chemical and physical forms, each one with different behaviour in terms of transport and environmental effects. Among the metals emitted to the atmosphere from natural and anthropogenic sources, highly toxic mercury is unique as being mainly released in its gaseous elemental state ( $\text{Hg}^0$ ) which represents 95-99 % of the Total Gaseous Mercury (TGM).  $\text{Hg}^0$  is relatively stable and has an atmospheric residence time of the order of one year. Deposition occurs after chemical conversion to divalent forms in the gaseous or aqueous phase. Reactive Gaseous

Mercury (RGM) and Particulate Mercury ( $\text{Hg-p}$ ) although representing only a small fraction of the total gaseous mercury (5-10 %), have moderate residence times in the atmosphere and a higher affinity to condensed phases thus playing a fundamental role in the wet and dry deposition processes to aquatic and terrestrial receptors. Therefore, the knowledge of atmospheric chemical and physical processes involving mercury species is essential to describe atmospheric transport and transformation and assessing the environmental fate of mercury. Two seasonal sampling campaigns of two-weeks were performed within the MERCYMS Project in order to carry out speciated mercury measure-

ments in the Mediterranean region. In this paper the application and comparison of manual and automated methods are described to assess RGM concentrations on a tyrrhenian coastal site in the southern of Italy (Fuscaldo, Calabria lat 39° - long 16°).

## EXPERIMENTAL

RGM measurements were carried out using KCl-coated annular denuders by both manual and automatic techniques. Field intercomparison exercises of different methods for the determination of RGM have previously been performed at Sassetta, Italy and Mace Head, Ireland, (EBINGHAUS ET AL., 1999; MUNTHE, 2001), which a really good precision for the denuder method was demonstrated without significant breakthrough. The findings of these field intercomparison studies have been reconfirmed by a laboratory study published by LANDIS ET AL. (2002). Annular denuders are first chemically pre-treated to clean them by soaking in concentrated HNO<sub>3</sub> for a week and then in dilute HCl for another week, then rinsed with Milli-Q water and argon-dried in the laboratory. These pre-treated denuders were then soaked in saturated KCl solution for 30 minutes at room temperature. Excess water inside the denuders was removed by heating to 500 °C with argon flowing through the denuder. During the campaign denuders were recoated and changed regularly in order to obtain a collection efficiency >99 %. The denuders collect oxidized gaseous mercury compounds with a diffusion coefficient >0.1 cm<sup>2</sup>/s that readily adhere to a KCl coating at 50 °C (LANDIS ET AL., 2002). The most probable candidate compounds are HgCl<sub>2</sub> and HgBr<sub>2</sub>; HgO is less likely. Automated sampling and analysis was performed using the

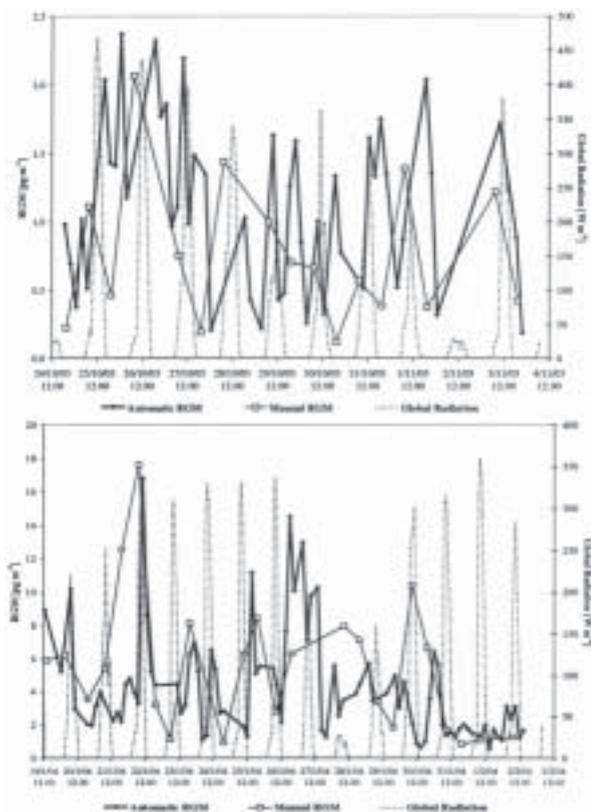
Tekran Model 1130 Mercury Speciation Unit coupled to a mercury vapour analyser (Tekran 2537A). RGM collected on the KCl-coated annular denuder at a flow rate of 10 Lpm, at 2 hour intervals, is thermally desorbed to 500 °C to decompose and reduce RGM to the elemental Hg for the analysis step by the Tekran 2537A CVAFS. After a cooling step (to 50 °C), the denuder is ready for another sampling cycle. Manual RGM were collected with 12-hours time resolution at a flow rate of 10 Lpm; after the sampling the denuders were desorbed at 500 °C and analysed by CVAFS using a Tekran 2537A analyser.

## RESULTS AND DISCUSSIONS

Figures 1 and 2 display the RGM concentration-time series obtained by both manual and automated techniques during the two seasonal campaigns. Both figures clearly show that both methods have produced comparable results. In particular, Figure 1 shows the diurnal variability of RGM levels collected during the fall experiment, from the 20<sup>th</sup> of October to 4<sup>th</sup> of November, 2003; RGM concentrations ranged from 0.2 to 2.4 pg m<sup>-3</sup> with a mean value of 1.12 pg m<sup>-3</sup>. Figure 2 shows RGM and global radiation during the winter campaign. The graph clearly shows that in contrast to the last sampling experiment, during the winter season higher RGM concentrations were observed with values ranged between 0.6 and 16.8 pg m<sup>-3</sup> and a mean value of 4.2 pg m<sup>-3</sup>. The diurnal pattern characterizing RGM levels, with the rapid morning increase reaching a maximum around midday and lower concentrations during the night could suggest that RGM is deposited to the ground beneath the nocturnal boundary layer and transported from above the

boundary layer during morning mixing. The source of this RGM may be direct emissions from point sources or formation in the free troposphere via photochemical oxidation (e.g. by OH radicals). In order to examine and interpret the results obtained during both seasonal campaigns, RGM concentrations have been compared with meteorological parameters and, in particular, air masses direction were also analysed by back-trajectories obtained using the Hybrid-single-particle lagrangian integrated trajectory (HYSPLIT) Model. The stability of the back trajectories was verified by expanding the starting area or by calculating at different ending heights. The results of this investigation strongly suggest that observed RGM concentrations and the behaviour observed was influenced by

transport of air coming from the sea (N-NW and NW, prevalently). These findings support the results obtained during recent studies (SPROVIERI ET AL., 2003) performed within an intensive cruise campaign over the Mediterranean Sea along 6000 km cruise path. In the MBL it has been shown (PIRRONE ET AL., 2000; PIRRONE ET AL., 2003; HEDGECOCK ET AL., 2001; SPROVIERI ET AL., 2003) that the extremely high chloride ion concentration in sea-salt aerosol is of a great importance in the cycling of RGM species. The sea salt aerosol provides a large excess of complexing ligands for  $\text{Hg}^{2+}_{(\text{aq})}$  and the aqueous phase concentration of Hg(II) in sea-salt aerosol can reach levels 100 times higher than those in other type of deliquesced aerosols or cloud droplets. The sea salt aerosol



as well as scavenging HgO produced by the reactions between  $\text{Hg}^0_{(g)}$  and  $\text{OH}_{(g)}$ ,  $\text{O}_{3(g)}$  and to a lesser extent  $\text{H}_2\text{O}_{2(g)}$  also releases RGM to the gas phase in the form of  $\text{HgCl}_2$  as a result of the high  $\text{Cl}^-_{(aq)}$  concentration in the sea-salt aerosol and the fact that the Henry's Law constant for  $\text{HgCl}_2$  although high is lower than that of HgO (SCHROEDER AND MUNTHE, 1998). From this point of view, the sea-salt aerosol represents not only a medium by which atmospherically produced Hg(II) could enter the sea, but is also a continuous source of RGM cycling HgO to  $\text{HgCl}_2$  in the MBL. Further studies are necessary to explain the reaction mechanisms and the kinetics in the production of oxidised Hg compounds. The RGM results provide necessary data to support the development of chemical models to clarify the role played by the RGM in the atmospheric mercury chemistry and its significance to the spatial distributions of Hg on hemispheric and global scales.

### Acknowledgements

This work is part of the MERCYMS (<http://www.cs.iaa.cnr.it/MERCYMS/project.htm>) funded by the European Commission (Contr. No. EVK3-2002-00070).

### REFERENCES

- EBINGHAUS, R., JENNINGS, S. G., SCHROEDER, W. H., BERG, T., DONAGHY, T., GUNTZEL, J., KENNY, C., KOCK, H. H., KVIETKUS, K., LANDING, W., MÜHLECK, T., MUNTHE, J., PRESTBO, E., SCHNEEBERGER, D., SLEMR, F., SOMMAR, J., URBA, A., WALLSCHLÄGER, D., XIAO, Z. (1999): *Atmos. Environ.*, Vol. 33, pp. 3063-3073.
- HEDGECKOCK, I. M., PIRRRONE, N. (2001): Mercury and photochemistry in the marine boundary layer: modelling studies suggest the in situ production of reactive gas phase mercury; *Atmos. Env.*, Vol. 35, pp. 3055-3062.
- HEDGECKOCK, I. M., PIRRRONE, N., SPROVIERI, F., PESENTI, E. (2003): Reactive gaseous mercury in the marine boundary layer: modelling and experimental evidence of its formation in the Mediterranean region; *Atmospheric Environment*, Vol. 37, pp. 41-49.
- LANDIS, M. S., STEVENS, R. K., SCHAEDLICH, F., PRESTBO, E. M. (2002): Development and characterization of an annular denuder methodology for the measurements of divalent inorganic reactive gaseous mercury in ambient air; *Environ. Sci. Technol.*, Vol. 36, No. 13, pp. 3000-3009.
- MUNTHE, J., WÄNGBERG, I., PIRRRONE, N., IVERFELDT, A., FERRARA, R., COSTA, P., EBINGHAUS, R., FENG, X., GARDFELT, K., KEELER, G., LANZILLOTTA, E., LINDBERG, S. E., LU, J., MAMANE, Y., NUCARO, E., PRESTBO, E., SCHMOLKE, S. R., SCHROEDER, W. H., SOMMER, J., SPROVIERI, F., STEVENS, R. K., STRATTON, W., TUNCEL, G., URBA, A. (2001): *Atmos. Environ.*, Vol. 35, No. 17, pp. 3007-3017.
- PIRRONE, N., HEDGECKOCK, I., FORLANO, L. (2000): The role of the ambient aerosol in the atmospheric processing of semi-volatile contaminants: a parameterised numerical model (GASPAR); *Journal of Geophysical Research* D105(8), pp. 9773-9790.
- PIRRONE, N., FERRARA, R., HEDGECKOCK, I. M., KALLOS, G., MAMANE, Y., MUNTE, J., PACYNA, J.M., PYTHAROULIS, I., SPROVIERI, F., VOUDOURI, A., WANGBERG, I. (2003): Dynamic processes of mercury over the Mediterranean region : results from the Mediterranean Atmospheric Mercury Cycle System (MAMCS) project; *Atmos. Environ.*, Vol. 37, pp. 21-39.
- SCHROEDER, W. H. AND MUNTHE, J. (1998): Atmospheric Mercury - an overview; *Atmos. Env.* 32(5), pp. 809-822.
- SPROVIERI, F., PIRRRONE, N., GÄRDFELDT, K., SOMMAR, J. (2003): Mercury speciation in the Marine Boundary Layer along a 6000 Km cruise path around the Mediterranean Sea; *Atmospheric Environment*, Vol. 37, pp.63-71.

## Some Sources and Sinks of Methyl and Inorganic Mercury on Ellesmere Island in the Canadian High Arctic

VINCENT L. ST. LOUIS<sup>1</sup>, MARTIN J. SHARP<sup>1</sup>, ALEXANDRA STEFFEN<sup>2</sup>, AL MAY<sup>1</sup>, JOEL BARKER<sup>1</sup>,  
JANE L. KIRK<sup>1</sup>, DAVID J. A. KELLY<sup>1</sup>, SHELLEY E. ARNOTT<sup>3</sup>,  
BRONWYN KEATLEY<sup>3</sup> & JOHN P. SMOL<sup>3</sup>

<sup>1</sup>University of Alberta, Edmonton, Alberta Canada;

E-mails: vince.stlouis@ualberta.ca; martin.sharp@ualberta.ca; AMay@ci.stamford.ct.us;  
jdbarker@ualberta.ca; jkirk@ualberta.ca; dkelly@ualberta.ca

<sup>2</sup>Meteorological Service of Canada, Environment Canada,

4905 Dufferin Street, Toronto, Ontario, Canada; E-mail: Alexandra.Steffen@ec.gc.ca

<sup>3</sup>Queen's University, Kingston, Ontario, Canada.

E-mails: arnotts@biology.queensu.ca; keatleyb@biology.queensu.ca; smolj@biology.queensu.ca

**Abstract:** On Ellesmere Island in the Canadian High Arctic, we found that Hg(II) deposited to snowpacks following atmospheric Hg depletion events was rapidly (photo)reduced to Hg(0). We also observed a significant correlation between concentrations of Cl and monomethyl Hg (MMHg) in snow deposited in the spring, suggesting a marine source of MMHg. We hypothesize that dimethyl Hg produced in deep northern oceans and fluxing through open water regions in the sea ice during winter is a primary source of MMHg to some high Arctic food webs. Concentrations of MMHg in warm and shallow freshwater ponds on Ellesmere Island were also quite high, leading us to conclude that there are very active regions of microbial Hg(II) methylation in freshwater systems during the short summer season in the high Arctic.

**Key words:** Arctic, methylmercury, atmospheric Hg depletion events, snow/snowmelt, lakes and ponds.

### INTRODUCTION

Even in remote regions such as the Canadian high Arctic, there is increasing evidence of contamination by persistent, toxic substances including Hg<sup>[1]</sup>. However, the degree of Hg deposition in certain regions of the High Arctic varies more seasonally than in southern ecoregions, with a recently discovered pulse of deposition after polar sunrise<sup>[2]</sup>. Gaseous elemental Hg(0) concentrations in the Arctic atmosphere normally range between 1-2 ng/m<sup>3</sup><sup>[2]</sup>. However, for three

months after polar sunrise (until the approximate timing of snowmelt), atmospheric Hg(0) levels frequently drop below 1 ng/m<sup>3</sup>, coinciding with a decrease in tropospheric ozone concentrations<sup>[2]</sup>. It is now believed that gaseous Hg(0) is oxidized by sunlight-induced heterogeneous reactions with the marine halogens Br and Cl to become reactive gaseous Hg and/or particulate Hg<sup>[3,4,5]</sup>. Both of these have dry-deposition velocities greater than gaseous Hg(0) and thus fall out into the snowpack. In fact, *atmospheric Hg depletion events* have been implicated as the

source of elevated concentrations of Hg(II) (100 ng/L) found in surface snow in the Arctic<sup>[5]</sup>. We studied the short-term fate of Hg(II) in snowpacks on Ellesmere Island in the Canadian high Arctic following atmospheric Hg depletion events. We also examined the deposition of MMHg to High Arctic snowpacks, as well as concentrations of MMHg in snowmelt and lakes and ponds on Ellesmere Island, to help understand why concentrations of MMHg in certain marine and freshwater organisms used as traditional food by aboriginal peoples of the north have increased over the past few decades.

## RESULTS AND DISCUSSION

Atmospheric Hg depletion events resulted in the deposition of Hg(II) into the upper layers of snowpacks, where concentrations of total Hg (THg; all forms of Hg) reached over 20 ng/L. However, our data suggests that much of this Hg(II) was subsequently (photo)reduced to Hg(0) which then evaded back to the atmosphere. As a result, we estimate that net deposition of Hg(II) during winter was lower at our sites (0.4 to 5.9 mg/ha) than wet deposition in more southerly locations in Canada and the United States. We also found quite high concentrations of MMHg in snowpacks (up to 0.26 ng/L), and at times, most of the Hg present in snowpacks was present as MMHg. On the Prince of Wales Icefield near the North Water Polynya, we observed a significant correlation between concentrations of Cl and MMHg in snow deposited in the spring, suggesting a marine source of MMHg. We hypothesize that through open leads in the ice and polynyas, dimethyl Hg fluxes from the ocean to the atmosphere

where it is rapidly photolysed to MMHg-Cl. We also found that concentrations of MMHg in initial surface snowmelt on John Evans Glacier (up to 0.24 ng/L) were higher than concentrations of MMHg in the snowpack (up to 0.11 ng/L), likely due to the preferential leaching of MMHg from snow in the early stages of melt. Concentrations of MMHg in warm and shallow freshwater ponds on Ellesmere Island were also quite high (up to 3.0 ng/L), leading us to conclude that there are very active regions of microbial Hg(II) methylation in freshwater systems during the short summer season in the high Arctic.

## CONCLUSIONS

Atmospheric Hg depletion events resulted in only a short-term deposition of Hg(II) into the upper layers of snowpacks at our sites on Ellesmere Island. Once deposited, the Hg(II) was quickly (photo)reduced to Hg(0), which then fluxed back to the atmosphere, resulting in low *net* deposition of Hg(II) during winter and spring. As a result, we do not believe that atmospheric Hg depletion events are the ultimate source of the high concentrations of MMHg found in certain Arctic marine and freshwater organisms. Instead, we present for the first time strong evidence that high concentrations of MMHg found in Arctic snowpacks have marine origins, leading us to hypothesize that DMHg produced in deep northern oceans and fluxing through open water regions in the sea ice during winter is a primary source of MMHg to some high Arctic food webs. Climate warming and the thinning and melting of sea ice may explain why concentrations of MMHg in certain marine mammals used as traditional food

by aboriginal peoples of the north have increased over the past few decades.

### Acknowledgements

This research was financially supported by, in no specific order, the Northern Contaminants Program (Department of Indian and Northern Affairs Canada), Meteorological

Service of Canada (Environment Canada), the Canadian Circumpolar Institute Circumpolar/Boreal Alberta Research (C/BAR) and Northern Scientific Training (NSTP) grant programs, NSERC Discovery Grants to V. St.Louis and M. Sharp, the Polar Continental Shelf Program for logistic support on John Evans Glacier and the Prince of Wales Icefield, and the Alberta Science Research Program.

### REFERENCES

- [1] Canadian Arctic Contaminants Assessment Report II; Highlights (2003): *Indian and Northern Affairs Canada*.
- [2] SCHROEDER, W.H., ANLAUF, K.G., BARRIE, L.A., LU, J.Y., STEFFEN, A., SCHNEEBERGER, D.R., BERG, T. (1998): Arctic springtime depletion of mercury. *Nature* 394, pp. 331-332.
- [3] BERG, T., BARTNICKI, J., MUNTHE, J., LATTILA, H., HREHORUK J., MAZUR, A. (2001): Atmospheric mercury species in the European Arctic: measurements and modeling. *Atmospheric Environment* 35, pp. 2569-2582.
- [4] LINDBERG, S.E., S.B. BROOKS, M. LANDIS, AND R. STEVENS. (2001): Comments on "Atmospheric mercury species in the European Arctic: measurements and modeling" by Berg et al. *Atmospheric Environment* 14 (2001), 2569-2582. *Atmospheric Environment* 35, pp. 5377-5378.
- [5] LINDBERG, S.E., BROOKS, S., LIN, C.-J., SCOTT, K.J., LANDIS, M.S., STEVENS, R.K., GOODSITE, M., RICHTER, A. (2002): Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise. *Environmental Science and Technology* 36, pp. 1245-1256.

## On-going Atmospheric Mercury Measurements in the High Arctic in Canada and Russia

ALEXANDRA STEFFEN<sup>1\*</sup>, WILLIAM SCHROEDER<sup>1</sup>, ROB MACDONALD<sup>2</sup>, AND ALEXEI KONOPLEV<sup>3</sup>

<sup>1</sup> Meteorological Service of Canada, 4905 Dufferin St., Toronto, Ontario, M3H 5T4

<sup>2</sup> Institute of Ocean Sciences, PO Box 6000, Sidney, British Columbia, V8L 4B2

<sup>3</sup> Center for Environmental Chemistry SPA “Typhoon”, 82 Lenin Av. Obninsk, Russia.

**Abstract:** Eight years of gaseous elemental mercury (GEM) concentration measurements from Alert, Nunavut, Canada (between 1995 to 2002) are presented. The annual time series shows a distinct repeating seasonal pattern with an overall annual median concentration for this time period of 1.58 (SD = 0.04 ng m<sup>-3</sup>). Strong seasonal variation was observed throughout the years. Preliminary results suggest that from 1995 to 2002 at Alert an increasing amount of the mercury lost from the atmosphere in the spring is not returned to atmosphere in summer. A comparison of GEM concentration data from Alert (Canada) and Amderma (Russia) demonstrated similar distribution of GEM. Mercury depletion events (MDEs) were found to occur at both sites in the spring and demonstrate both similar and differing characteristics.

**Key Words:** mercury, gaseous elemental mercury, mercury depletion events, arctic mercury.

### INTRODUCTION

Mercury (Hg) is a toxic metal that has been found at elevated concentrations in the tissues of aquatic animals from the Canadian Arctic. Atmospheric elemental mercury can undergo long range transport because it has a long atmospheric residence time allowing it to be carried by air currents far from emission sources to remote regions like the Arctic.

In 1995, studies were initiated at Alert (Nunavut, Canada - 82.5 °N; 62.3 °W) and then subsequently at Amderma (Russia - 69.72°N; 61.62°E) to measure atmospheric trends of Hg in the Arctic and to evaluate the role of the atmosphere in transferring Hg to Arctic ecosystems by investigating how atmospheric chemical processes in the Arctic might act to enhance the capture of Hg

from the global atmosphere. In this research, the discovery of mercury depletion events (MDEs) was made and has since revolutionized our understanding of how mercury cycles in Arctic regions and has since engendered an increase in mercury research in polar regions.

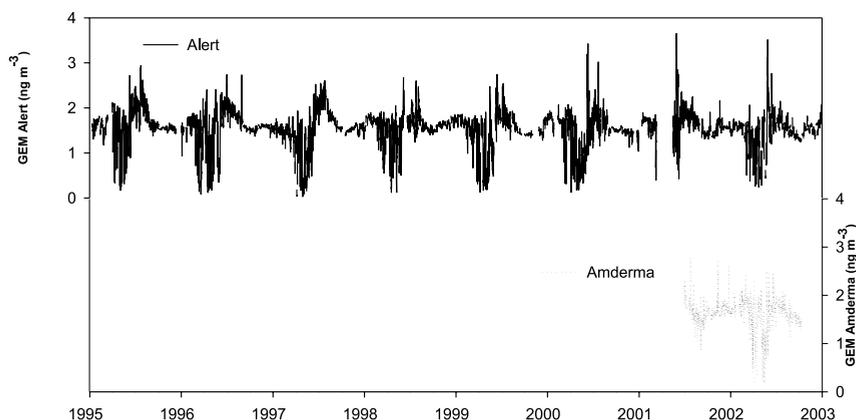
### RESULTS AND DISCUSSION

The atmospheric Hg record at Alert between 1995 - 2002 is the longest set of continuous measurements from an Arctic location (Figure 1 top panel). The distinct seasonal patterns, which repeat annually at Alert, suggest the presence of predictable behaviour of the mercury cycle at this high Arctic location. The annual average median mercury concentration for Alert from 1995-2002 is

1.58 (SD = 0.04 ng m<sup>-3</sup>) with a range in the data from 0.03 – 4.09 ng m<sup>-3</sup>. Between 1995 and 2002, there is no statistically significant trend (95 % CI) in the annual median. This agrees with others who have investigated time trends of GEM in Arctic locations (BERG ET AL.(2004), TEMME ET AL. (2004)). However, seasonal trends are very evident in these data and hence merit more detailed discussion. From 1995-2002, winter at Alert has an average median concentration of 1.63 (SD = 0.08) ng m<sup>-3</sup>. At the beginning of January the GEM data show low variance and continue to increase until early March. The average spring median concentration is 1.39 (SD = 0.19 ng m<sup>-3</sup>) and this season shows the highest variance in the data including highest maximum concentration. Despite the variability in the signal during summer, the average median GEM concentration increases to 1.67 (SD = 0.11) ng m<sup>-3</sup>. Finally, during the fall, the GEM exhibit a small vari-

ance about an average median value of 1.54 (SD = 0.06 ng m<sup>-3</sup>).

If we look at the repeating annual pattern of GEM at Alert it is tempting to suggest that the increase of GEM in the summer is simply the release of the mercury previously deposited in the springtime. To address this simple proposition the relationship between the magnitude of the springtime depression and the magnitude of the summer enhancement were compared. Results from this data showed a change in the behaviour of GEM in summer relative to spring at Alert over an 8 year period. From 1995 to 2002, progressively less mercury lost from the atmosphere in the spring appears to have been returned to atmosphere in summer. Given that mercury deposited in spring is potentially bioavailable, it appears important to conduct further investigations aimed at accounting for the missing mercury.



**Figure 1:** Time series of GEM concentration at Alert (top) and Amderma (bottom).

GEM at Alert varies between seasons within a given year but there are also variations in these seasons between years. Figure 2 represents the inter-quartile range as an estimation of the dispersion of the GEM concentration data. From this plot the winter GEM data show some variation in the concentration and range and are generally dispersed to the lower concentrations. The springtime data are also dispersed towards the lower concentrations with little variation between years and show no significant increase or decrease (95 % CI) in the median concentration. The summer data are dispersed towards the higher concentrations and the median concentration values indicate a slight

but statistically significant (within a 95 % CI) decrease from 1995 to 2002. The fall results show an inter-annual consistency of GEM from year to year.

**Comparison of Alert and Amderma.** The record of GEM data from Amderma suggests that this site exhibits annual and seasonal patterns more closely aligned with those of Alert (Figure 1 – bottom panel). Slightly higher than Alert, the annual median concentration for Amderma is  $1.7 \text{ ng m}^{-3}$  with a range of  $0.01 - 4.6 \text{ ng m}^{-3}$ . Amderma and Alert show similar patterns which include a low in the springtime, elevated concentrations in the summer (less pronounced at

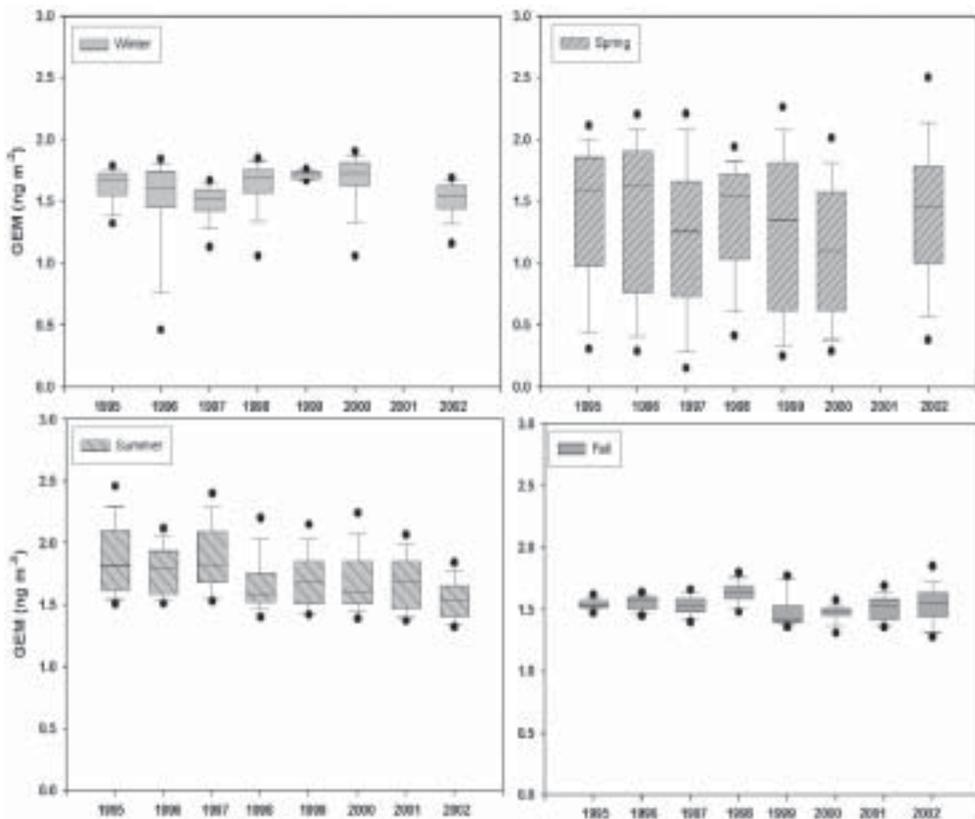


Figure 2: Inter-quartile range as box and whisker plots of Alert seasonal data 1995-2002.

Amderma), relatively invariant GEM distributed in the fall and a slight increase in GEM in the winter.

While MDEs have been confirmed at both Alert and Amderma and have now been studied in many polar areas (SCHROEDER ET AL., 2003), there has been little attempt to investigate MDE data collectively from different locations. This study found that most conditions reported to initiate MDEs occur similarly at both these high Arctic sites but differed slightly on the presence of sunlight. Although MDEs initiate at the same time of the year, Alert has a rapid transition from 24 hour dark to 24 hour light but at Amderma this transition takes a few months. Alert and Amderma revealed similar average number of MDEs per season (10 and 11, respectively) but the length and sharpness of these events differed at each site. The end of the depletion events at both Alert and Amderma is characterized by the onset of sustained air temperatures above 0 °C which, in turn, coincides with snowmelt. Following snowmelt, GEM concentrations in the air increase at these high Arctic locations, although they differ in magnitude. The impact of mercury in the melt water is yet unclear but it has been suggested that it may be significant as a viable means by which mercury can enter the ecosystem (Dommergue et al. 2003). Such impact of snowmelt on the Arctic ecosystem will differ for each location depending on the amount of mercury that is deposited in the spring from the atmosphere, the

amount that is released back to the atmosphere and how much is leached into the spring run-off. Further investigations are required to establish a relationship between elevated snowmelt concentrations and the frequency and extent of MDEs.

## CONCLUSIONS

This study investigated 8 years of GEM concentration measurements from Alert from 1995 to 2002. Results showed that there is an annually reoccurring pattern in this data but no statistically significant long term trend of GEM concentration in time was observed. Strong seasonal variation was evident at Alert throughout the years. A comparison of GEM concentrations at Alert and Amderma indicates that the high Arctic sites show a similar behaviour in the cycling of GEM although some interesting differences are indicated. The study of MDEs throughout polar regions are ongoing and warranted, but it is insufficient to observe and study these events solely at one given site to elicit impacts on the polar and global environments. Therefore a more cohesive approach to this type of study is recommended.

## Acknowledgements

This research has been funded by the Northern Contaminants Program of the Department of Indian and Northern Affairs Canada, Environment Canada and the Danish EPA.

**REFERENCES**

- BERG, T., KALLENBORN, R. AND MANŘ, S. (2004) Temporal trends in atmospheric heavy metal and organochlorine concentrations at Zeppelin, Svalbard. *Arctic, Antarctic, and Alpine Research Vol 2, Nr 2, May 2004*. In press.
- DOMMERGUE, A., FERRARI, C.P., GAUCHARD, P-A, BOUTRON, C.F., POISSANT, L., PILOTE, M., JITARU P. AND ADAMS F.C. (2003) The fate of mercury species in a sub-arctic snow pack during snow-melt. *Geophys. Res. Lett.*30:1621-1624.
- MACDONALD, R.W., HARNER, T., FYFE, J., LOENG, H. AND WEINGARTNER, T. (2003) The Influence of Global Change on Contaminant Pathways to, within and from the Arctic, in *AMAP Assessment 2002 Arctic Monitoring and Assessment Programme*, Oslo, Norway. 65.
- SCHROEDER, W.H., STEFFEN, A., SCOTT, K., BENDER, T., PRESTBO, E., EBINGHAUS, R., LU, J.Y. AND LINDBERG, S.E. (2003) Summary report: first international Arctic atmospheric mercury research workshop. *Atmos. Environ.* 37:2551-2555.
- TEMME, C., EBINGHAUS, R., EINAX, J.W., STEFFEN, A. AND SCHRODER, W.H. (2004) Application of time series analysis on long-time data sets of atmospheric mercury concentrations at two sites. In preparation.

## Characterizing Mercury Depletion Events in Ny-Ålesund, 2003

ALEXANDRA STEFFEN<sup>1</sup>, KATRINE ASPMO<sup>2</sup>, CATHARINE BANIC<sup>1</sup>, TORUNN BERG<sup>2</sup>, RALF EBINGHAUS,  
CHRISTOPHE FERRARI<sup>4</sup>, PIERRE-ALEXIS GAUCHARD<sup>4</sup> AND CHRISTIAN TEMME<sup>2</sup>

<sup>1</sup>Environment Canada (MSC), Canada.

<sup>2</sup>Norwegian Institute for Air Research (NILU), Norway.

<sup>3</sup>GKSS-Forschungszentrum Geesthacht GmbH, Germany.

<sup>4</sup>CNRS, Grenoble, France.

**Abstract:** An inter-comparative and processes study was undertaken at Ny-Ålesund, Svalbard (78°54'N, 11°53'E) in April 2003. During the study time period 4 mercury depletion events (MDEs) were recorded. Mercury species determined during these events include total atmospheric mercury (using a cold regions pyrolysis unit), reactive gaseous and particulate mercury (using automated and manual methods). Particle number concentration was also determined during these MDEs. The importance of reliable and comparable methods in which to measure mercury species is great and this study further developed our understanding of the currently used methodologies. By combining data sets a clearer picture of the characteristics of MDEs occurring during this study emerged. The distribution of mercury in the reactive gas phase and mercury on particles can be a key aid in understanding different types of depletion events that occur and ultimately their impacts on the environment. The recovery of depleted mercury in the air during MDEs ranged from less than 10 to almost 90 %.

**Key Words:** mercury depletion events, mercury speciation, inter-comparison

### INTRODUCTION

Since the discovery of mercury depletion events (MDEs) at Alert, Nunavut there has been considerable research on this atmospheric phenomenon and its implications to the Arctic environment (SCHROEDER ET AL., 2003). Since different groups have been undertaking a variety of atmospheric mercury measurements to study MDEs at various locations in Polar Regions, a collaborative project was required to ensure comparable data sets. To fill this need, researchers from 6 countries collected measurements at

3 different sites in Ny-Ålesund, Svalbard in the spring of 2003.

Mercury measurements included gaseous elemental mercury (GEM), reactive gaseous mercury (RGM), particulate-phase mercury (PM) and total atmospheric mercury (TAM). Additionally, size distribution and particle number concentration data were collected. The data collected by 4 of the research groups are presented and compared here. The species measured and the methods used are shown in Table 1.

**Table 1.** Summary of methods used by 3 research groups for Hg species determinations

Hg Species	MSC	GKSS	NILU
GEM	Tekran 2537A	Tekran 2537A	Tekran 2537A
RGM	Manual* (KCl denuder)	Automated Tekran 1130	Manual* (KCl denuder)
PM	Manual quartz filter*	Not collected	Manual quartz filter*
TAM	CRPU	Not collected	Not collected

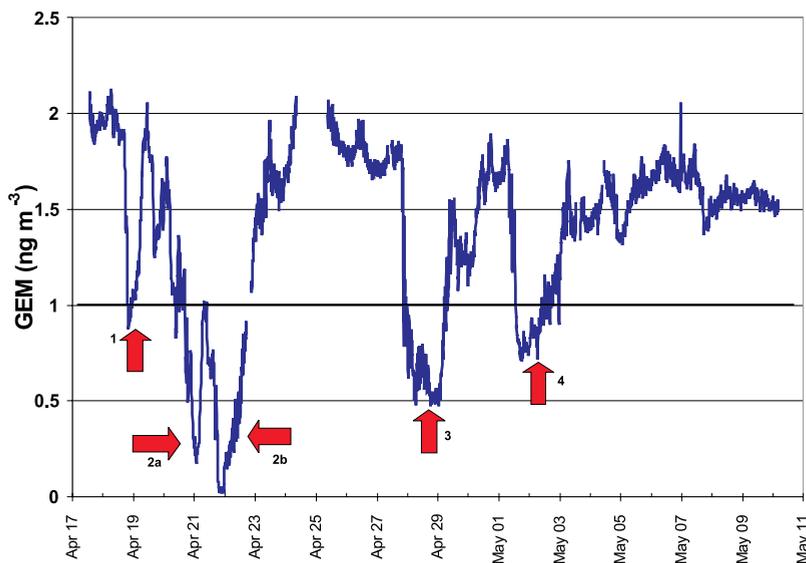
\*The size of the MSC and NILU deuders and filters are different but the general methods for collection and analysis is the same

## RESULTS AND DISCUSSION

The 4 MDEs that occurred during the study period are indicated in the GEM concentrations in Figure 1. MDEs are considered to occur if the GEM concentrations decrease to below  $1 \text{ ng m}^{-3}$ .

*Summary of events:* MDEs occur during different meteorological conditions and the characteristics of these events, with respect to the distribution of mercury, are shown in Table 2. Event 1 is considered a small MDE

where low PM and RGM concentrations were recorded during blowing snow conditions. As well, the number of particles present was low and less than 20 % of the depleted ambient mercury was recovered with the CRPU. Event 2a occurred during relatively high winds where elevated numbers of particles (mostly less than  $0.5 \mu\text{m}$  in size), high PM concentration, higher RGM (than Event 1) were recorded. Approximately 50 % of the Hg in the air was recovered by CRPU. PM and RGM (in general) were higher during Event 2b but the particle



**Figure 1.** GEM over Ny-Alesund field campaign with 4 recorded mercury depletion events

number concentration did not change. The winds decreased during this event and the range of percent Hg recovered increased up to 90 %. RGM concentrations increased in comparison to PM and the particle number concentration decreased during Event 3. The percent of Hg recovered in the air dropped to less than 40 %. Finally, Event 4 shows similar characteristics to Event 3 where RGM was relatively high, PM was low, number of particles was low and the percent of Hg recovered in the air by pyrolysis remained at less than 40 %. When the data are compared it can be seen that there are some differences between results using the different methods but in general the pattern of the distribution of mercury are similar. Further investigation into a comparison of the methodologies is being done elsewhere.

*Characterization of the MDEs:* Event 1 displayed small concentrations of both RGM

and PM as well as a low recovery of Hg in the air with the CRPU. Since blowing wet snow was falling throughout this event, any RGM and PM present during the MDE are thought to have been scavenged by the snow and thus not detected in the air. A further look at the Hg concentrations in the snow is warranted to confirm this conclusion.

Reactive (oxidized) gaseous mercury produced during a MDE can easily associate to particles or can remain in the air. It is thought that if the distribution of mercury during a depletion event is higher in PM relative to RGM this may indicate that the RGM produced during a MDE has had more opportunity to associate to particles. This is considered an indication that the depletion occurred elsewhere and was transported to the measurement site. Conversely, if the distribution of mercury species is higher in RGM than PM, the oxidized mercury has had less

**Table 2.** Summary of measurement results for the 4 mercury depletion events.

	Wind Speed (m/s)	RGM (GKSS) (pg/m <sup>3</sup> )	RGM (MSC) (pg/m <sup>3</sup> )	RGM (NILU) (pg/m <sup>3</sup> )	PM (MSC) (pg/m <sup>3</sup> )	PM (NILU) (pg/m <sup>3</sup> )	Particles #/L average	TAM* Rec. (%)	Other
<b>Event 1</b>	6-12	<16	< 16	n/a	<35	n/a	a. 5903 b. 1667 c. 2	<20	wet snow
<b>Event 2a</b>	6-13	25-75	3 - 78	3-10	10-150	n/a	a. 10282 b. 1775 c. 1.5	50-60	“double dip” blowing snow, windy
<b>Event 2b</b>	6-13	50-200	9 - 66	10-200	10-225	n/a	a. 10348 b. 1441 c.1.5	25-90	“double dip” blowing snow
<b>Event 3</b>	1-6	35-300	10-300	14-200	8-80	14-75	a. 4923 b. 509 c. 0.6	10-40	mid to low winds
<b>Event 4</b>	5-7	50-225	n/a	10-150	n/a	<50	a. 6066 b. 838 c. 1.2	20-50	medium winds

For particle counts a= 0.3-0.5 µm; b=0.5-5 µm; c=>5 µm; n/a data not available

TAM % recovered calculation: [(heated-ambient)/ (avg. non MDE [Hg]-ambient)]\*100

\*TAM recoveries calculated from data collected with CRPU

opportunity to associate to particles and can thus be an indication of a more local event (STEFFEN ET AL., 2003a). During Event 2 higher concentrations of both PM and particle number concentration were recorded. The wind speed was high for Event 2a but decreased at the onset of Event 2b. In addition, Event 2a found higher PM relative to RGM than during Event 2b. Thus, Event 2a is the result of advection of a depleted air mass in from elsewhere whereas Event 2b was a more local event. The highest percent recovered of Hg in the air was seen during Event 2, which includes the highest particle concentration numbers.

Events 3 and 4 show higher concentrations of RGM relative to PM, lower wind speeds, low number of particles and lower percent Hg recovered in the air. These results indicate that these events could be more local events. Further investigation into the significance of these differing events is warranted.

These results indicate that there are different types of depletion events with varying characteristics and an in depth analysis of these differences are needed. Understanding the distribution of mercury during different environmental and meteorological conditions can play a significant role in understanding the impact of MDEs on the Arctic at different locations with different climate conditions.

## CONCLUSIONS

An inter-comparative and processes study was undertaken at Ny-Ålesund, Svalbard in April 2003. Results from this campaign indicate that while there are differences in current methodologies for measuring atmospheric mercury during MDEs the distribution of Hg species is similar. Since the distribution of mercury during MDEs is not well understood at this point, a closer look at the characteristics of MDEs reveals that different environmental and meteorological conditions yield a different distribution of mercury. The characterization of MDEs is important in order to fully understand the impact of MDEs under different climate conditions and at different locations throughout Polar Regions.

## Acknowledgments

This research has been funded by the Northern Contaminants Program of the Department of Indian and Northern Affairs Canada and Environment Canada. Special thanks go to CNR Italy for their support and hospitality at the Italian Dirigibile station at Ny-Ålesund; John Deary for his invaluable support during the field campaign and Torunn Berg and NILU for organizing this whole campaign.

## REFERENCES

- SCHROEDER, W. H., STEFFEN, A., LAWSON, G. AND STRACHAN, W. (2001): Mercury measurements at Amderma, Russia; In (KALHOK, S., Editor) *Synopsis of Research Conducted Under the 2000-20001 Northern Contaminants Program*, Indian and Northern Affairs Canada, Ottawa, pp. 130-135.
- SCHROEDER, W. H., STEFFEN, A., SCOTT, K., BENDER, T., PRESTBO, E., EBINGHAUS, R., LU, J. Y. AND LINDBERG, S. E. (2003): Summary report: First International Arctic Atmospheric Mercury Research Workshop; *Atmos. Environ.* 37, pp. 2551-2555.
- STEFFEN, A., SCHROEDER, W. H., POISSANT, L. AND MACDONALD, R. (2003a): Mercury in the arctic atmosphere; In (BIDLEMAN, T., MACDONALD, R. AND STOW, J., Eds.) *Canadian Arctic Contaminants Assessment Report II*, Indian and Northern Affairs Canada, Ottawa, pp. 124-142.
- STEFFEN, A., SCHROEDER, W. H., EDWARDS, G. AND BANIC, C. (2003b): Mercury throughout polar sunrise 2002; *J. Phys.* IV(107), pp. 1267-1270.

## Role of Ocean-Atmosphere Exchange in a Global Mercury Model

SARAH STRODE<sup>1</sup>, LYATT JAEGLÉ<sup>1</sup>, NOELLE ECKLEY<sup>2</sup>, ROKJIN PARK<sup>2</sup> AND DANIEL JACOB<sup>2</sup>

<sup>1</sup>Department of Atmospheric Sciences, University of Washington, Seattle, Washington, USA; E-mail: sstrode@atmos.washington.edu

<sup>2</sup>Division of Engineering and Applied Sciences and Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA

**Abstract:** This study examines the flux of elemental mercury between the ocean and atmosphere in a global model. We determine the seasonal and spatial distribution of the flux as a function of solubility and temperature only and also as a function of biological and photochemical oceanic production.

**Key Words:** mercury, ocean, global model

### INTRODUCTION

Oceanic evasion plays an important role in the biogeochemical cycling of mercury and the long-range transport of anthropogenic mercury. Since the oceanic flux of mercury depends on the relative concentrations of elemental mercury in the atmosphere and ocean, as well as temperature and wind speed, we expect to see both spatial and seasonal variability in the flux. Observations suggest that production of elemental mercury in the ocean may be photochemically and/or biochemically mediated, and is limited by the supply of mercury via deposition (e.g., MASON AND SHEU, 2002).

We are developing a mercury simulation in the GEOS-CHEM global chemical transport model (BEY ET AL., 2001). The model is driven by assimilated meteorological data from the Goddard Earth Observing System (GEOS) Global Modeling and Assimilation Office. Our simulation of atmospheric mercury in-

cludes elemental ( $\text{Hg}^0$ ), reactive ( $\text{Hg}(\text{II})$ ), and particulate ( $\text{Hg}(\text{p})$ ) mercury. The model includes anthropogenic, land, and ocean emissions, oxidation of elemental mercury, and wet and dry deposition. We are comparing four different formulations of the air-sea exchange. In the base case (C1), the oceanic flux is a function of latitude only, with emissions decreasing with distance from the equator, following BERGAN ET AL. (1999). In all other versions, mercury evasion is determined from temperature-dependent Henry's Law and the temperature and wind-speed dependent gas exchange coefficient. In the second case (C2), the aqueous concentration of  $\text{Hg}^0$  is treated as constant in space and time. Cases C3 and C4 allow the aqueous  $\text{Hg}^0$  concentration to vary spatially and temporally by including an aqueous  $\text{Hg}^0$  production term throughout the mixed layer, and assuming steady state between production and evasion. In C3, the production of  $\text{Hg}^0$  is linearly proportional to radiation only, while in C4 it is proportional to both radiation and net primary productivity

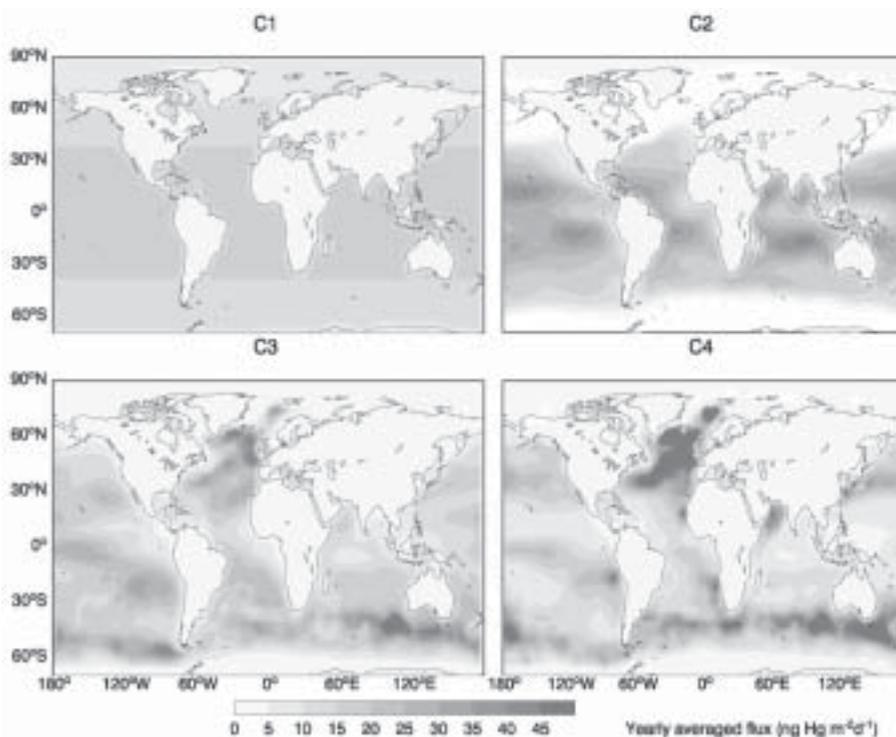
(NPP). In all cases we scale the annual global oceanic  $\text{Hg}^0$  emissions to  $2 \times 10^6$  kg/yr, and examine the spatial and seasonal variability in the air-sea exchange.

## RESULTS AND DISCUSSION

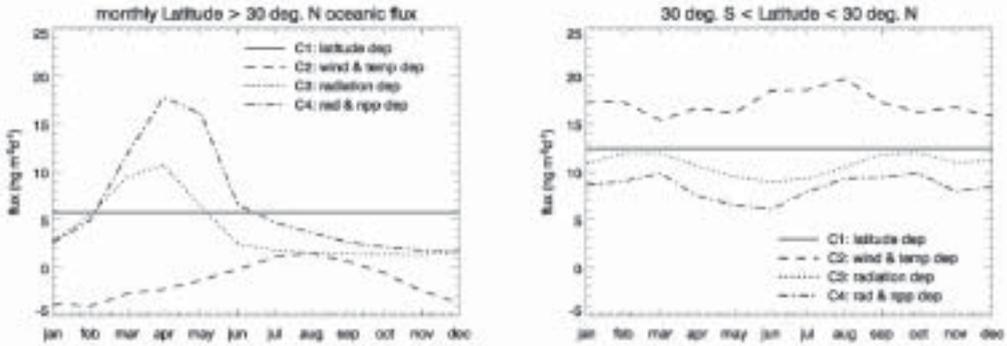
Figure 1 presents the global annual flux of elemental mercury for the 4 model cases. While in C1 the flux varies sinusoidally with latitude, the other cases show more complicated patterns of evasion. C2 illustrates the influence of temperature and wind-speed on the flux, with emissions being largest in the warm tropical waters near the trade winds. At high latitudes, the cold temperatures drive

a net flux of  $\text{Hg}^0$  into the ocean. When we allow aqueous  $\text{Hg}^0$  concentrations to vary as a function of solar radiation and mixed layer depth (C3), emissions shift away from the tropical regions. This shift to higher latitudes is further accentuated in C4 under the influence of NPP, particularly over the North Atlantic and Southern Ocean. The low evasion rates in the tropical Pacific and elevated North Atlantic rates of C4, 11 and 51  $\text{ng}/\text{m}^2/\text{day}$  respectively, seem to best match existing observations (MASON & FITZGERALD, 1995; LAURIER ET AL., 2003).

The seasonal cycle of the ocean flux is presented in Figure 2 for tropical regions and high latitudes.



**Figure 1.** Annual sea-air flux of  $\text{Hg}^0$  for the 4 model cases: C1 (function of latitude), C2 (fixed aqueous  $\text{Hg}^0$ ), C3 (aqueous  $\text{Hg}^0$  due to radiation), and C4 (aqueous  $\text{Hg}^0$  due to radiation and NPP). Values have been capped at 0-50  $\text{ng}/\text{m}^2/\text{day}$ .

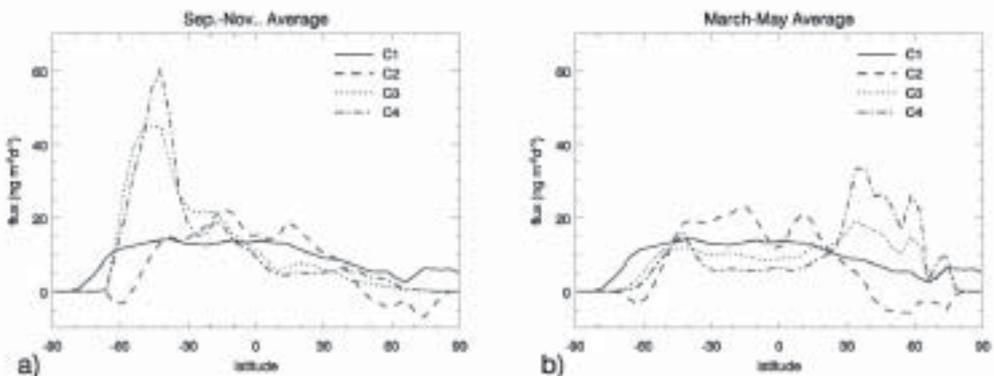


**Figure 2.** Seasonal cycle of the ocean to atmosphere Hg<sup>0</sup> evasion. The left panel is for the oceans north of 30°N, while the right panel is for the tropical oceans (30°N-30°S).

The Hg<sup>0</sup> evasion flux at mid and high latitudes exhibits a strong seasonal cycle. For C2, cold temperatures drive a negative evasion flux in the North Atlantic in winter, while the maximum sea-air flux is found during the warm summer months. The negative flux does not occur in C3 or C4, and the seasonal cycle of mixed layer depth and radiation shifts the maximum for these cases to the Northern Hemisphere spring. In the Tropics, warm temperatures and high wind speeds between June and August drive a strong oceanic flux in the C2 simulation. For cases 3 and 4, there is a maximum in March due to the deepening of the mixed layer and

increase in NPP and radiation in the Northern Tropics, and a second maximum in October, when these effects occur in the Southern Tropics. Overall, the amplitude of the seasonal cycle is much smaller than at higher latitudes.

Figure 3 shows oceanic evasion averaged by latitude for September-November and March-May. The strongest peak occurs in September-November for C4 around 40°S. At this point, strong NPP, intense radiation, and deep mixed layers are collocated, leading to elevated aqueous Hg<sup>0</sup> concentrations. C3 has the same general shape but less sharp



**Figure 3.** Oceanic flux averaged by latitude for autumn (panel a) and spring (panel b).

peaks due to the lack of dependence on NPP. In contrast, C2 shows the strongest flux in the tropics, driven by warm tropical temperatures and the trade winds.

The March-May flux is a mirror image of Sep.-Nov., with the maximum for C3 and C4 shifting to the Northern Hemisphere, following the shift in mixed layer depth and NPP.

## CONCLUSIONS

We examined the ocean to atmosphere flux of elemental mercury using 4 different model formulations. When the oceanic concentration of elemental mercury is held constant and the flux is a function only of solubility and windspeed, the flux is greatest in the tropics and decreases at high latitudes, with a small seasonal cycle. However, when the oceanic concentration of elemental mercury

varies as a function of mercury production rate and mixed layer depth, the maximum evasion flux shifts poleward and peaks in the spring hemisphere. Future work will include coupling of wet deposition of atmospheric Hg(II) to the evasion flux. We will validate our different formulations of air-sea exchange by comparisons to flux observations and existing atmospheric Hg<sup>0</sup> observations. We will also examine the potential role of rapid oxidation of Hg<sup>0</sup> in the marine boundary layer in the export of ocean emissions to the global atmosphere.

## Acknowledgements

This work was supported by funding from the National Science Foundation (NSF0238520). The GEOS-CHEM model is managed by the Atmospheric Chemistry Modeling group at Harvard University with support from the NASA Atmospheric Chemistry Modeling and Analysis Program.

## REFERENCES

- BERGAN, T., GALLARDO, L., AND RODHE, H. (1999): Mercury in the global troposphere: a three-dimensional model study; *Atmospheric Environment*, Vol. 33, pp. 1575-1585.
- BAY, I., JACOB, D. J., YANTOSCA, R. M., LOGAN, J. A., FIELD, B. D., FIORE, A. M., LI, Q., LIU, H. Y., MICKLEY, L. J. AND SCHULTZ, M. G. (2001): Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation; *J. Geophys. Res.*, Vol. 106, No. D19, pp. 23,073-23,095.
- LAURIER, F. J. G., MASON, R. P. AND WHALIN, L. (2003): Reactive gaseous mercury formation in the North Pacific Ocean's marine boundary layer: a potential role for halogen chemistry; *J. Geophys. Res.*, Vol. 108, No. D17, 4529, doi: 10.1029/2003JD003625.
- MASON, R. P. AND FITZGERALD, W. F. (1995): Sources, sinks, and biogeochemical cycling of mercury in the ocean; In *Global and Regional Mercury Cycles: Sources, Fluxes, and Mass Balances* (Ed. by BAEYENS, W., EBINGHAUS, R. AND VASILIEV, O.), pp. 249-272.
- MASON, R. P. AND SHEU, G.-R. (2002): Role of the ocean in the global mercury cycle; *Global Biogeochemical Cycles*, Vol. 16, No. 4, 1093, doi:10.1029/2001GB001440.

# Distribution of Mercury in Surface Dust and Topsoil in Slovenian Rural and Urban Areas

ROBERT ŠAJN

Geological survey of Slovenia, Dimičeva 14, 1000 Ljubljana, Slovenia,  
E-mail: robert.sajn@geo-zs.si

**Abstract:** The aim of this study was to establish contents and distribution of mercury in surface dust in Slovenia, and to define them according to geology and anthropogenic influence. Sampling locations in the rural area of Slovenia were set within settlements with less than 2000 inhabitants and without known pollution, and in six largest towns in Slovenia. The distribution of mercury in all used materials shows a strong Hg anomaly in the south-western part of Slovenia. The Hg distribution pattern is the result of the impacts of the Hg ore deposit, mine and mercury smelter in Idrija. The use of Hg rich blasting material used in the WW I had also contributed to the heightened contents of Hg, especially in the Soča Valley. The highest contents of Hg in sampling materials collected in town centres were determined in the samples from the Koper area. The causes for those high concentrations were Hg rich sediments brought to the Bay of Trieste by the Soča River. High Hg contents in the area of Jesenice show the impact of metallurgic industry.

**Key words:** mercury, pollution, dwelling dust, soil, Slovenia

## INTRODUCTION

Attic dust is a substance that is formed mostly by sedimentation of small particles onto exposed surfaces. Its formation is influenced by numerous factors, such as concentration of particles in the air, precipitations and the processes of condensation, in urban environments also weathering of building materials, soil and street dust and mostly human activities. According to FERGUSSON<sup>[4]</sup> 40 to 50 % is contributed by weathering of soils, 3-5 % by fossil fuels combustion, and 10-15 % by transport emissions. The remaining part is contributed by other less important sources.

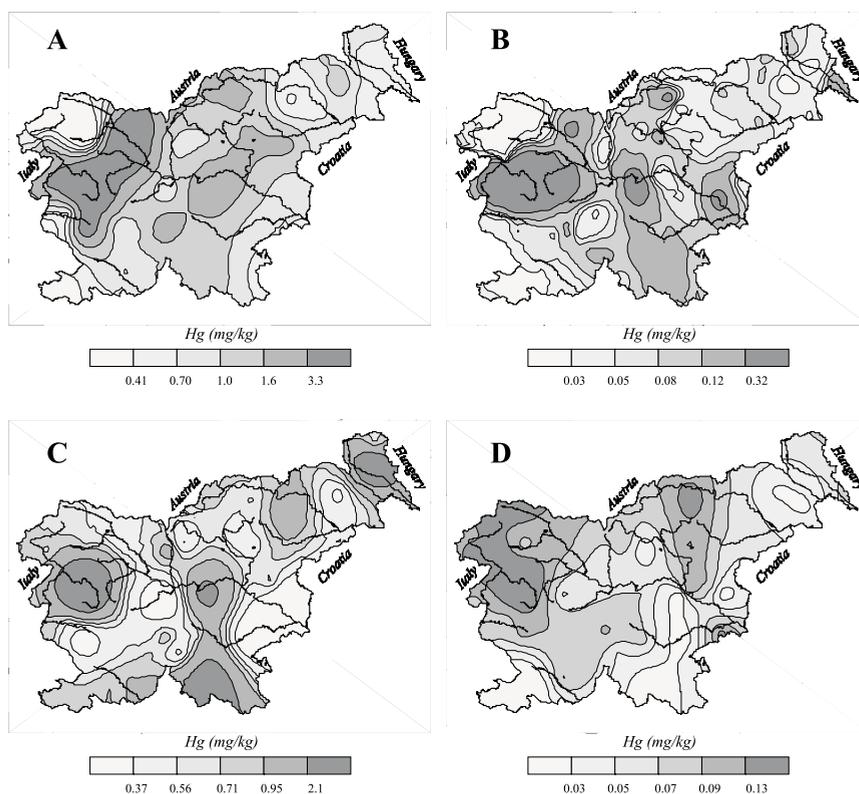
Surface dust can be divided into street dust, which is dust deposited in the open air, and dwelling dust (household and attic dust). Street dust is a typical product of urban environment. Its composition changes as to climatic conditions and time. Dust that can be found exclusively in rooms in which people actually spend their time is called household dust. The composition of that type of dust depends strongly on habits and types of activity of the inhabitants<sup>[5]</sup>. Attic dust represents dust deposited in abandoned attics, so that influence of inhabitants is minimized. Attic dust originates predominantly from external sources and less from household activities<sup>[9, 10]</sup>.

## RESULTS AND DISCUSSION

Sampling locations in the rural area of Slovenia were set within settlements with less than 2000 inhabitants and without known industry or pollution, following the scheme developed by PIRC<sup>[7]</sup>, and in six largest towns in Slovenia: Celje, Jesenice, Koper, Ljubljana, Maribor and Novo Mesto. 269 samples of street, household, attic dust and topsoil (0-5 cm) were collected<sup>[9, 10]</sup>.

Soil was sampled from the surface to the depth of 5 cm; the possible organic horizon was excluded. Within towns, we sampled urban soil such as soil in the gardens and on the grass verges. We collected the sample of

street dust by sweeping dips in pavements and along curbs. The sample was a composite of about 20 subsamples. The sample of household dust was a composite of the contents of sacks from vacuum cleaners, which were used exclusively in households. The attic dust samples were brushed from wooden constructions that were not in immediate contact with roof tiles or floors. Buildings as old as possible were selected for sampling locations<sup>[9, 10]</sup>. All samples were air-dried. A fraction smaller than 0.125 mm was prepared for the chemical analyses by sieving. Soil samples were gently crushed, then fraction smaller than 2 mm was pulverised. Hg was determined with CV-AAS after aqua regia digestion.



**Figure 1.** Areal distribution of mercury in attic dust<sup>[10]</sup> (A), household dust<sup>[9]</sup> (B), overbank sediment<sup>[9]</sup> (C) and topsoil<sup>[10]</sup> (D) in Slovenia

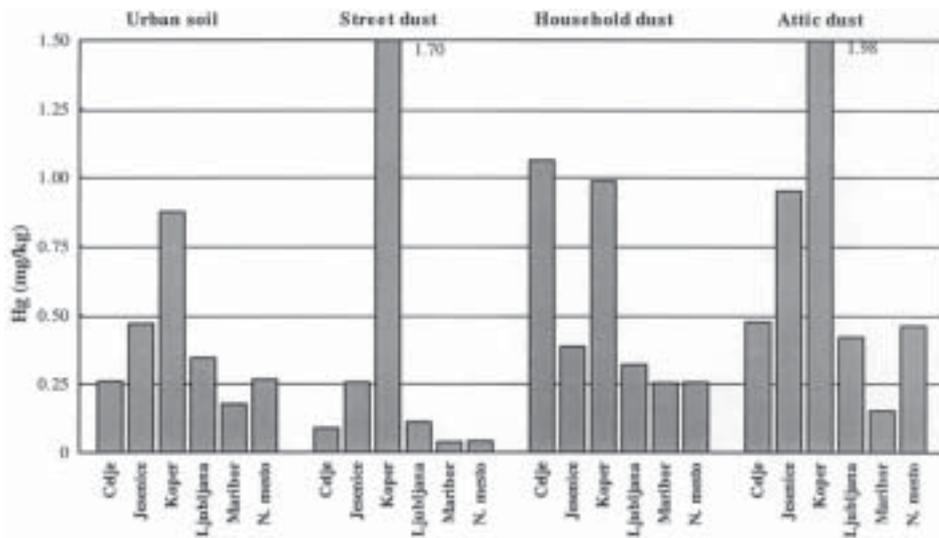


Figure 2. Distribution of mercury in sampling materials of Slovenian towns<sup>[9]</sup>

According to BOWEN<sup>[2]</sup>, a clarke of Hg distribution in unpolluted soils is 0.06 mg/kg and oscillates between 0.01 and 0.05 mg/kg. In the Slovenian countryside, the estimated median of the contents of Hg in soils is 0.07 mg/kg. The samples of household (0.69 mg/kg) and attic dust (1.03 mg/kg) showed the highest medians. The samples collected in town centres showed a median of 0.44 mg/kg for household and 0.46 mg/kg for attic dust. It is interesting that the estimated medians in the centres of towns are distinctively lower than the estimated averages for Slovenia.

The distributions of Hg in attic and household dust of the Slovenian countryside agree very well with one another. The same can be determined if they are compared with the distributions of Hg in natural sampling materials such soils<sup>[10]</sup> and overbank sediment<sup>[1]</sup>. Samples of all four materials show a strong Hg anomaly in the south-western part of

Slovenia (Fig. 1). The Hg distribution pattern is the result of the impacts of the Hg ore deposit, mine and mercury smelter in Idrija<sup>[6]</sup>. A possible source of Hg can also be natural evaporation from rocks. That source, however, is of secondary importance. The use of Hg rich blasting material used in the WW I had also contributed to the heightened contents of Hg, especially in the Soča Valley<sup>[8]</sup>.

The highest contents of Hg in sampling materials collected in town centres were determined in the samples from the Koper area (Fig. 2). The causes for those high concentrations were Hg rich sediments brought to the Bay of Trieste by the Soča River<sup>[3]</sup>. High contents of Hg were also determined in the soil and attic dust samples collected in Ljubljana<sup>[11]</sup>. The mechanisms of Hg enrichment of the banks of the Ljubljanica River are hitherto unclear. High Hg contents in the area of Jesenice show the impact of metallurgic industry<sup>[12]</sup>.

## CONCLUSIONS

The results of our study show a strong resemblance between the distribution of Hg in household and attic dust and natural sampling materials, such as soil and overbank sediments, with the average content of Hg in attic dust being considerably higher. Contrary to our expectation, the Hg content in surface dust was much higher in the Slovenian countryside than in town centres.

The only exception was the town of Koper, where relatively high values were found in all sampling materials. An important outcome of our study is also the confirmation of surface dust, especially attic dust, to be a very good and sensitive sampling material for the identification of Hg pollution. Attic dust together with other sampling materials, especially soils, ensures distinctive separation between anthropogenic and natural sources of Hg in the environment

## REFERENCES

- [1] BIDOVEC, M., ŠAJN, R. AND GOSAR, M. (1998): The use of recent overbank sediments in geochemical mapping of Slovenia; *Geologija*, Vol. 41, pp. 275-317.
- [2] BOWEN, H. J. (1979): *Environmental chemistry of the elements*; Academic Press, 318 p., London.
- [3] COVELLI, F., FAGANELI, J., HORVAT, M. AND BRAMBATI, A. (2001): Mercury contamination of coastal sediments as the result of long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic sea; *Applied geochemistry*, Vol. 16, No. 4, pp. 541-558.
- [4] FERGUSSON, J. E. (1992): *Dust in the environment, elemental composition and sources*; The science of global change, the impact of human activities on the environment. Portland State University, 116-133 p., Washington, D.C.
- [5] FERGUSSON, J. E. AND KIM, N. D. (1991): Trace elements in street and house dusts: Sources and speciation; *The science of the total environment*, Vol. 100, pp. 125-150.
- [6] GOSAR, M. AND ŠAJN, R. (2001): Mercury in soil and attic dust as a reflection of Idrija mining and mineralization (Slovenia); *Geologija*, Vol. 44, pp. 137-159.
- [7] PIRC, S. (1993): *Regional geochemical surveys of carbonate rocks; final report*; USG Project Number: JF 881-0, Report, Ljubljana: University of Ljubljana 1993; 30 p.
- [8] PIRC, S. AND BUDKOVIČ, T. (1997): Remains of world war I geochemical Pollution in the landscape; *Environmental xenobiotics*, pp. 375-418, Rickmansworth.
- [9] ŠAJN, R. (1999): *Geochemical properties of urban sediments on the territory of Slovenia*; Ljubljana: Geological survey of Slovenia, 1999, 136 p.
- [10] ŠAJN, R. (2003): Distribution of chemical elements in attic dust and soil as reflection of lithology and anthropogenic influence in Slovenia; *Journal de Physique*, Vol. 107, pp. 1173-1176.
- [11] ŠAJN, R., BIDOVEC, M., ANDJELOV, M., PIRC, S. AND GOSAR, M. (1998): *Geochemical atlas of Ljubljana and environs*; Ljubljana: Geological survey of Slovenia, 1998, 34 p.
- [12] ŠAJN, R., BIDOVEC, M., GOSAR, M. AND PIRC S. (1998): Geochemical soil survey at Jesenice area, Slovenia; *Geologija*, Vol. 41, pp. 319-338.

## Aircraft Measurements of Atmospheric Mercury over the Antarctic Shelf Ice and the Atka Bay

CHRISTIAN TEMME & RALF EBINGHAUS

Institute for Coastal Research, GKSS Research Centre, Max-Planck-Str. 1, D-21502 Geesthacht, Germany; E-mail: christian.temme@gkss.de

**Abstract:** The concentration of atmospheric mercury was measured on 29<sup>th</sup> of January 2001, during a level flight in the vicinity of Neumayer station, Antarctica. GEM concentrations at 8 different flight levels were highly comparable with GEM concentrations at ground-level, obtained with an independent instrument. The vertical distribution of atmospheric mercury was homogeneous from ground-level to the maximum altitude of about 4000 meter a.s.l. at the prevailing weather conditions during Antarctic summer without any significant inversion layer in the lower troposphere.

**Key words:** Atmospheric mercury, Antarctica, Vertical profile, Aircraft measurements

### INTRODUCTION

Unlike other heavy metals that are associated with atmospheric aerosols, mercury exists in ambient air predominantly in the gaseous form ( $\text{Hg}^0$ ) which is estimated to have a mean global tropospheric residence time of 1 year, making it subject to long range atmospheric transport. Because of its toxicity and high tendency to bioaccumulate in the food chain, mercury is a pollutant of global concern.

The background concentration of Gaseous Elemental Mercury (GEM) in the lower troposphere of the northern hemisphere is generally around  $1.9 \text{ ng m}^{-3}$  and  $1.2 \text{ ng m}^{-3}$  in the southern hemisphere respectively (SLEMR ET AL., 2003; TEMME ET AL., 2003).

Since almost all our knowledge is derived from ground-based measurements the vertical distribution of mercury in the troposphere

is not sufficiently known. One of the rather few studies in this field was carried out by GKSS Research Centre in cooperation with the Fraunhofer-Institute for Atmospheric Environmental Research in 1996 over southern and eastern Germany, giving experimental evidence for a homogeneous vertical distribution between 400 and 4000 meter a.s.l. (EBINGHAUS AND SLEMR, 2000). Aircraft measurements of atmospheric mercury in Antarctica are not known by now.

Aircraft measurements were carried out at the German Antarctic research station Neumayer ( $70^{\circ}39'S$ ,  $8^{\circ}15'W$ ) during Australian summer 2000/01 with an automated mercury monitor TEKRAM 2537A, based on atomic fluorescence detection (AFS) and operated with a time resolution of 5 min. The altitude of the station is about 40 meter a.s.l.. Measurements were performed with an aircraft Dornier 228 at 8 different altitudes in 8 consecutive legs. A PTFE-lined stainless-



**Figure 1.** Ekströmsisen shelf ice around Neumayer station (NM) and the path of the flight undertaken on 29<sup>th</sup> of January 2001.

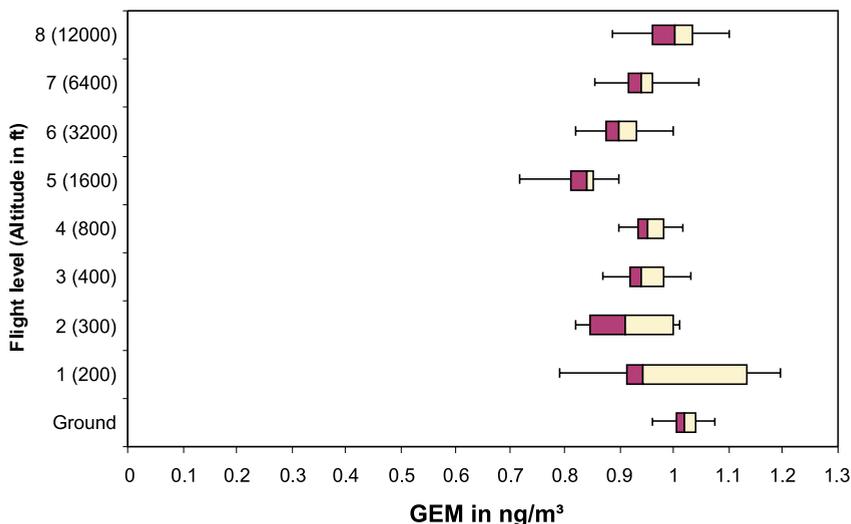
steel tubing was used as a sampling inlet. Before ascending to the next higher level, the aircraft remained on isobaric level for about 100 km at a ground speed of approximately 250 km/h (Figure 1). Therefore, horizontal sampling at one level includes up to 5 GEM values.

The results from the flight over the Ekströmsisen shelf ice and the Atka Bay should give a better understanding of the vertical distribution of mercury during Antarctic summer in order to explain the diurnal variabilities of GEM observed in late January and February 2000 at Neumayer sta-

tion (EBINGHAUS ET AL., 2002). The aircraft measurements were accompanied by simultaneous ground-based measurements of GEM concentrations with a second TEKTRAN 2537A.

## RESULTS AND DISCUSSION

The analytical instruments were operated at ambient pressure which changes with the flight altitude. Detailed laboratory studies were carried out in order to obtain information about the pressure dependence of the TEKTRAN analyser. An almost linear rela-



**Figure 2.** Box and whisker plot of GEM concentrations at different flight levels during the measurement flight at Neumayer station. The boxes enclose 50% of data (interquartile range) with the median displayed as a line. The horizontal lines extending outside the boxes, marks the minimum and maximum values of the flight level.

tion between the AFS detector response and the ambient pressure was observed over the entire pressure range with a decrease of about 0.1 %/mbar. The linear equation of the regression was used for the correction of the signals obtained during the flight. All concentrations reported here are given in ng/m<sup>l</sup> (STP) units, where STP means standard temperature of 0 °C and standard pressure of 1013 mbar.

The synoptic weather situation on the 29<sup>th</sup> of January 2001 was dominated by clear sky and cold temperatures (-5 °C at ground-level). The radiosounding from the Alfred Wegener Institute during midday showed no strong inversion up to 4000 meter a.s.l. and therefore a well mixed boundary layer during the flight.

Figure 2 shows the vertical distribution of GEM during the measurement flight with POLAR 4 carried out on the 29<sup>th</sup> of January 2001. It reveals a very homogenous distribution of GEM at different flight levels. A robust statistic with median instead of the mean was used with a number of 4 to 9 data points used for one level. The median GEM concentrations between 80 and 4000 meter a.s.l. are in the range of 0.85 and 1.01 ng/m<sup>l</sup> respectively with lowest concentrations at 1600 meter a.s.l.. However, no significant difference between the GEM-concentrations at different altitudes and the independent measurements at ground-level can be detected.

The strong variability in the GEM concentrations at flight level 1 may be due to the influence of the aircraft emissions during take off and landing.

## CONCLUSIONS

Presented aircraft measurements of atmospheric mercury were the first carried out in Antarctica. We verified the pressure dependency of the TEKRAN analyser and compared the results from the flight with the GEM level obtained with a second ground-based instrument. For typical meteorological conditions of Antarctic summer, the GEM concentrations at altitudes up to 4000 meter a.s.l. exhibited no significant gradient or pattern compared to the ground-level concentrations. Additional flights at different weather conditions and at different locations can help to

better understand the vertical distribution of atmospheric mercury and the dynamic processes leading to concentration gradients in the boundary layer of the troposphere.

## Acknowledgements

The authors thank the Alfred Wegener Institute for providing the aircraft POLAR 4 for the measurement flight at Neumayer station. We also thank Aerodata Flugmesstechnik GmbH for the support with the technical equipment. Last but not least we would like to thank the DLR crew and especially the captains, Andreas Knüppel and Ralf Böhler.

## REFERENCES

- EBINGHAUS, R., KOCK, H. H., TEMME, C., EINAX, J. W., LOEWE, A. G., RICHTER, A., BURROWS, J. P. & SCHROEDER, W. H. (2002): Antarctic springtime depletion of atmospheric mercury; *Environmental Science and Technology*, Vol. 36, pp. 1238-1244.
- EBINGHAUS, R. & SLEMR, F. (2000): Aircraft measurements of atmospheric mercury over southern and eastern Germany; *Atmospheric Environment*, Vol. 34, pp.895-903.
- SLEMR, F., BRUNKE, E.-G., EBINGHAUS, R., TEMME, C., MUNTHE, J., WÄNGBERG, I., SCHROEDER, W. H., STEFFEN, A. & BERG, T. (2003): Worldwide trend of atmospheric mercury since 1977; *Geophysical Research Letters*, Vol. 30, No.10, pp.1516-1519.
- TEMME, C., SLEMR, F., EBINGHAUS, R. & EINAX, J. W. (2003): Distribution of mercury over the Atlantic Ocean in 1996 and 1999-2001; *Atmospheric Environment*, Vol. 37, pp. 1889-1897.

# Modeling of Mercury Intercontinental Atmospheric Transport in the Northern Hemisphere

OLEG TRAVNIKOV

Meteorological Synthesizing Centre – East of EMEP, Arhitektor Vlasov 51, 117393 Moscow, Russia; E-mail: oleg.travnikov@msceast.org

**Abstract:** Dispersion of mercury in the atmosphere of the Northern Hemisphere is studied by means of atmospheric modelling. Mercury concentration in the ambient air and deposition levels are investigated as well as the intercontinental transport of mercury is assessed. It is demonstrated that contribution of external anthropogenic and natural sources to mercury deposition to different continents varies from 30 % to 70 % of total value. Besides, about half the mercury deposition to such a remote region as the Arctic is due to the transport from anthropogenic emission sources. Thus, it is concluded that the intercontinental transport plays significant role in atmospheric mercury pollution of the environment.

**Key words:** Atmospheric modeling, mercury depositions, intercontinental transport

## INTRODUCTION

Global character of mercury dispersion in the atmosphere makes possible transport of the pollutant between continents and impact of anthropogenic emission sources on vulnerable ecosystems of remote regions. Because of restricted abilities of monitoring networks and field measurements to cover significant areas numerical modeling becomes an essential instrument for assessing pathways of mercury dispersion in the atmosphere. A hemispheric model of mercury airborne transport and deposition (MSCE-Hg-Hem) was used for assessment of mercury contamination levels in the Northern Hemisphere and, in particular, for evaluation of role of the intercontinental transport in regional pollution. Depositions of mercury to the continents of the Northern Hemisphere from anthropogenic and natural emission sources were analysed.

## MODELING APPROACH

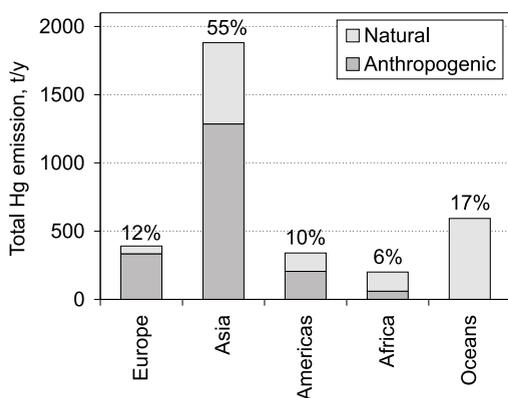
The MSCE-Hg-Hem is a three-dimensional chemical transport model of Eulerian type. The model domain covers the whole Northern Hemisphere with resolution  $2.5^{\circ} \times 2.5^{\circ}$ . The terrain-following pressure-based vertical coordinate consists of eight irregular layers up to the lower stratosphere. The model considers mercury emissions from anthropogenic and natural sources, transport in the atmosphere, chemical transformations both in gaseous and aqueous phases, and deposition to the ground. Physical and chemical transformations include dissolution in cloud droplets, gas-phase and aqueous-phase oxidation by ozone and chlorine, aqueous-phase reduction of mercury, formation of chloride complexes, and adsorption by soot particles in cloud water. Simplified description of the phenomenon of mercury depletion events (MDE) in the Arctic is also incorporated.

Detailed description of the model in use is published by TRAVNIKOV AND RYABOSHAPKO (2002).

Anthropogenic emission of mercury in the Northern Hemisphere was evaluated basing on the global emission inventory for 1995 published by PACYNA ET AL. (2003). According to these data, anthropogenic emission of mercury in the Northern Hemisphere is about 1900 t/y.

Available data on the natural emission of mercury are rather uncertain. To take into account natural emission of mercury we used global estimates by LAMBORG ET AL. (2002). Spatial distribution of natural emission fluxes (including re-emission) was obtained by scattering the total value throughout the globe depending on mercury content in soils and the surface temperature. The total natural emission and re-emission of mercury in the Northern Hemisphere is estimated as much as 1600 t/y.

Contributions of particular regions to the total (anthropogenic and natural) emission of mercury in the Northern Hemisphere are



**Figure 1.** Contribution of different regions to the total annual mercury emission in the Northern Hemisphere

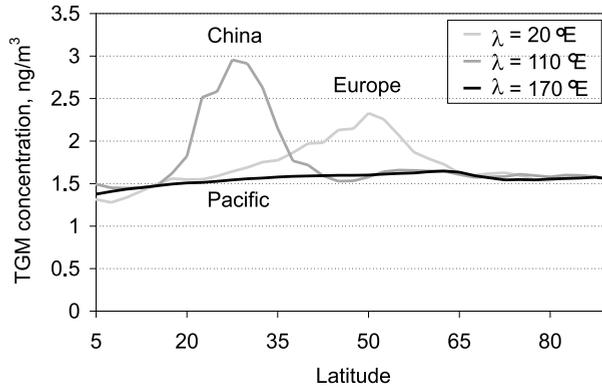
shown in Fig. 1. The predominant contributors are Asian sources (55 % of the total emission). Besides, European (11 %) and American (10 %) sources make the significant inputs as well as mercury evasion from the ocean surface (17 %).

## RESULTS AND DISCUSSION

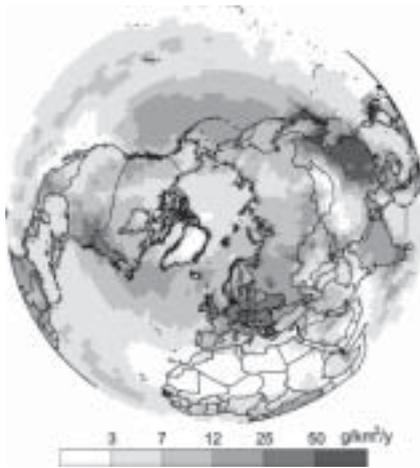
Transport of mercury in the atmosphere of the Northern Hemisphere has been assessed for 1996. Modeling results show that elevated mercury concentrations in the ambient air are characteristics of regions with high emissions such as Europe, South-eastern Asia and eastern part of North America. Figure 2 shows total gaseous mercury concentration profiles coming along meridians through two the most contaminated and one background region. As one can see from the figure even in the remote parts of the Pacific Ocean, as well as in the Arctic, mercury concentration in the ambient air does not fall below 1.5 ng/m<sup>3</sup>. Spatial distribution of total annual mercury deposition (wet and dry) in the Northern Hemisphere is illustrated in Fig. 3.

High deposition fluxes were obtained for contaminated regions but also for some background regions characterized by large precipitation amount (North Atlantic and Pacific). This can be explained by wide dispersion of atmospheric mercury over the globe and prevailing role of wet scavenging in mercury removal from the atmosphere.

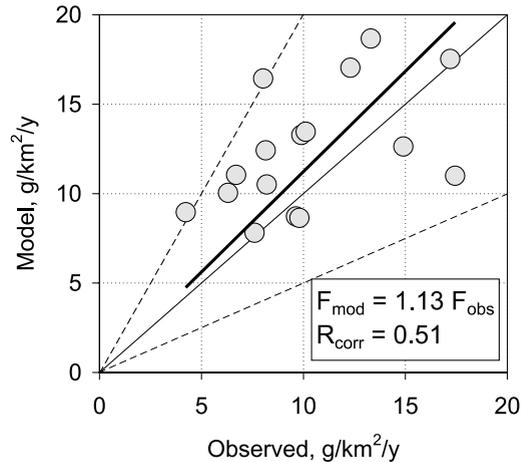
Comparison of modelled and measured values of mercury wet deposition is presented in Figure 4. Measurements from European (EMEP network) and North American (NADP/MDN network) monitoring sites was



**Figure 2.** Profiles of total gaseous mercury concentration in the ambient air of the Northern Hemisphere



**Figure 3.** Spatial distribution of total annual mercury deposition (wet and dry) in the Northern Hemisphere



**Figure 4.** Calculated versus measured values of annual wet deposition of mercury. Dashed line shows the two-fold difference

used in the comparison. As seen the mean ratio between measured and calculated values is close to unity; the maximum difference between them does not exceed a factor of two.

The role of the intercontinental atmospheric transport of mercury in pollution of different regions of the Northern Hemisphere is illustrated in Fig. 5. As one can see North America is most significantly subjected to influence

of emission sources from other continents: up to 67 % of total depositions to the continent are from external anthropogenic and natural sources. Among them about 24 % are from Asian sources and 14 % from European ones. In contrast, contribution of all external sources for Asia does not exceed 32 %. As to Europe, about 40 % of annual mercury depositions are from external sources including 15 % from Asia and 5 % from North America. The Arctic has no significant sources of mercury emis-

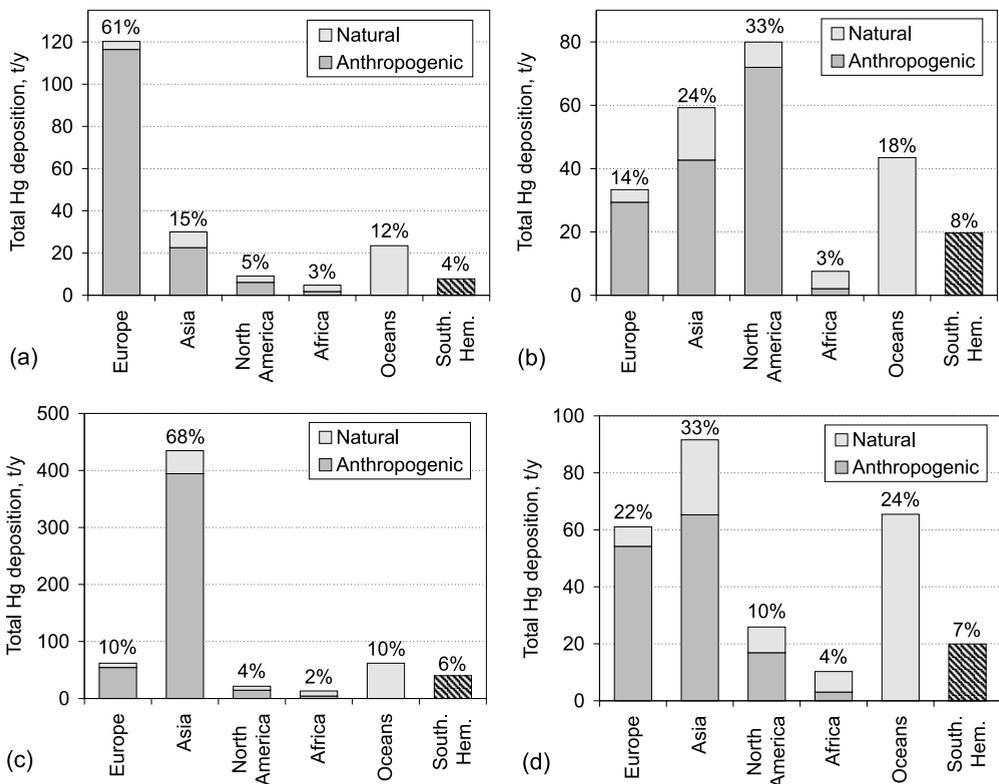
sion. However, about half the mercury deposition to the Arctic is due to the atmospheric transport from anthropogenic emission sources, of which the greatest contribution is made by Asian (33 %) and European sources (22 %).

The phenomenon of Mercury Depletion Events (MDE) accompanied by the active deposition and accumulation of mercury in snow plays a special role in the mercury pollution of the Arctic ecosystems. The effect of MDE on the Arctic pollution with mercury was estimated using simplified phenomenological approach described by TRAVNIKOV AND RYABOSHAPKO (2002). According to the

estimates MDE contributes additionally about 20 % of annual mercury deposition to the Arctic as a whole. However, its contribution can exceed 50 % in coastal areas (Queen Elisabeth Islands, coastal areas of the White, Kara, and Laptev Seas etc.).

## CONCLUSIONS

The atmospheric transport and deposition of mercury in the Northern Hemisphere has been assessed by means of atmospheric modelling. In particular, the role of the intercontinental transport in regional pollution has been evaluated. It was demonstrated that



**Figure 5.** Contribution of different regions to the total annual mercury deposition to Europe (a), North America (b), Asia (c) and the Arctic (d).

contribution of external anthropogenic and natural sources to mercury deposition to different continents varies from 30 % to 70 % of total value. Besides, about half the mercury deposition to such a remote region as

the Arctic is due to the transport from anthropogenic emission sources. Thus, it could be concluded that the intercontinental transport plays significant role in atmospheric mercury pollution of the environment.

## REFERENCES

- LAMBORG, C. H., FITZGERALD, W. F., O'DONNELL, J., TORGERSEN, T. (2002): A non-steady-state compartmental model of global-scale mercury biogeochemistry with interhemispheric atmospheric gradients; *Geochimica et Cosmochimica Acta*, Vol. 66, pp. 1105-1118.
- PACZYNA, J. M., PACZYNA, E. G., STEENHUISEN, F., WILSON, S. (2003): Mapping 1995 global anthropogenic emissions of mercury; *Atmospheric Environment*, Vol. 37, Supplement No. 1, pp. 109-117.
- TRAVNIKOV, O., RYABOSHAPKO, A. (2002): *Modelling of mercury hemispheric transport and depositions*; EMEP/MSC-E Technical Report 6/2002, Meteorological Synthesizing Centre - East, Moscow, Russia.

# Modelling the Atmospheric Emission, Dispersion, Transformation and Deposition of Mercury on a Mediterranean Scale

GIUSEPPE A. TRUNFIO, IAN M. HEDGECK, FRANCESCA SPROVIERI AND NICOLA PIRRONE

CNR - Istituto sull'Inquinamento Atmosferico, 87036 Rende, Italy

E-mail: a.trunfio@cs.ia.cnr.it

**Abstract:** Chemistry, photolysis, emissions and deposition models have been linked to a prognostic atmospheric meteorological / dispersion model. The result is an integrated modelling system potentially capable of long-term simulations of regional deposition patterns, and emission reduction scenario analysis. The first results are consistent with measured  $\text{Hg}^0_{(g)}$  concentrations in the Mediterranean and with box modelling studies of the atmospheric chemistry of Hg.

**Key words:** mercury, modelling, regional, Mediterranean

## INTRODUCTION

The cycling of mercury in the Mediterranean region has been studied experimentally during two European Community funded projects (PIRRONE ET AL., 2003), one of which is still ongoing and includes not only coastal but shipboard measurement campaigns, continuing the work first performed during the Med-Oceanor campaign in the summer of 2000 (SPROVIERI ET AL., 2003). The experimental results show that there are consistent and significant concentrations of  $\text{Hg}^{\text{II}}_{(g)}$  over the Mediterranean Sea, as well as an important contribution to  $\text{Hg}^0$  from marine emissions. Box modelling studies of the photochemistry of the Mediterranean Marine Boundary Layer (MBL) indicate that in situ production of  $\text{Hg}^{\text{II}}$  is a major contributor to the total  $\text{Hg}^{\text{II}}_{(g)}$  (HEDGECK ET AL., 2003). The Mediterranean appears to differ from other marine environments in that the major contribution to  $\text{Hg}^0$  oxidation is made by OH oxidation rather than the reaction with the

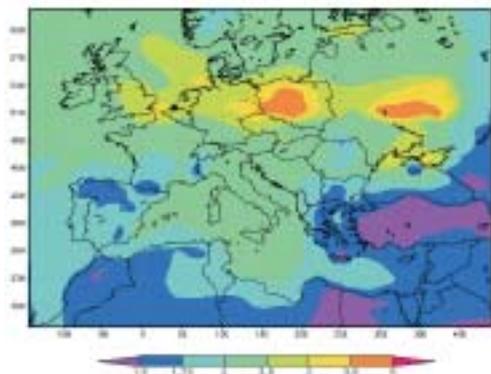
Br atom (HEDGECK ET AL., 2004) which is currently the most probable reaction behind the mercury depletion events observed in the Arctic and also the elevated RGM concentrations observed in more remote marine environments, specifically the Atlantic near Bermuda (MASON ET AL., 2001) and the North Pacific between Japan and Hawaii (LAURIER ET AL., 2003). The Regional Atmospheric Modelling System (RAMS) (ATMET, 2004) has been used in conjunction with an up to date Hg emission inventory, which provides annually averaged emissions from point and area sources. The emission inventory also provides information on Hg speciation (i.e., the proportions of  $\text{Hg}^0$ ,  $\text{Hg}^{\text{II}}$  and Hg associated with particulate material depending on emission source category). The Hg atmospheric chemistry model currently used in this initial version of the integrated modelling system has been designed specifically for the purpose and includes both gaseous and aqueous phase chemistry relevant to Hg and its oxidation and deposition. Oxidation

is fundamental to Hg deposition (both dry and wet) as RGM species are much less volatile and much more soluble than  $\text{Hg}^0$ . Given the importance of Hg oxidation by OH, the production of O ( $^1\text{D}$ ) needs to be well described as does the  $\text{O}_3$  concentration. Therefore,  $\text{O}_3$  fields from the European Centre for Medium range Weather Forecasting (ECMWF) have been included in the input to RAMS, and an on line photolysis rate constant calculation procedure is used. The program fast-j (WILD ET AL., 2000) has been linked to the meteorological model in order to provide photolysis rate constants which are a function of latitude, longitude, date, time of day, altitude and column optical depth, as described in more detail below. Model output will eventually include gas phase concentration fields of  $\text{Hg}^0$  and  $\text{Hg}^{\text{II}}$ , concentration of  $\text{Hg}^{\text{II}}$  in rain water and deposition rates of  $\text{Hg}^{\text{II}}$  to terrestrial receptors as a function of land use type, and of course rates of deposition to the Mediterranean Sea. The initial trial runs presented here are however more concerned with the direct comparison of concentration fields and the models response to meteorological conditions in order to validate the combination of models. The initialization of RAMS has been adapted to include 6 hourly  $\text{O}_3$  concentration fields from ECMWF. In order to reduce the calculation time required by the model, operator splitting between the meteorological model and the chemistry model has been employed. RAMS typically uses 90s time steps for the grid resolution chosen for these simulations, but the chemistry model is called every 15 minutes. The chemistry model is run for each cell, whilst fast-j is called for each column, the altitude dependent photolysis rate constants being stored in a temporary array.  $\text{Hg}^{\text{II}}_{(\text{aq})}$  represents the sum of oxidised Hg

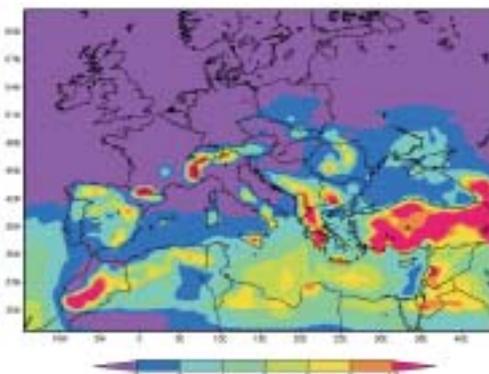
species in the aqueous phase, and in the absence of liquid water, for instance, after the evaporation of non-precipitating cloud droplets is transported as if it were  $\text{Hg}^{\text{P}}$ . However, unlike  $\text{Hg}^{\text{P}}$ , it is considered soluble so that should it once again be in the presence of liquid water it is assumed to be scavenged and returns to the aqueous phase. The non-Hg chemistry includes detailed HOx and SOx chemistry in both the gas and aqueous phases. More detailed NOx chemistry will be introduced following the inclusion of NOx emissions for the model region.

## RESULTS AND DISCUSSION

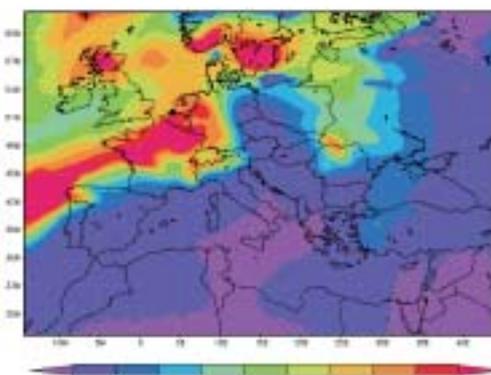
The model has been run from the 15<sup>th</sup> January 1999 until the 31<sup>st</sup> of March, the first four weeks are a spin-up period during which the results are still influenced by the initial conditions. The modelling region covers the Mediterranean and Europe as can be seen in the figures below. The modelling grid is made up of 130 ´ 125, 50 km ´ 50 km cells and 25 vertical levels. The ten week simulation took less than 24 hours on a 25 node Linux cluster. The figures below have been chosen to illustrate the interplay between meteorology, photochemistry, and the  $\text{Hg}^0_{(\text{g})}$  and  $\text{Hg}^{\text{II}}_{(\text{g})}$  concentration fields. Figures 1 and 2 show the  $\text{Hg}^0_{(\text{g})}$  and  $\text{Hg}^{\text{II}}_{(\text{g})}$  concentrations in the bottom model layer respectively whilst figure 3 shows the cloud cover fraction, and figure 4 the air temperature, also in the bottom model layer. All the figures refer to mid-day on the 8<sup>th</sup> of March. The correlation between  $\text{Hg}^{\text{II}}$  production and the factors that influence  $\text{O}_3$  and OH production can be seen.  $\text{O}_3$  production is favoured by high temperatures and  $\text{O}_3$  photolysis leading to OH production is clearly a function of cloud cover.



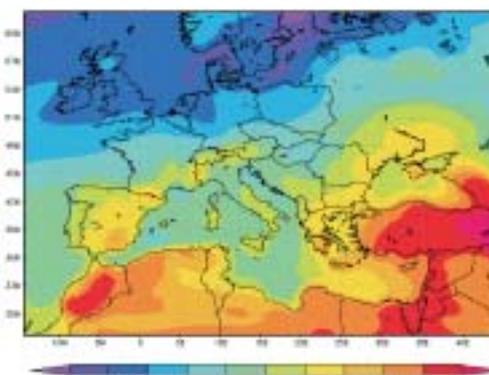
**Figure 1.** The modelled  $\text{Hg}^0_{(g)}$  concentration.



**Figure 2.** The modelled  $\text{Hg}^{\text{II}}_{(g)}$  concentration.



**Figure 3.** Cloud cover data from RAMS



**Figure 4** . Bottom layer temperature from RAMS

Figures 1 and 2 illustrate a phenomena which became evident during the MAMCS and MOE projects (PIRRONE ET AL., 2003, MUNTHE ET AL., 2003); that in spite of the higher  $\text{Hg}^0_{(g)}$  concentrations to be found in the north of Europe,  $\text{Hg}^{\text{II}}_{(g)}$  concentrations were found to be consistently higher in the Mediterranean region.

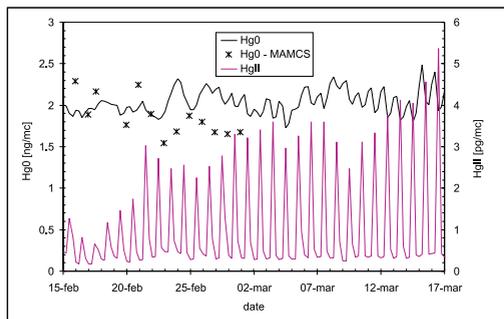
The model output can be compared to the daily average  $\text{Hg}^0_{(g)}$  data obtained at Fuscaldo (Calabria, Italy,  $39^\circ 25'N$ ,  $16^\circ 00'E$ ) during the 2<sup>nd</sup> MAMCS measurement campaign (15<sup>th</sup> Feb - 1<sup>st</sup> March, 1999), figure 5.

The results are certainly of the right order but over the campaign period the modelled  $\text{Hg}^0_{(g)}$  values are less variable than the measured val-

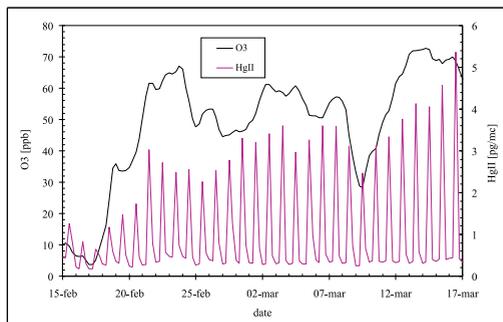
ues. Figure 6 shows the variation of  $\text{Hg}^{\text{II}}_{(g)}$  with the  $\text{O}_3$  concentration. The model as expected predicts greater  $\text{Hg}^{\text{II}}_{(g)}$  concentrations with higher  $\text{O}_3$ , the relationship is obviously not perfect because it is the photolysis of  $\text{O}_3$  and subsequent reaction with  $\text{H}_2\text{O}_{(g)}$ , which produces OH, so that  $\text{Hg}^{\text{II}}_{(g)}$  concentrations also depend on cloud cover and humidity.

## CONCLUSION

The various models required to model Hg chemistry on a regional scale have been linked and give results that are consistent with measurements and our understanding of the atmospheric chemistry of Hg. More



**Figure 5** . Modelled  $\text{Hg}^0$  (g) and  $\text{Hg}^{\text{II}}$  (g) and MAMCS data.



**Figure 6**. Modelled  $\text{Hg}^{\text{II}}$  (g) and ECMWF  $\text{O}_3$

tests are required to assess the importance of boundary and initial conditions for all the model components; fortunately there is a good amount of data now available for Europe and the Mediterranean to simplify.

## REFERENCES

- ATMET (2004): *Atmospheric Meteorological and Environmental Technologies*.
- HEDGECOCK, I. M., PIRRONE, N. (2004): Chasing Quick-silver: Modelling the atmospheric lifetime of in the marine boundary layer; *Env. Sci. Technol.*, Vol. 38, pp. 69-76.
- HEDGECOCK, I. M., TRUNFIO, G. A., SPROVIERI, F., PIRRONE, N., LAURIER F. J. G., MASON, R. P. (2004): Modelled Reactive Gaseous Mercury Concentrations in the Marine Boundary Layer: A Comparison with Measurements from the Pacific and the Mediterranean; Submitted to *Env. Sci. Technol.*
- HEDGECOCK, I. M., PIRRONE, N., SPROVIERI, F., PESENTI, E. (2003): Reactive gaseous mercury in the marine boundary layer: Modelling and experimental evidence of its formation in the Mediterranean region; *Atmos. Environ.*, Vol. 37, pp. 41-49.
- LAURIER, F. J. G., MASON, R. P., WHALIN, L., KATO, S. (2003): Reactive gaseous mercury formation in the North Pacific Ocean's marine boundary layer: A potential role of halogen chemistry; *J. Geophys. Res.*, Vol. 108(D17), p. 4529.
- MASON, R. P., LAWSON, N. M., SHEU, G.-R. (2001): Mercury in the Atlantic Ocean: factors controlling air-sea exchange of mercury and its distribution in the upperwaters; *Deep-Sea Res. II*, Vol. 48, pp. 2829-2853.
- MUNTHE, J., WÄNGBERG, I., IVERFELDT, L., LINDQVIST, O., STRÖMBERG, D., SOMMAR, J., GLRDFELDT, K., PETERSEN, G., EBINGHAUS, R., PRESTBO, E., LARJAVA, K., SIEMENS, V. (2003): Distribution of atmospheric mercury species in Northern Europe: final results from the MOE project; *Atmos. Environ.*, Vol. 37, S9-S20.
- PIRRONE, N., FERRARA, R., HEDGECOCK, I. M., KALLOS, G., MAMANE, Y., MUNTHE, J., PACYNA, J.M., PYTHAROULIS, I., SPROVIERI, F., VOUDOURI, A., WANGBERG, I. (2003): Dynamic Processes of Mercury Over the Mediterranean Region; *Atmos. Environ.* 37, S21-39.
- SPROVIERI, F., PIRRONE, N., GLRDFELDT K., SOMMAR, J. (2003): Mercury speciation in the marine boundary layer along a 6000 km cruise path around the Mediterranean Sea; *Atmos. Environ.*, Vol. 37, S63-71.
- WILD, O., X. ZHU AND M. J. PRATHER, FAST-J (2000): Accurate simulation of in- and below-cloud photolysis in global chemical models; *J. Atmos. Chem.* 37, pp. 245-282.

## Acknowledgements

This work is part of the MERCYMS <http://www.cs.iaa.cnr.it/MERCYMS/project.htm/>, funded by the European Commission (Contr. No. EVK3-2002-00070).

## Sensitivity of Mercury Atmospheric Deposition to Anthropogenic Emissions in the United States

KRISH VIJAYARAGHAVAN<sup>1</sup>, KRISTEN LOHMAN<sup>1</sup>, SHU-YUN CHEN<sup>1</sup>, PRAKASH KARAMCHANDANI<sup>1</sup>, CHRISTIAN SEIGNEUR<sup>1</sup>, ANNE SMITH<sup>2</sup>, JOHN JANSEN<sup>3</sup> AND LEONARD LEVIN<sup>4</sup>

<sup>1</sup>Atmospheric & Environmental Research, Inc., San Ramon, CA, USA; E-mail: krish@aer.com

<sup>2</sup>Charles River Associates, Inc., Washington, DC, USA

<sup>3</sup>Southern Company, Birmingham, AL, USA

<sup>4</sup>EPRI, Palo Alto, CA, USA

**Abstract:** A multi-scale modeling system is used to simulate the atmospheric fate and transport of atmospheric mercury over the globe and, in particular, its deposition over the eastern United States. Following satisfactory performance evaluation, the model is applied to simulate the effect of various emission control strategies for U.S. coal-fired power plants on mercury deposition in the eastern United States. Proposed NO<sub>x</sub> and SO<sub>2</sub> emission controls are shown to lead to co-benefits in terms of decreased mercury deposition due to concomitant mercury emission controls. A mercury Cap & Trade approach for further mercury emission controls is shown to be more effective than an approach based on maximum achievable control technology (MACT).

**Key words:** mercury deposition, power plants, emission control, United States, modeling

### INTRODUCTION

The atmospheric deposition of mercury to watersheds in the United States results from a combination of natural emissions, re-emissions of deposited mercury, anthropogenic emissions from other continents and other North American countries (i.e., Canada and Mexico), and emissions from the United States (SEIGNEUR ET AL., 2003, 2004a). It is, therefore, of interest to evaluate the relative effects that various emission control scenarios for U.S. anthropogenic sources may have on mercury deposition within the United States. We examine here three emission control scenarios that have been proposed by the U.S. Environmental Protection Agency (EPA) for coal-fired power plants.

### BASE MODEL SIMULATION

The multi-scale modeling system consists of a global model with a spatial resolution of about 1000 km, a nested continental model that covers North America with a 100 km spatial resolution and a nested regional model that covers the central and eastern United States with a 20 km resolution (SEIGNEUR ET AL., 2004a; VIJAYARAGHAVAN ET AL., 2004). It was applied using 1998 meteorology and 1998/1999 emissions. This modeling system provided satisfactory performance when compared to available data. For example, comparison with wet deposition data from the Mercury Deposition Network (MDN) showed a coefficient of determination of 0.55, an error of 26 % and a bias of 12 %.

A new base simulation was developed using projected 2004 emissions for power plants as a basis to compare various emission control scenarios. Coal-fired power plant emissions of mercury were estimated to amount to 42.8 Mg/yr for 2004. The simulated total (i.e., both wet and dry) deposition of divalent and particle-bound mercury over the eastern United States is presented in Figure 1. The western part of the domain shows deposition of less than 10 mg/m<sup>2</sup>-yr. Most of the domain has mercury deposition of less than 50 mg/m<sup>2</sup>-yr. The maximum deposition of 383 mg/m<sup>2</sup>-yr occurs in Maryland and is due primarily to a medical waste incinerator located in the southern part of Baltimore.

## EMISSION CONTROL SCENARIOS

EPA has proposed emission control regulations for U.S. coal-fired power plants. The corresponding emission scenarios were modeled in this study and are presented here for 2020. For each scenario, only coal-fired U.S. utility emissions of mercury were altered; emissions from all other sources were left unchanged from their base case rates.

The Interstate Air Quality Rule (IAQR) pertains to the control of SO<sub>2</sub> and NO<sub>x</sub> emissions through a Cap & Trade program. These emission controls will take place primarily via the installation of selective catalytic reduction (SCR) devices for NO<sub>x</sub> control and wet scrubbers for SO<sub>2</sub> control. Wet scrubbers have been shown to remove a large fraction of Hg(II) because of its high solubility. SCRs have been shown to lead to some oxidation of Hg(0) to Hg(II) under particular conditions of fuel chemistry and, when

placed upstream of a scrubber, will enhance Hg removal. Therefore, the IAQR scenario is estimated to lead to some co-benefits for mercury emission control that amount to a reduction of 13.1 Mg/yr by 2020.

Two alternative mercury emission control approaches have been considered by EPA. The Maximum Achievable Control Technology (MACT) approach would require emission control requirements based on power plant type and would amount to an additional reduction of coal-fired power plant emissions of mercury of 1.9 Mg/yr by 2020. The mercury “Cap & Trade” (C&T) approach would result in an additional reduction from IAQR for coal-fired power plant emissions of mercury of 16.0 Mg/yr by 2020 in order to meet a national cap of 13.6 Mg/yr (i.e., 15 short tons/yr). C&T, however, would allow the industry to distribute, via trading, those emission reductions among power plants in a cost-effective manner. (It was assumed here that C&T participation would be by all applicable units in all relevant U.S. states, with no “opt-out” being exercised by any state.)

Figures 2, 3 and 4 present the relative differences (%) in mercury total deposition between each emission control scenario (IAQR, MACT and C&T, respectively) and the 2004 base scenario. The IAQR scenario shows decreases in mercury deposition in most parts of the modeling domain and increases in some limited areas due to increased demand for electricity generation. However, the areas with increases are not typically areas of high mercury deposition in the base case (see Figure 1). The MACT scenario is similar to the IAQR scenario but with slightly greater decreases. Moreover, the MACT scenario has fewer areas where mercury deposition

increases from the base case. The C&T scenario shows the largest decreases occurring over a wider area in the eastern United States,

with isolated areas showing negligible increases in mercury deposition. Note that the largest decreases in all emission control sce-



**Figure 1.** Total annual deposition ( $\text{mg}/\text{m}^2\text{-yr}$ ) of atmospheric mercury in the eastern United States with projected 2004 emissions.



**Figure 2.** Relative difference (%) between the IAQR emission control scenario and the base simulation.



**Figure 3.** Relative difference (%) between the MACT emission control scenario and the base simulation.



**Figure 4.** Relative difference (%) between the C&T emission control scenario and the base simulation.

narios are likely to be overestimated because grid models tend to overestimate the local mercury deposition due to elevated point sources (SEIGNEUR ET AL., 2004b).

The MACT and C&T emission control scenarios considered here lead to decreases in mercury deposition in some areas that currently have high deposition fluxes. No new areas of high simulated mercury deposition (“hot spots”) are created under either of these scenarios.

## CONCLUSIONS

A multi-scale system that includes a global model and nested continental and regional models was applied to simulate the atmo-

spheric deposition of mercury to the eastern United States. Three emission control scenarios for U.S. coal-fired power plants were simulated. The IAQR scenario that pertains to SO<sub>2</sub> and NO<sub>x</sub> emission controls was shown to lead to co-benefits in terms of mercury deposition. Among the two approaches considered for mercury emission controls, the Cap & Trade scenario leads to greater overall decreases in mercury deposition than the MACT scenario. Neither of those emission control scenarios leads to new simulated areas or “hot spots” of mercury deposition.

## Acknowledgements

This work was supported by EPRI, Palo Alto, CA, USA under Contracts EP-P11144/C5579 and EP-P14738/C7238.

## REFERENCES

- LOHMAN, K., SEIGNEUR, C., LOHMAN, K., VIJAYARAGHAVAN, K. & SHIA, R.-L. (2003): Contributions of global and regional sources to mercury deposition in New York State; *Environ. Pollut.*, Vol. 123, pp. 365-373.
- SEIGNEUR, C., VIJAYARAGHAVAN, K., LOHMAN, K., KARAMCHANDANI, P. & SCOTT, C. (2004a): Global source attribution for mercury deposition in the United States; *Environ. Sci. Technol.*, Vol. 38, pp. 555-569.
- SEIGNEUR, C., LOHMAN, K., VIJAYARAGHAVAN, K., JANSEN, J. & LEVIN, L. (2004b): Comparison of grid-based and plume modeling to estimate the local impacts of large mercury point sources; *7<sup>th</sup> International Conference on Mercury as a Global Pollutant*, 27 June-2 July 2004, Ljubljana, Slovenia.
- VIJAYARAGHAVAN, K., SEIGNEUR, C., LOHMAN, K., KARAMCHANDANI, P., LEVIN, L. & JANSEN, J. (2004): Modeling the impact of mercury speciation in power plant plumes on mercury deposition over the eastern U.S.; *7<sup>th</sup> Electric Utilities Environmental Conference*, 19-22 January 2004, Tucson, Arizona, USA.

## Estimate of Mercury Emission from Different Sources to Atmosphere in Chongqing, China

DINGYONG WANG<sup>1</sup> & LEI HE<sup>1</sup>

<sup>1</sup>College of Resources and Environment, Southwest Agricultural University, Chongqing 400716, P. R. China, e-mail: wangdy@swau.cq.cn

**Abstract:** Mercury is emitted to the atmosphere by the anthropogenic and natural sources. The present study includes an inventory of anthropogenic mercury emissions and mercury fluxes from selected natural sources to the atmosphere for a typical acid deposition region, Chongqing, China in 2001. Anthropogenic emissions totaled approximately 8.12 t; more than 50 % of this total originated in coal combustion and 23.7 % of this total emission in the industrial process (include cement production, metal smelting and chemical industry). Natural emissions represented approximately 14.3 % of total emissions (1.36 t per annum). The total mercury emission to atmosphere in Chongqing in 2001 was 9.48 t.

**Key words:** acid deposition area, anthropogenic mercury emission, natural mercury emission

## Exchange Flux of Mercury on the Interface and its Source and Sink

QICHAO WANG

**Abstract:** The exchange flux of mercury in the Changchun City of China was estimated in this paper, according to the discharged flux of polluted source, wet/dry deposition flux, emitting flux on the surface of water and land, and the runoff flux of mercury. About 425.6 kg/a mercury was emitted by the combustion of coal in Changchun. Mercury emitted from the dust was 5.5 kg/a, and the dry and wet depositions of mercury were 11.72 kg/a and 23.09 kg/a individually. Mercury emitted from the surface of water and land was 9.46 kg/a. The runoff flux of mercury was 3.8 kg/a. All the city area was the source of mercury in the global and regional cycle of mercury. Components of the city ecology system had the characteristic of sink, for example mercury accumulated clearly in the waters, soil and plant. The trend of mercury pollution became more and more serious.

**Key words:** mercury, flux, interface exchange, Changchun

## Mercury Emission to Atmosphere from Geologically Enriched Area in Southwest Guizhou, China

SHAOFENG WANG<sup>1,2</sup>, XINBIN FENG<sup>1,\*</sup>, GUANGLE QIU<sup>1,2</sup>, SHUNLIN TANG<sup>1,2</sup>,  
YAMIN HOU<sup>1,2</sup>, TANGFU XIAO<sup>1,2</sup>

<sup>1</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, P.R. China

<sup>2</sup>Graduate School of the Chinese Academy Sciences, Beijing, 100039

\*Corresponding author; E-mail address: xinbin.feng@mail.gyig.ac.cn

**Abstract:** More and more attention are being paid to mercury natural enriched areas since these areas are huge atmospheric sources. Mercury emission fluxes from soil were measured in Lanmuchang Hg-Tl mine area, southwest Guizhou, China. The results showed that mercury exchange between soil and air in this area are greatly stronger than the background areas. Mercury concentration in soil is a dominate factor impacting mercury emission. Various environmental factors have strong impacts to mercury emission too.

**Key words:** mercury, Lanmuchang Hg mine, exchange fluxes, environmental factors

### INTRODUCTION

Geologically mercury enriched area has been thought as a huge atmospheric mercury source in a long time<sup>[1, 2]</sup>. There are three mercuriferous belts associated with plates tectonic boundries. Many big mercury mines locate in these mercury belts, such as Almadén, Spain, Mt. Amiata, Italy, Wanshan, China and so on. In the past several years, with the development of mercury fluxes measurement technology, considerable progress has been made in understanding mercury geochemistry in these mercury mines. Most studies showed that mercury emission from those mercury enriched area is greater than predicted. FERRARA ET AL. (1998) estimated the total mercury emission rate to atmosphere from Almadén in the range 600—1200g h<sup>-1</sup> by Lidar technique.

The province of Guizhou (N24°30'—29°13', E103°1'—109°30', 1100m above sea level, subtropical humid climate) in Southwestern China is a most important mercury product center over the world. There are 88100 tonnes of cinnabar deposits in Guizhou, which are approximately 70 % of total in China. Lanmuchang Hg-Tl mine (as shown in Fig. 1) located in southwest Guizhou, is a typical faults-controlled mineralized Hg-Tl deposits. Lanmuchang normal fault and Huangnjiang reverse fault controlled this mineralized belt. The regional karstic topography mainly includes peaks, karstic graves, valleys and so on. The hills are bare in Lanmuchang, and are covered by a little of shrubs and crop. The main minerals containing Hg, Tl, As are cinnabar, sulfides lorandite, realgar, orpiment, and arsenopyrite and pyrite. The maximum Hg grade



**Figure 1.** Sampling sites of Hg fluxes in Lanmuchang Hg-Tl mine district.

reaches 3 wt. %, and is between 0.08 wt. % and 0.3 wt. % normally. Through geological exploration, the total mercury reserve is about 3140 tonnes in Lanmuchang Hg-Tl mine. According to recordation, from Ming Dynasty to 1958, mercury had been smelted in a long period in this area. We measured Mercury emission fluxes from soil in this area using Dynamic Flux Chamber-Automatic Mercury Analyzer Method in December of 2002 and May of 2003, respectively.

## RESULTS AND DISCUSSION

All sampling results are summarized in Tab. 1. Even though there is no anthropogenic activity in a long time in Lanmuchang Hg mine, the natural emission of mercury from mercury geologically enriched soil has resulted in high mercury content in the ambient air ( $209.8 \sim 79.1 \text{ ng} \cdot \text{m}^{-3}$  in sampling site F3 in warm season). The maximum of mercury emission flux reaches  $10543.7 \text{ ng m}^{-2} \text{ h}^{-1}$ , and the maximum of average mercury emission flux is  $2283.3 \sim 2434.2 \text{ ng m}^{-2} \text{ h}^{-1}$  ( $n=152$ ) in five

sampling sites. On the other hand, atmospheric mercury deposits quickly too, the maximum dry deposition flux is  $1502.6 \text{ ng m}^{-2} \text{ h}^{-1}$ . The results show that mercury exchange between soil and air in this area is much stronger than that in background areas. At the same time, it is shown in Tab. 1 that Hg emission fluxes from soil change with season.

It has been accepted widely that mercury evaporated from soil was elemental mercury ( $\text{Hg}^0$ ) and a small portion of methyl mercury. Factors controlling the emission of volatile  $\text{Hg}^0$  from soil are various. The dominating factor is obviously the concentration and speciation of mercury in matrix, and other physical factors such as solar radiation, soil temperature, TGM in air near soil surface can influence as well  $\text{Hg}^0$  emission strongly.

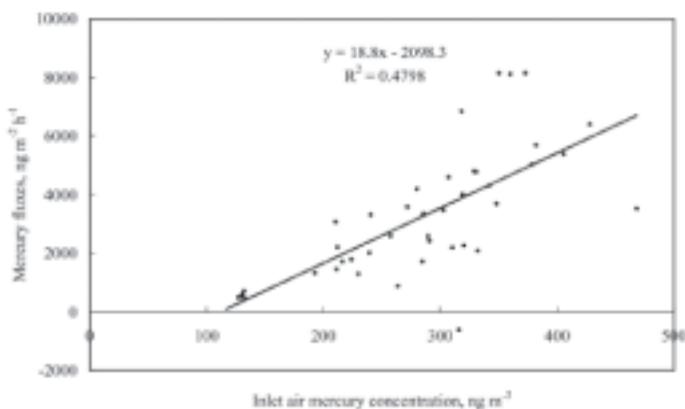
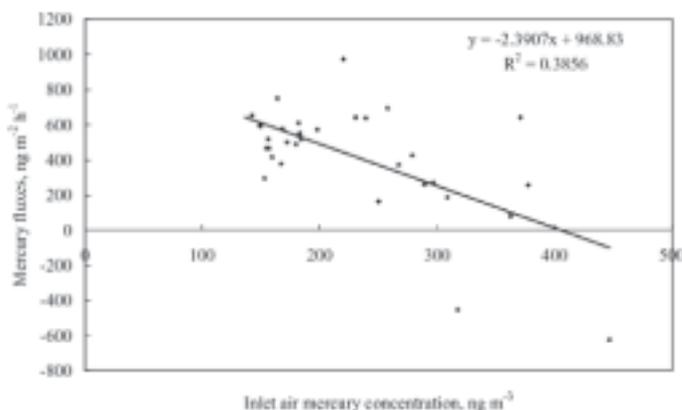
Sunlight induced Hg emission from soil has been proved by many field and laboratory studies. Our measurement results obviously supported this conclusion. It is shown from Table 1 that the light intensity of solar radiation correlated significantly with the Hg

**Table 1.** Hg fluxes, average inlet air Hg concentration, total Hg concentration in soil and average light intensity in all sampling sites.

Sampling site	Time		Hg flux ( $\text{ng m}^{-2} \text{h}^{-1}$ )			Average inlet air Hg content ( $\text{ng m}^{-3}$ )	Soil Hg content ( $\text{ng g}^{-1}$ , dry wt)	Average light intensity ( $\text{W m}^{-2}$ )	$\eta_{\text{emission}}$	$\eta_{\text{deposition}}$
	Form	To	Max	min	Average					
F1	2002-12-4	2002-12-5	3525.5	694.7	919.4±1137.9	48.6±40.8	223 000	257	71	10
	2003-5-17	2003-5-18	1508	553.6	241.7±376.6	42.0±28.9	—	54	70	9
F2	2002-12-5	2002-12-6	2097.4	8.3	482.3±517.7	24.5±13.0	247 000	161	64	1
	2003-5-15	2003-5-16	6922.3	1502.6	782.7±1711.8	117.8±43.3	—	217	51	22
F3	2002-12-6	2002-12-8	3864.3	222.3	861.9±807.1	31.7±7.8	614 000	30	113	0
	2003-5-6	2003-5-8	10543.7	622.9	2283.3±2434.2	209.8±79.1	—	145	147	5
F4	2003-5-9		1047.4	153.4	247.0±326.3	35.6±8.5	—	182	27	4
F5	2003-5-13	2003-5-15	4717.8	279.4	729.2±1039.5	43.6±27.4	291 000	79	104	4

emission fluxes in all sampling sites, and the correlation coefficients are greater than 0.82,  $p < 0.05$ . There is a positive correlation between mercury concentration in ambient air

and mercury flux during daytime, and a negative correlation between them at night, respectively (Figs. 2 and 3). From the linear equation of mercury deposition and mercury

**Figure 2.** The plot of mercury fluxes versus inlet air mercury concentration in the sampling site of F3, Lanmuchang in May, 2003 (in daytime).**Figure 3.** The plot of mercury fluxes versus inlet air mercury concentration in the sampling site of F3, Lanmuchang in May, 2003 (in night).

concentration, we estimate that about 16 % of total gaseous mercury flowing through the field chamber is absorbed by soil surface. Rainfall event facilitated mercury emission, this indicated that physical degassing of soil and photo-reduction of  $\text{Hg}^{2+}$  were approaches of mercury diffusing from soil.

## CONCLUSIONS

Geologically mercury enriched area in global mercury belts in southwest Guizhou is a huge atmospheric source of mercury. In this area, a great amount of  $\text{Hg}^0$  (of several hundred to tens of thousand ng per square meter per hour) are evaporating from soil to atmosphere. The strong  $\text{Hg}^0$  emission from soil will definitely lead the elevation of mercury

concentration in ambient in geologically mercury enriched area.

Mercury exchange between soil and air is bi-directional and is controlled by many factors including geological, meteorological, biological, anthropogenic conditions. In all factors, mercury contents in substrate and light intensity play a significant role in accelerating mercury emission from the substrates, whereas mercury concentration in ambient air may constrain mercury diffusion from soil effectively.

## Acknowledgements

This work was financially supported by Chinese National Natural Science Foundation (No. 40173037), and also by Chinese Academy of Sciences through “Hundred Talent Plan”.

## REFERENCES

- [1] SCHROEDER, W. H. AND MUNTHER, J. (1998): Atmospheric mercury—an overview; *Atmospheric Environment*, pp. 809-822.
- [2] SCHLÜTER, K. (2000): Review: evaporation of mercury from soils. An integration and synthesis of current knowledge; *Environmental Geology*, pp. 249-271.

# Oxidation of Elemental Mercury by Aqueous Bromine: Atmospheric Implications

ZHI WANG AND SIMO O. PEHKONEN\*

Dept. of Chemical and Biomolecular Engineering, National University of Singapore,  
10 Kent Ridge Crescent, Singapore, 119260; \*E-mail: chesop@nus.edu.sg

**Abstract:** The special characteristics of mercury, such as, its long-range atmospheric transport, its transformation between various species, biomagnification, and its role as a neurotoxin make it a pollutant of global concern. The chemical processes that take place in the atmosphere and water systems are closely linked and affect the transport of mercury. The kinetics of aqueous elemental mercury oxidation by aqueous bromine species detected by dithizone-Hg(II) complexation-UV-VIS spectroscopy was extensively investigated in this study. The second order oxidation rate constants at room temperature (294–296K) for the  $\text{Hg}_{(\text{aq})}^0\text{-Br}_2$ ,  $\text{Hg}_{(\text{aq})}^0\text{-HOBr}$  and  $\text{Hg}_{(\text{aq})}^0\text{-OBr}$  are determined to be  $0.20 \pm 0.03$ ,  $0.28 \pm 0.02$  and  $0.27 \pm 0.04 \text{ M}^{-1}\text{s}^{-1}$ , respectively. Such small oxidation rate constants also mean that the important atmospheric “sink” for mercury, which was discovered in the Arctic and sub-Arctic regions, is not caused by aqueous bromine, but other oxidizing bromine species (e.g., gaseous phase bromine species).

**Key words:** redox, mercury, bromine, hypobromous, kinetics

## INTRODUCTION

Mercury is emitted into the atmosphere from various anthropogenic and natural sources and is removed through dry and wet deposition. Deposition rates of mercury from the atmosphere to soil and surface waters depend on the chemical and physical forms of mercury. The wet deposition efficiency is governed by divalent mercury, while particulate mercury is often removed from the atmosphere via dry deposition. Understanding the chemical and physical transformation pathways that govern the atmospheric behavior of mercury is a key point to assess its fate and lifetime in the atmosphere.

The chemistry of mercury in the atmospheric environment may take place in the gas or in

the aqueous phase as well as in the heterogeneous phase in aerosol. Aqueous phase reactions can occur in cloud, fog and/or rain-water and in films of moisture on hygroscopic aerosols (Seigneur et al., 1994). Table 1 summarizes the reactions identified to be relevant in the aqueous phase chemistry of Hg, including the disproportionation of monovalent mercury into its elemental and divalent forms; the oxidation of elemental mercury to divalent mercury by ozone, hypochlorite ions, and some free radicals and the reduction of divalent mercury to elemental mercury (SANEMASA ET AL., 1983; MUNTHE ET AL., 1991; MUNTHE 1992; MUNTHER AND McELROY, 1992; LIN AND PEHKONEN, 1997, 1998; PEHKONEN AND LIN, 1998).

Unexpected and rapid mercury deposition from the atmospheric boundary layer through-

out the Arctic and sub-Arctic during the spring has been reported since 1998 (SCHROEDER ET AL., 1998; LU ET AL., 2001 AND LINDBERG ET AL., 2002). It has been lately discovered that reactive bromine and chlorine from the vaporized sea-salt aerosols and ice algae and through photocatalyzed activation usually appear upon the first sunlight of spring and are likely the active species for this surprising reaction, which takes place in the atmosphere between mercury and halogens (MOZURKEWICH, 1995; SCHROEDER ET AL., 1998; CAPOZZA AND FELLOW, 2001 AND ARIYA ET AL., 2002).

Reactions of gaseous mercury with molecular and atomic chlorine and bromine in the atmosphere have been previously carried out in the laboratory and these studies indicate that atomic bromine with a rate constant of  $3.2 \pm 0.3 \times 10^{-12} \text{ cm}^3/(\text{molecule}\cdot\text{s})$  is the only likely candidate to explain the rapid depletion of mercury in the Arctic (ARIYA ET AL., 2002). The reaction between gaseous elemental mercury and molecular chlorine is quite unusual, with two kinetic regimes, one is a gas-phase reaction with a rate constant of  $2.62 \pm 0.08 \times 10^{-18} \text{ cm}^3/(\text{molecule}\cdot\text{s})$ , the other is a surface-catalyzed reaction, with a rate constant of  $4.63 \pm 0.28 \times 10^{-18} \text{ cm}^3/(\text{molecule}\cdot\text{s})$ , which is believed to occur after the reactor wall is covered by a product, which is identified to be  $\text{HgCl}_2$ . However, for the reaction with molecular bromine (no bi-kinetic regimes appeared), it was found that the reaction is significantly faster than with molecular chlorine with a rate constant of  $0.9 \pm 0.2 \times 10^{-16} \text{ cm}^3/(\text{molecule}\cdot\text{s})$  (ARIYA ET AL., 2002). Furthermore, the reported rate constants for the atomic chlorine and bromine are  $1.0 \pm 0.2 \times 10^{-11} \text{ cm}^3/(\text{molecule}\cdot\text{s})$  and  $3.2 \pm 0.3 \times 10^{-12} \text{ cm}^3/(\text{molecule}\cdot\text{s})$ , respectively. The major reaction product was

identified as  $\text{HgCl}_2$  or  $\text{HgBr}_2$ . Later, RAOFIE AND ARIYA (2003) have reported the rate constant between gaseous elemental mercury and BrO radicals with a value of  $1.1 \times 10^{-13} \sim 1.1 \times 10^{-15} \text{ cm}^3/(\text{molecule}\cdot\text{s})$ . Moreover, the GOME satellite observation recorded a positive correlation between MDEs and vertical column BrO (LU ET AL., 2001; LINDBERG ET AL., 2002). Those findings provide evidence that atomic halogens and BrO are the responsible species for MDEs in the surface marine boundary layer in the Arctic and Sub-Arctic (LU ET AL., 2001; LINDBERG ET AL., 2002). But there is still a lack of reliable experimental kinetic data on the reactions that proceed in the aqueous phase.

To better understand the global cycle of this toxic metal in the environment and the species responsible for the polar spring mercury increases, the kinetics and mechanisms of aqueous elemental mercury oxidation by aqueous bromine species (i.e., bromine, hypobromous acid and hypobromite ion) need to be studied.

## RESULTS AND DISCUSSION

The first series of experiments were performed to investigate the reaction between  $\text{Hg}^0$  and bromine at pH of 2 by using the initial concentrations of elemental mercury of 0.13-0.21  $\times 10^{-7} \text{ M}$  and the concentration of bromine at 1.125 and 2.25 mM at room temperature (294~296 K) in the dark. Perchloric acid was used to control the pH value, and pH change during the course of the experiments was limited to  $\pm 0.1$  units. The predominant species at this pH is aqueous bromine,  $\text{Br}_2(\text{aq})$ . The color of the reaction solution is pale yellow.

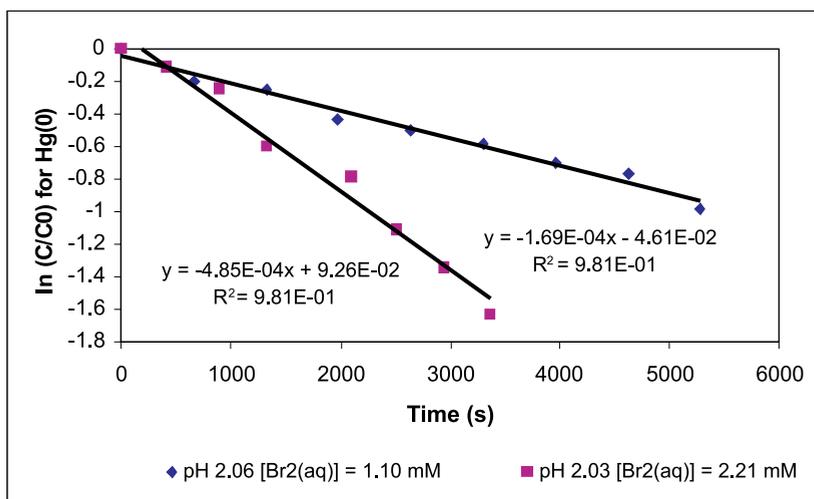
Figure 1 shows the  $\ln(C/C_0)$  vs. time reaction profile of aqueous elemental mercury and aqueous bromine conducted at two different bromine concentrations. According to this figure, elemental mercury can be oxidized in the presence of aqueous bromine. The figure indicates a pseudo first-order behavior in our experiments. The slopes of the plots were taken as the observed pseudo first-order rate constants.

The rate of oxidation of elemental mercury in the presence of excess bromine was measured and the derived second-order rate constant was found to be  $0.20 \pm 0.03 \text{ M}^{-1}\text{s}^{-1}$ .

For oxidation of aqueous elemental mercury with hypobromous acid at pH of 6.8, keeping the same experimental conditions as those at pH of 2, except using a buffer of 12.25 mM sodium dihydrogen phosphate and 7.75 mM sodium phosphate salts to maintain neutral pH. Under such conditions, the

predominant bromine species is hypobromous acid. Because Dithizone decomposes much more readily under alkaline conditions, the more concentrated Dithizone was used at pH of 6.8 and 11.7 with a concentration of up to  $2.76 \times 10^{-4} \text{ M}$ . The rate of the reaction between aqueous elemental mercury and hypobromous acid at pH of 6.8 was measured. It was demonstrated that hypobromous acid can also oxidize aqueous elemental mercury. The slopes of the plots were taken as the observed rate constants. The second-order rate constant of the reaction between aqueous mercury and hypobromous acid is  $0.28 \pm 0.02 \text{ M}^{-1}\text{s}^{-1}$ .

For the experiments conducted at pH of 11.7 between aqueous elemental mercury and hypobromite, sodium hydroxide was used to adjust and maintain the pH. Under such conditions, the predominant bromine species is hypobromite. It is interesting to note that hypobromite also has an oxidation potential



**Figure 1.** The pseudo first-order plot of the oxidation of  $\text{Hg}^0$  by aqueous bromine ( $\text{Br}_2$ ) at pH 2. Initial reactant concentrations: pH 2.06  $[\text{Hg}^0] = 0.21 \mu\text{M}$ ,  $[\text{Br}_2] = 1.10 \text{ mM}$ ; pH 2.03  $[\text{Hg}^0] = 0.13 \mu\text{M}$ ,  $[\text{Br}_2] = 2.21 \text{ mM}$ . The slopes of the regressed lines are  $k_{\text{obs}}$ .

sufficiently high to oxidize aqueous elemental mercury rapidly. The slopes of the plots were again taken as the observed rate constants. The derived second-order rate constant is found to be  $0.27 \pm 0.04 \text{ M}^{-1}\text{s}^{-1}$ .

The stoichiometry of elemental mercury oxidation with  $\text{OBr}^-$  at pH of 12 was also determined. The reaction time was 336 hours and the results clearly show that the ratio is 1:1 for the  $\text{Hg(II)}$  formed vs.  $\text{OBr}^-$  present. This result is consistent with the two-electron transfer that one would expect between the oxidant and the reactant in this case.

A sudden mercury increase is observed in the Arctic ecosystem and ice surfaces during the polar sunrise. The increase is mainly due to reactions of halogen species, such as  $\text{BrO}$ ,  $\text{ClO}$ ,  $\text{Cl}$  and  $\text{Br}$ , these species probably originate from marine aerosol, the acidification of snowpack and some ice algae harnessed by vanishing of multi-year ice coverage subsequently depositing on the snowpack (SCHROEDER ET AL., 1998; LU ET AL., 2001; LINDBERG ET AL., 2002). The levels of reactive bromine in terrestrial regions are low owing to the very low concentrations of bromide in urban clouds (HERRMANN ET AL., 2003) and their measured concentrations are not available; moreover  $\sim 70\%$  of the earth's surface is covered by oceans, a reaction involving bromine released from sea salt aerosols is of potential global importance. The following discussion only focuses on the typical conditions within the marine boundary layer.

The most important source of bromine in the atmosphere over the oceans is from wave breaking, which contains high concentrations of  $\text{NaBr}$  with a  $\text{Br}^-/\text{Na}^+$  ratio of 6.25 g/kg

(GABRIEL ET AL., 2002). The most relevant bromine species are the chemically reactive ones, such as  $\text{BrO}$ ,  $\text{Br}$  and  $\text{Br}_2$ . One pathway of such conversion is through the acidification of snowpack as marine aerosol contains sea-salt and sulfate, which will be frozen when encountering cold temperatures and depositing to the snowpack, where it can be photolysed by visible light (SUMNER AND SHEPSON, 1999). The crucial species for enabling the halogen cycling is  $\text{HOBr}$ , which is identified in the Arctic boundary layer with a concentration of 270 pppt (IMPEY ET AL., 1999).  $\text{BrCl}$  is another important species, which is a by-product for this important acid-catalyzed reaction in the presence of  $\text{Br}^-$  (KATRIB ET AL., 2001). Some ice algae communities also produce photolyzable bromine (LINDBERG ET AL., 2002). In polluted air containing nitrogen oxides can also release reactive halogen atoms, but this is not the case in Arctic, since nitrogen oxides are not very abundant there. The model by VON GLASOW AND SANDER (2002) shows that during daylight, photolysis is the driving force for the net transport of bromine from the aqueous to the gas phase, as the formation of  $\text{HOBr}$  is dependent on photolytically produced  $\bullet\text{HO}_2$ . The main  $\text{Br}$  species are  $\text{HOBr}$ ,  $\text{HBr}$  and  $\text{BrO}$ . At night, this is shifted toward  $\text{Br}_2$  and  $\text{BrCl}$ , which are readily photolyzed during daylight.

To evaluate the importance of bromine reactions of mercury in light of this kinetic study, eight atmospherically important oxidants are selected and used to estimate the contribution of each to oxidized mercury in the atmosphere. The selected oxidants in the aqueous phase are ozone, hypochlorite species, hydroxyl radical, hydrogen peroxide, hypobromous acid, bromine and hypobro-

mite. Comparing the concentrations of bromine species present in the atmosphere and the relevant kinetic data, the reactions of aqueous bromine species are far too slow to be important atmospheric "sinks" for mercury. Oxidation of mercury in the gas phase by halogen species is considerably faster than its oxidation in the aqueous phase.

## CONCLUSIONS

Reactive bromine and chlorine are known to be released through acid-catalyzed activations in the marine boundary layer; this results in significant mercury depletion in the springtime near Arctic and Sub-Arctic. In this study, the pseudo first-order rate constants

of aqueous elemental mercury with aqueous bromine, hypobromous acid and hypobromite have been determined to be  $0.20 \pm 0.03$ ,  $0.28 \pm 0.02$  and  $0.27 \pm 0.04 \text{ M}^{-1}\text{s}^{-1}$ , respectively. Results from the comparison of identified oxidants (i.e.,  $\text{O}_3$ ,  $\bullet\text{OH}$ ,  $\text{H}_2\text{O}_2$ , chlorine and bromine) of atmospheric mercury indicate that the aqueous bromine species are not the main scavengers of elemental mercury in the Arctic and Sub-Arctic regions, gaseous bromine species are more likely to cause this oxidative scavenging.

## Acknowledgements

This work was supported by a grant R-279-000-054-112 from the National University of Singapore

## REFERENCES

- ARIYA, P. A., KHALIZOV, A., GIDAS, A. (2002): Reactions of gaseous mercury with atomic and molecular halogens: kinetics, product studies, and atmospheric implications; *Journal of Physical Chemistry A* 106, pp. 7310-7320.
- CAPOZZA, K., FELLOW, P. (2001): *Polar spring arrives, mercury rises - in sky. Environmental News Network, Canada* [On Line]; Available: <http://pewfellowships.org/stories/canada/polarspring.html>.
- GABRIEL, R., VON GLASOW, R., SANDER, R., ANDREAE, M. O., CRUTZEN, P. J. (2002): Bromide content of sea-salt aerosol particles collected over the Indian Ocean during INDOEX 1999; *Journal of Geophysical Research* 107, Art. No. 8032 SEP-OCT 2002.
- HERRMANN, H., MAJDIK Z., ERVENS B., WEISE D. (2003): Halogen production from aqueous tropospheric particles; *Chemosphere* 52, pp. 485-502.
- IMPEY, G. A., MIHELE, C. M., ANLAUF, K. G., BARRIE, L. A., HASTIE, D. R., SHEPSON, P. B. (1999): Measurements of photolyzable halogen compounds and bromine radicals during the Polar Sunrise Experiment 1997; *Journal of Atmospheric Chemistry* 34(21).
- KATRIB, Y., DEIBER, G., SCHWEITZER, F., MIRABEL, P., GEORGE, C. (2001): Chemical transformation of bromine chloride at the air/water interfacel; *Journal of Aerosol Science* 32, pp. 893-911.
- LIN, C. J., PEHKONEN, S. O. (1997): Aqueous free radical chemistry of mercury in the atmosphere; *Atmospheric Environment* 32, pp. 2543-2558.
- LIN, C. J., PEHKONEN, S. O. (1998): Oxidation of elemental mercury by aqueous chlorine: implications for troposphere mercury chemistry; *Journal of Geophysical Research - Atmosphere* 103, pp. 28093-28102.
- LINDBERG, S. E., BROOKS, S. B., LIN, C.-J., SCOTT, K. J., LANDIS, M. S., STEVENS, R. K., GOODSITE, M., RICHTER, A. (2002): Dynamic oxidation of gaseous mercury in the Arctic atmosphere at polar sunrise; *Environmental Science and Technology* 36, pp. 1245-1256.

- LU, J. Y., SCHROEDER, W. H., BARRIE, L. A., STEFFEN, A., WELCH, H. E., MARTIN, K., LICKHART, L., HUNT, R. V., BOILA, G., RICHTER, A. (2001): Magnification of atmospheric mercury deposition to polar regions in springtime: the link to tropospheric ozone depletion chemistry; *Geophysical Research Letters* 28, pp. 3219-3222.
- MOZURKEWICH, M. (1995): Mechanisms for the release of halogens from sea-salt particles by free radicals reactions; *J. Geophysical Research* 100(14), pp. 199-14,207.
- MUNTHE, J. (1992): Aqueous oxidation of elemental Hg by O<sub>3</sub>; *Atmospheric Environment* 26A, pp. 1461-1468.
- MUNTHE, J., MCELROY, W. J. (1992): Some aqueous reaction of potential importance in the atmospheric chemistry of mercury; *Atmospheric Environment* 26A, pp. 553-557.
- MUNTHE, J., XIAO, Z. F., LINDQVIST, O. (1991): The aqueous reduction of divalent mercury by sulfite; *Water, Air and Soil Pollution* 56, pp. 621-630.
- PEHKONEN, S. O., LIN, C. J. (1998): Aqueous photochemistry of divalent mercury with organic acids; *Journal of the Air and Waste Management Association* 48, pp. 144-150.

## The Local Environmental Impact from a Mercury Cell Chlor-Alkali Plant in Sweden

INGVAR WÄNGBERG<sup>1</sup>, JOHN MUNTHE<sup>1</sup>, JONAS SOMMAR<sup>2</sup> & BRUCE DENBY<sup>3</sup>

<sup>1</sup>IVL Swedish Environmental Research Institute, P.O. Box 47086, S-402 58 Göteborg, Sweden,  
e-mail: ingvar.wangberg@ivl.se

<sup>2</sup>Department of Chemistry, Göteborg University, S-412 96 Göteborg, Sweden

<sup>3</sup>Norwegian Institute for Air Research, PO Box 3000, 2027 Kjeller, Norway

**Abstract:** Air measurements of mercury inside the cell house and in the surroundings of a Mercury Cell Chlor-Alkali plant (MCCA) in Bohus, Sweden has been performed. The work was made in the frame of the European founded EMECAP project (European Mercury Emission from Chlor-Alkali Plants). Within the project air measurements were also conducted at MCCA plants in Italy and Poland. The aim of project was to achieve relevant information on human health risks due to mercury emissions from European MCCA plants. The entire project included field measurements, extensive epidemiological studies, dispersion modelling, development of technological and data base software tools. The methods developed within EMECAP project are not restricted to study effects from chlor-alkali industry only but can also be applied to assess the influence from other anthropogenic mercury sources.

The Swedish chlor-alkali plant was established 1924 and is situated on the east shore of the Göta Älv river, 20 km North of Göteborg. The chlorine production amounts 100,000 ton per year. Five field campaigns were made in which TGM, RGM and TPM were measured at different sites around the plant including one site in the Bohus village. One year monthly precipitation sampling at four strategically chosen sites were also made. Due to the point source character of the emission mercury concentrations were found to be very dependent on the wind direction. Maximum concentrations of TGM, RGM and TPM measured in outside air 70 m from the cell house were 500, 1 and 0.2 ng m<sup>-3</sup>, respectively. The maximum concentrations observed of the same mercury species at the site in the Bohus village 600 m from the source were 40, 0.1 and 0.01 ng m<sup>-3</sup>, respectively. Concerning TGM and RGM these values are about 20 times higher than the background in this area of Sweden. The measurement result was combined with dispersion modelling using the TAPM model from which yearly average geographical distributions of TGM and RGM could be calculated. The result shows that despite frequent occasions of strongly elevated mercury concentrations the average influence is quite limited. The yearly average concentration of TGM within a radius of 1 km (including residential areas in Bohus) is 2.5 - 3.5 ng m<sup>-3</sup>. The background concentration of TGM in the area is about 1.7 ng m<sup>-3</sup>. The relatively small influence from the MCCA plant is, as will be shown, also reflected in the mercury precipitation data. RGM emission and wet and dry deposition of RGM are likely to be the most important parameters determining the impact on the local environment. The RGM emission factor at the Swedish plant was determined to 0.007 g per ton Cl<sub>2</sub> produced. The corresponding emission factor obtained at the Polish plant is 2.7 g per ton Cl<sub>2</sub> produced. The origin of RGM from the chlor-alkali process has also been studied and the result will be presented.

**Key words:** mercury emission, RGM, MCCA

## Mercury Monitoring in Ambient Air in the Minamata Area

AKIRA YASUTAKE<sup>1</sup>, AKITO MATSUYAMA<sup>1</sup>, NIKOLAY MASHYANOV<sup>2</sup>,  
VLADIMIR RYZHOV<sup>3</sup>, ALEXEY NIKIFOROV<sup>2</sup>

<sup>1</sup>National Institute for Minamata Disease, Minamata, Japan; E-mail: mail@nimd.go.jp;

<sup>2</sup>St. Petersburg State University, St. Petersburg, Russia; E-mail: nrm@lumex.ru;

<sup>3</sup>Lumex Ltd., St. Petersburg, Russia; E-mail: hg@lumex.ru

**Abstract:** The results of long-term mercury monitoring in ambient air in the Minamata area using a Lumex RA-915<sup>+</sup> mercury analyzer are presented. Due to statistical data acquisition the detection limit for continuous measurements was attained to be as low as 0.3 ng/m<sup>3</sup>. The average mercury concentration was equal to 2 ng/m<sup>3</sup> with current values varying from 1 to 4 ng/m<sup>3</sup>. Maximum values of the mercury concentration in ambient air were associated with the wind directions outward landfills and the Minamata Bay. The dependence of the mercury concentration in air on the wind direction is evidence of small-scale mercury emission from buried sediments.

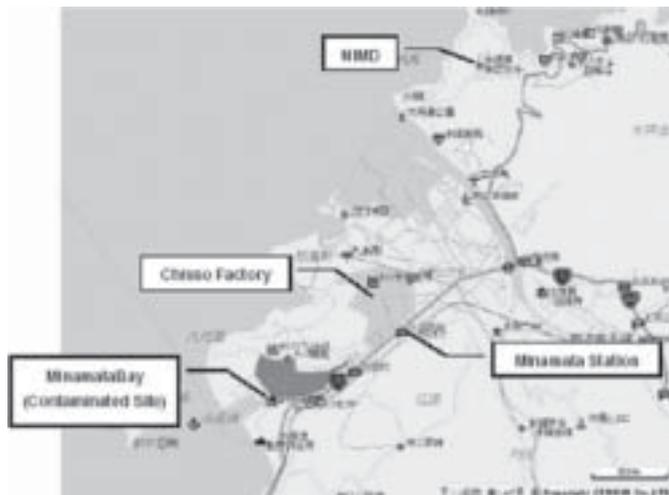
**Key words:** mercury in air, background monitoring, Minamata

### INTRODUCTION

More than half a century has elapsed since the Minamata Bay was heavily polluted by methylmercury discharged from a chemical factory. The first Minamata disease patient with methylmercury-caused neurological symptoms was reported in 1956. In 1974, Kumamoto Prefecture started a project to restore the polluted environment by dredging and landfilling. The government funded removal of 1,500,000 cubic meters of bottom sediments from the Minamata Bay that contained more than 25 ppm of total mercury by 1990 (Fig. 1).

According to the official data, no fish with mercury content above 0.4 ppm, which is Japanese provisional regulation level, was found in the bay since 1994<sup>[1]</sup>. This means that most part of mercury was removed from marine biogeochemical cycling. However,

there is no regular data on the mercury concentration in the atmosphere in the Minamata area, which can indicate mercury dissipation from buried highly contaminated sediments. We conducted continuous automobile survey and stationary long-term mercury monitoring in ambient air in the Minamata area using a Lumex RA-915<sup>+</sup> mercury analyzer<sup>[2]</sup>. According to the automobile surveys conducted in 2001-2003, no significant regional or local anomalies were revealed in the area of Minamata city and sites of contaminated waste burial. The first measurements of the mercury concentration in ambient air in the Minamata area were fulfilled in 2001 and the regular long-term background air monitoring was started in February 2003 at the facility of National Institute for Minamata Disease (NIMD) for investigation of possible emission of mercury to the atmosphere from marine and terrestrial environment.



**Figure 1.** Location of the initial pollution source (Chisso factory), landfills and air monitoring point (NIMD) in the Minamata area.

## RESULTS AND DISCUSSION

Lumex RA-915<sup>+</sup> Zeeman analyzer provides continuous determination of the mercury concentration with a detection limit (DL) of 1.5 – 2 ng/m<sup>3</sup>, the response time being 1 s. The DL is calculated as threefold standard error and depends on averaging time ( $t_{av}$ ) as:

$$DL(t_{av}) = \frac{DL_1}{\sqrt{t_{av}}},$$

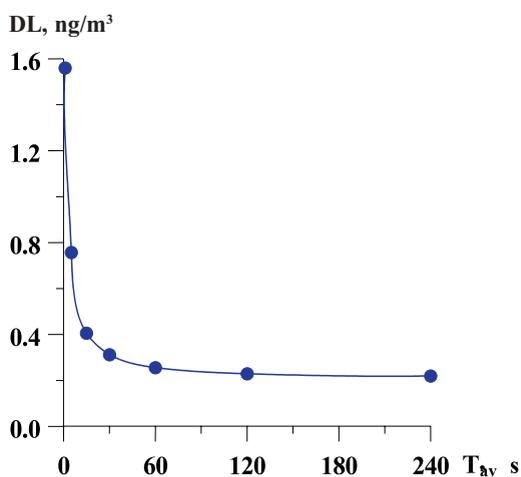
where  $DL_1$  is determined for the averaging time of 1 s.

Statistical accumulation of the analytical signal by the RA-919P software enables a decrease in the real DL of measurements (Fig. 2).

In background air monitoring, the average mercury concentration was detected every 30 s during permanent air pumping through the multi-path analytical cell of the RA-915<sup>+</sup>

at a rate of 25 L/min. The detection limit was attained to be as low as 0.32 ng/m<sup>3</sup> due to the data acquisition during the response time of 30 s.

The monitoring point was located at about 4 km NNE from the Minamata Bay (see

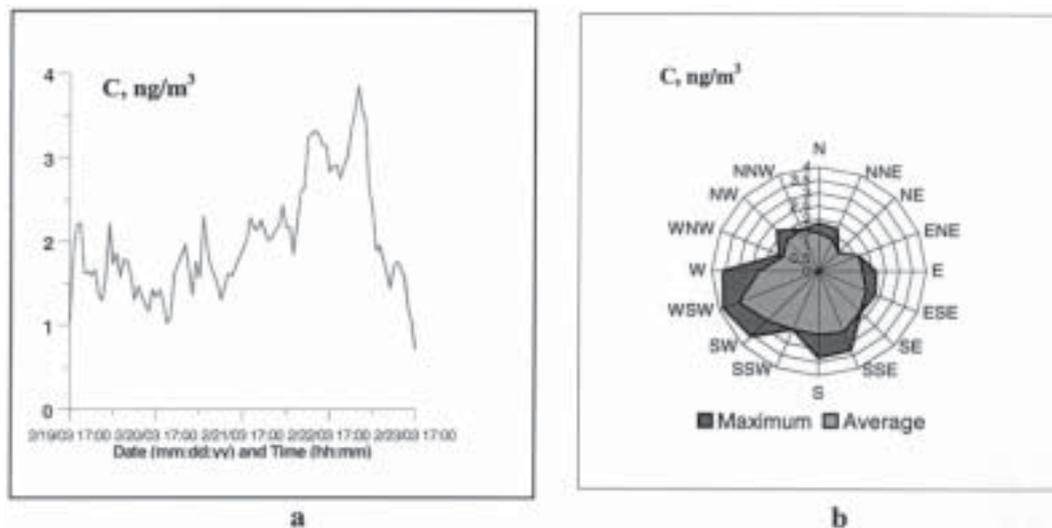


**Figure 2.** Dependence of the RA-915<sup>+</sup> detection limit on the averaging time. Experimental data.

Fig. 1). The measurements were performed continuously in off-hand mode for 5-10 days in February, April, June and December 2003, and January 2004.

An example of the behavior of the average mercury concentration obtained throughout 5-days monitoring in February 2003 is shown in Fig. 3. During these days the average concentration was equal to  $2 \text{ ng/m}^3$  with current values varying from 1 to  $4 \text{ ng/m}^3$  (average over 12-hours intervals ranged from 1.3 up to  $3.1 \text{ ng/m}^3$ ).

When compared with the weather data, collected in 1-hour intervals, the mercury concentration in ambient air exhibited definite correlation with the temperature, pressure, humidity and wind direction. The maximum values of the mercury concentration in ambient air were associated with W-WSW-SW wind directions (outward landfills and the Minamata Bay, see Fig. 1), whereas the minimum values were observed during N-NE-E wind. The dependence of the mercury concentration in air on the wind direction suggests a possible small-scale mercury emission from buried contaminated sediments.



**Figure 3.** Monitoring data during 19 – 23 February 2003. a) Variations of the mercury concentration in ambient air, b) dependence of the maximum and average mercury concentrations on the wind direction. Detection limit is  $0.3 \text{ ng/m}^3$ .

## CONCLUSIONS

The developed technique of air monitoring using the RA-915<sup>+</sup> Zeeman analyzer enables the long-term measurements of the mercury concentration at a sub-nanogram level. Continuous observations for many days fulfilled in 2003 and 2004 revealed noticeable varia-

tion of the mercury concentration within  $1 - 4 \text{ ng/m}^3$  depending on weather conditions. The maximum values of the mercury concentration in ambient air were associated with the wind directions outward the contaminated site in Minamata area.

## Acknowledgements

This work was supported by the National Institute for Minamata Disease, Japan, and Lumex Ltd., Russia. The authors are thankful to Dr. H. Akagi, Dr. S. Pogarev, Dr. S. Sholupov and Dr. S. Belov for their help in research and fruitful discussions.

## REFERENCES

- <sup>[1]</sup> *Minamata Disease: The History and Measures* (2002); Environmental Health Department, Ministry of the Environment, Japan, 20 p.
- <sup>[2]</sup> GANEEV, A. A., SHOLUPOV, S. E., SLYADNEV, M. N. (1996): Zeeman modulation polarization spectrometry as a version of atomic-absorption analysis: potential and limitations; *J. Analytical Chemistry* 51, N6, pp.788-796.

# Statistical Analysis of Total Gaseous Mercury in the Great Lakes and St. Lawrence River Basin

HONGYU YOU<sup>1\*</sup>, XIAOHONG XU<sup>1</sup>, RAM BALACHANDAR<sup>1</sup> HAYLEY HUNG<sup>2</sup>, PIERRETTE BLANCHARD<sup>2</sup>, FRANK FROUDE<sup>2</sup>, CATHY BANIC<sup>2</sup> LAURIER POISSANT<sup>3</sup>

<sup>1</sup>Department of Civil and Environmental Engineering, University of Windsor, 401 Sunset Ave., Windsor, Ontario, Canada N9B 3P4; \*E-mail: you1@uwindsor.ca

<sup>2</sup>Meteorological Service of Canada, Environment Canada, 4905 Dufferin Street, Toronto, Ontario, Canada M3H 5T4

<sup>3</sup>Meteorological Service of Canada, Environment Canada, 105 McGill (7<sup>th</sup> floor), Montréal, Québec, Canada H2Y 2E7

**Abstract:** Total gaseous mercury (TGM) measurements have been conducted by the Canadian Atmospheric Mercury Network (CAMNet) since 1997. In this study, a statistical analysis was carried out using 6 years of TGM monitoring data at three CAMNet sites in the Great Lakes basin and 3 years data at two CAMNet sites in the St. Lawrence River basin. The mean of TGM concentrations ranged from  $1.59 \pm 0.24$  to  $1.85 \pm 0.39$  ng/m<sup>3</sup> at the five sites. Point Petre and St. Anicet have a significantly higher ( $p < 0.01$ ) TGM concentration in the Great Lake and St. Lawrence River basin, respectively. Large Hg evasion from Lake Ontario might be a primary contributor for the former site, while nearby industrial and metropolitan areas of the latter site contribute more anthropogenic inputs. Seasonal variability was detected at all 5 sites with a similar winter high/summer-fall low pattern. Diurnal distribution was characterized by minimum concentration occurring at early morning and maximum at noon. The diurnal pattern during summer is much more pronounced than that in other seasons. Long-term trend analysis for TGM concentrations of Burnt Island from 1998-2003 was carried out using the digital filter technique. There was a slight decreasing rate in TGM concentration from 1998 to 2001, and afterward, an increase took place in 2002, followed by a decrease in 2003.

**Key words:** total gaseous mercury (TGM), seasonal variability, diurnal variability, trend, Great Lakes

## INTRODUCTION

Mercury (Hg) exists primarily in gaseous elemental form (Hg<sup>0</sup>) in the atmosphere and is released by natural and anthropogenic sources. Atmospheric mercury is highly stable and has residence time in the order of 1 year (Lindqvist and Rodhe, 1985); therefore it can be transported over a long distance regionally, even globally. Canadian Atmospheric Mercury Network (CAMNet)

was established in 1997 to provide long-term measurements of total gaseous mercury (TGM) concentration across Canada and offer a better understanding of trend, pathways, behaviours and fate of atmospheric mercury from both natural and anthropogenic sources (KELLERHASLS ET AL., 2003).

Five of the CAMNet sites in the Great Lakes and St. Lawrence River basin were chosen in this study, as listed in Table 1. Each site

utilizes a Tekran™ 2537A analyzer for TGM measurement. The sampling time interval is 15 minutes, the data were quality controlled using procedures developed by Environment Canada, and were averaged into hourly values (KELLERHASLS ET AL., 2003).

Descriptive statistics was applied to characterize seasonal and diurnal variability of TGM concentrations. A digital filter (DF) technique described by NAKAZAWA ET AL. (1997) was employed in this study to perform long-term trend analysis of TGM concentrations. This technique has been effectively used to detect a 4-year trend of TGM at Egbert and Point Petre (BLANCHARD ET AL., 2002) and trend in other studies such as Polychlorinated Biphenyls measurement (HUNG ET AL., 2001).

## RESULTS AND DISCUSSION

The descriptive statistics of TGM concentrations of the all five sites were shown in Table 1. In the Great Lake basin, Point Petre has a significantly higher ( $p < 0.01$ ) TGM concentration than that in Burnt Island and Egbert. In St. Lawrence River basin, St.

Anicet site has significantly higher ( $p < 0.01$ ) TGM concentrations than that in Mingan.

Point Petre is a small peninsula on the eastern end of Lake Ontario, which is surrounded by urban and industrial centers. POISSANT (2002) has reported that Hg evasion flux is one order magnitude larger than deposition flux at Lake Ontario. The large amount of re-emission from water body increases TGM concentration in the boundary layer above the Lake, which might be the primary factor for higher TGM concentration at this site. St. Anicet site is near industrial areas and metropolitan area of Montréal (population ~3,000,000); therefore inputs of local anthropogenic sources might be responsible for higher TGM concentration.

Seasonal variability was detected as a winter high/summer low pattern in all five sites. Figure 1 shows monthly concentration at Burnt Island from 1998 to 2003, as an example. The TGM concentration decreases and reaches the minimum during late summer and early fall, increases afterward and reaches the maximum in February. In winter, the increasing coal consumption for heating systems (ROTTY, 1987) could be a factor

**Table 1.** Statistical summary of TGM concentrations (ng/m<sup>3</sup>)

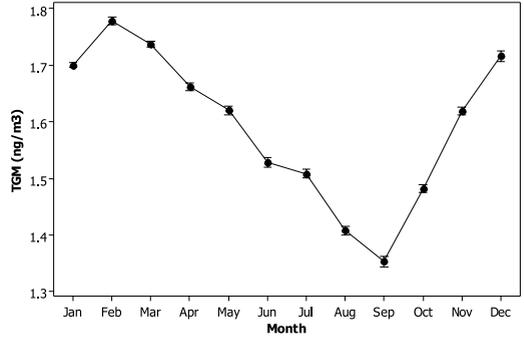
Station	Lat/Long	Mean	Std. Dev.	Median	Max.	Min.	Site category*
Burnt Island	45.81N/82.95W	1.59	0.24	1.60	4.38	0.47	RR
Egbert	44.23N/79.78W	1.70	0.41	1.69	25.8	0.76	RA
Point Petre	43.84N/77.15W	1.85	0.39	1.79	8.50	0.60	RR
Mingan	50.00N/64.00W	1.61	0.23	1.65	3.07	0.36	RR
St. Anicet	43.00N/77.00W	1.71	0.79	1.65	53.0	0.59	RA

Note: \* RR = Rural remote and RA = Rural sites expected to be affected by nearby anthropogenic Hg emission, as in KELLERHASLS ET AL. (2003)

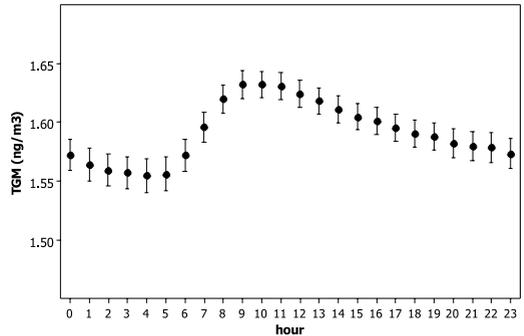
for the high concentration, and lower air mixing height of winter may lead to TGM concentration build up near the surface.

Figure 2 shows the diurnal variation of TGM in Burnt Island. The minimum occurs at early morning; the concentration then increases and approaches the maximum near solar noon. The result suggests that depletion of TGM takes place at nighttime and stronger solar radiation enhances activity of surface re-emission of Hg during daytime. Further analysis indicates that the diurnal pattern in summer is much more pronounced than that in other seasons. Through the other four sites, the similar diurnal distribution was found as well.

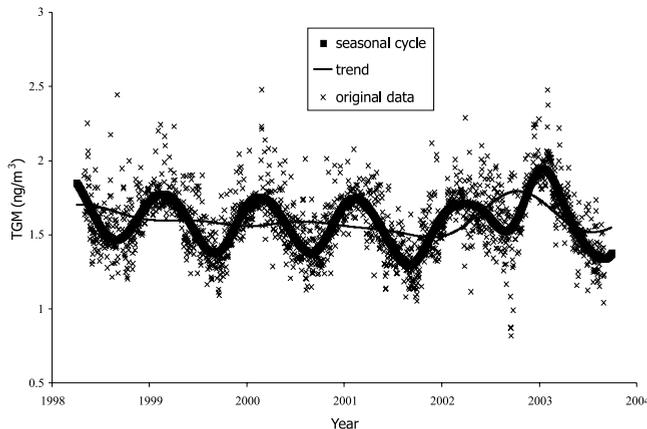
Long-term trend analysis of TGM concentration was conducted at the Burnt Island site. As shown the Figure 3, there was a slight decreasing trend of TGM concentration during 1998 to 2001 ( $p < 0.01$ ), and then an increasing took place in the year of 2002, followed by a decrease in 2003. Yearly mean of TGM concentration increased significantly ( $p < 0.01$ ) from 1.52 ng/m<sup>3</sup> in 2001 to 1.68 ng/m<sup>3</sup> in 2002. Seasonal variability is shown clearly in Figure 3 as well.



**Figure 1.** Seasonal variability of TGM concentrations in Burnt Island, data from 1998 to 2003. Solid circle indicates mean, vertical error bars are 95 % confidence interval for mean.



**Figure 2.** Diurnal variability of TGM concentrations in Burnt Island, data from 1998 to 2003. Solid circle indicates mean, vertical error bars are 95 % confidence interval for mean.



**Figure 3.** Trends and seasonal cycles of TGM concentrations for Burnt Island from 1998 to 2003.

## CONCLUSIONS

Statistical analysis was carried out using TGM concentrations at the five CAMNet sites in the Great Lakes and St. Lawrence River basin. Point Petre has a higher TGM concentration likely due to Hg evasion from Lake Ontario. Local anthropogenic sources are responsible for higher concentration at St. Anicet. Similar seasonal pattern of the 5 sites indicates that the seasonal variability depends on both anthropogenic emission and meteorological factors. Depletion of TGM at nighttime and increasing daytime re-emis-

sion with solar radiation may lead to the observed diurnal pattern, especially in summer. For Burnt Island, there were four-year of slight decreasing in TGM during 1998-2001, followed by an increase in 2002 then a decrease in 2003.

## Acknowledgements

The authors would like to thank Celine Audette for providing the meteorological data. The project is funded by the Natural Sciences and Engineering Research Council of Canada and Environment Canada.

## REFERENCES

- BLANCHARD, P., FROUDE, F. A., MARTIN, J. B., DRYFHOUT-CLARK, H., WOODS, J. T. (2002): Four years of continuous total gaseous mercury (TGM) measurements at sites in Ontario, Canada; *Atmospheric Environment* 36, 3735-3743.
- HUNG, H., HALSALL, C. J., BLANCHARD, P., LI, H. H., FELLIN, P., STERN, G., ROSENBERG, B. (2001): Are PCBs in the Canadian Arctic Atmosphere Declining? Evidence from 5 years of monitoring; *Environmental Science and Technology* 35, 1303-1311.
- KELLERHALS, M., BEAUCHAMP, S., BELZER, W., BLANCHARD, P., FROUDE, F., HARVEY, B., McDONALD, K., PILOTE, M., POISSANT, L., PUCKETT, K., SCHROEDER, B., STEFFEN, A., TORDON, R. (2003): Temporal and spatial variability of total gaseous mercury in Canada: preliminary results from the Canadian atmospheric mercury measurement network (CAMNet); *Atmospheric Environment* 37, 1003-1011.
- LINDQVIST, O., RODHE, H. (1985): Atmospheric Mercury – a review; *Tellus*, 37B, 136-159.
- NAKAZAWA, T., ISHIZAWA, M., HIGUCHI, K., TRIVETT, N. B. A. (1997): Two curve fitting methods applied to CO<sub>2</sub> flask data; *Environmetrics* 8, 197-218.
- POISSANT, L. (2002): Mercury surface-atmosphere gas exchange in Lake Ontario/St. Lawrence river ecosystem; *Rev. Sci. Eau* 15 (Special), 229-239.
- ROTTY, R. M. (1987): Estimates of Seasonal Variation in Fossil Fuel CO<sub>2</sub> Emission; *Tellus* 39B, 184-202.

## Mercury Air-Water Gas Exchanges: Modeled Vs. Observed Flux in the Bay Saint-François Wetlands

HELEN HONG ZHANG<sup>1</sup>, LAURIER POISSANT<sup>2, 3, 4\*</sup>, XIAOHONG XU<sup>1</sup>, MARTIN PILOTE<sup>2</sup>, CONRAD BEAUVAIS<sup>2</sup>, MARC AMYOT<sup>5</sup>, EDENISE GARCIA<sup>5</sup> AND JEROME LAROULANDIE<sup>6</sup>

<sup>1</sup>Department of Civil and Environmental Engineering, University of Windsor, Canada.

<sup>2</sup>Environment Canada, 105 McGill (7<sup>th</sup> floor), Montréal, Québec, H2Y 2E7, Canada;  
E-mail: Laurier.Poissant@EC.GC.CA.

<sup>3</sup>Institut des sciences de l' environnement, Université du Québec à Montréal, Canada.

<sup>4</sup>Collaborative Mercury Research Network Initiative, Canada.

<sup>5</sup>Université de Montréal, Canada.

<sup>6</sup>Institut national de la recherche scientifique - centre Eau, Terre, Canada.

**Abstract:** An intensive field study on mercury (Hg) air-water exchange flux was conducted in the Bay St-Francois (BSF) wetlands in summer 2003. Hg air-water flux was measured using a dynamic flux chamber (DFC) coupled with a Tekran® analyzer. Based on a two-layer model and a model by BOUDALA (2000), several new models were developed and used for Hg flux estimation. The predicted Hg flux using the original and the improved models were compared with the measured one. Great improvements (62%–95%) were made by using the newly improved models. These newly developed models could help us in estimating Hg emission from water body to the atmosphere in wetlands, which is an important part of Hg global budget.

**Keywords:** Mercury, Two-layer model, Wetlands, Air-water exchange flux

### INTRODUCTION

Mercury (Hg) is a well-known hazardous, bio-accumulative global pollutant. Aquatic ecosystem and especially wetlands are important environments for Hg biochemical transformation and cycling. Hg air-water flux was measured in the Bay St-Francois (BSF) wetlands (Figure 1) on the Lake St. Pierre, Quebec, Canada (46°06'53.5"N,

72°55'45.8"W) in July 2003. Hg flux was measured by using a dynamic flux chamber (DFC) coupled with a Tekran® analyzer. Detailed flux calculation using DFC can be found in POISSANT (1998). Some meteorological factors such as net radiation, air and water temperature were monitored to investigate environmental effects on Hg air-water exchange flux.

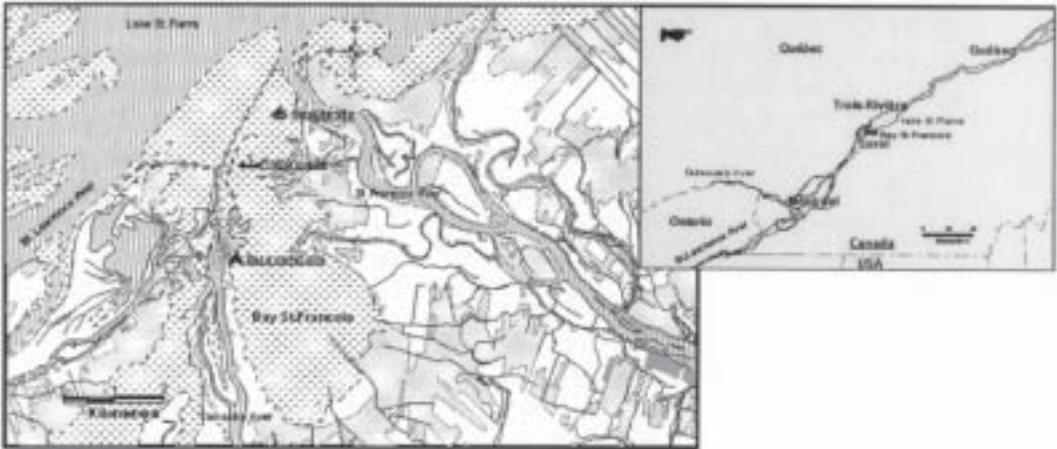


Figure 1. Map of the study site at the Bay St. Francois (Quebec, Canada).

Several new models based on a two-layer gas-exchange model and a model by BOUDALA (2000) were developed and applied to predict Hg flux over water. The flux calculated using the newly developed models were compared with the observed flux. The two-layer model is based on Hg concentration equilibrium between the vapor and dissolved phase and can be expressed as:

$$F = K (C_w - C_a / H') \quad (1)$$

where  $F$  is the predicted Hg air-water flux ( $\text{ng}/\text{m}^2/\text{h}$ ),  $K$  is the mass transfer coefficient ( $\text{m}/\text{h}$ ),  $C_w$  and  $C_a$  are the dissolved gaseous mercury (DGM,  $\text{pg}/\text{l}$ ) in water and the total gaseous mercury (TGM,  $\text{ng}/\text{m}^3$ ) in air, respectively,  $H'$  is the dimensionless Henry's Law constant and is a temperature-adjusted parameter. In a study conducted by POISSANT (2000), the following equation was used to calculate  $K$  value for Hg flux estimation over the Upper St. Lawrence River and Lake Ontario:

$$K = (0.45U_{10}^{1.64}) [Sc_w(\text{Hg}) / Sc_w(\text{CO}_2)]^{0.5} \quad (2)$$

where  $U_{10}$  is the wind speed at 10 m height,  $S_w(\text{Hg})$  and  $S_w(\text{CO}_2)$  are Schmidt numbers for  $\text{Hg}^0$  and  $\text{CO}_2$ , respectively. Equation (2) is used to predict Hg emission from open water and the estimated flux is wind speed dependent. However, this equation might not be applied to BSF site, which is covered by water, soil and vegetation. After rearranging Equation (2), a simple and explicable equation is derived as follows:

$$K = K'S \quad (3)$$

where  $K'$  is a meteorological dependent parameter, and  $S$  represents the term:  $[Sc_w(\text{Hg}) / Sc_w(\text{CO}_2)]^{0.5}$ . The improvements of  $K'$  were sought in this study.

Hg flux ( $F$ ) over water was also estimated using a model by BOUDALA (2000) based on the strong correlation of Hg flux with wind speed and solar radiation:

$$F = BRU_{10}^i + c \quad (4)$$

where  $R$  is the net radiation ( $\text{kW}/\text{m}^2$ ),  $B$ ,  $i$  and  $C$  are fitted constants.

The empirical parameters in the two models (eq. 3 and 4) were derived from the data obtained during the first sampling period (June 14~16,2003), then the developed models

were applied to the second study period (June 18~20,2003). The newly developed models were then evaluated by using the statistical indexes shown in Table 1.

**Table 1.** Statistical indexes used for model evaluation

Index	Mean Absolute Error (MAE)	Root Mean Square Error (RMSE)	Normalized Mean Square Error (NMSE)
Equation	$MAE = \frac{1}{N} \sum  C_0 - C_p $	$RMSE = \sqrt{\sum \frac{1}{N} (C_0 - C_p)^2}$	$NMSE = \frac{(C_0 - C_p)^2}{C_0 C_p}$

Note:  $C_0$  and  $C_p$  are the observation and prediction values, respectively, N is the sample number

## RESULTS AND DISCUSSION

The following equations summarized in Table 2 were the newly developed models for Hg air-water exchange flux. Equations (5) ~ (7) were the K value used in the two-

layer model and equation (8) is the modified model based on the one by BOUDALA (2000). The predicted Hg fluxes using the original and the improved models were compared with the measured flux. The statistical evaluation of each model is shown in Table 3.

**Table 2.** The newly developed models based on the two-layer model and the one proposed by Boudala

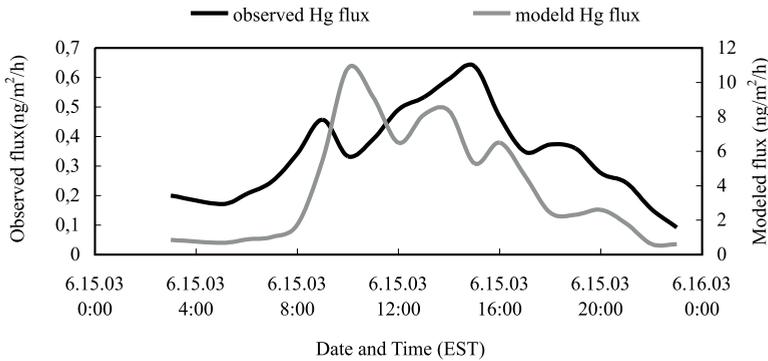
Developed models	(Eqn.)	Description
$K = U_{10}^{0.03} S$	(5)	$U_{10}$ (m/s) is the wind speed at 10 m height
$K = 0.535 \exp^{2.8R} S$	(6)	R is the net radiation (kW/m <sup>2</sup> )
$K = 0.005 \exp^{0.25T} S$	(7)	T is the water temperature (°C)
$F = 1.7RU_{10}^{0.005} + 0.5$	(8)	R is the net radiation (kW/m <sup>2</sup> ); $U_{10}$ (m/s) is the wind speed at 10 m

**Table 3.** Statistical evaluation of original and newly developed models during the two study periods

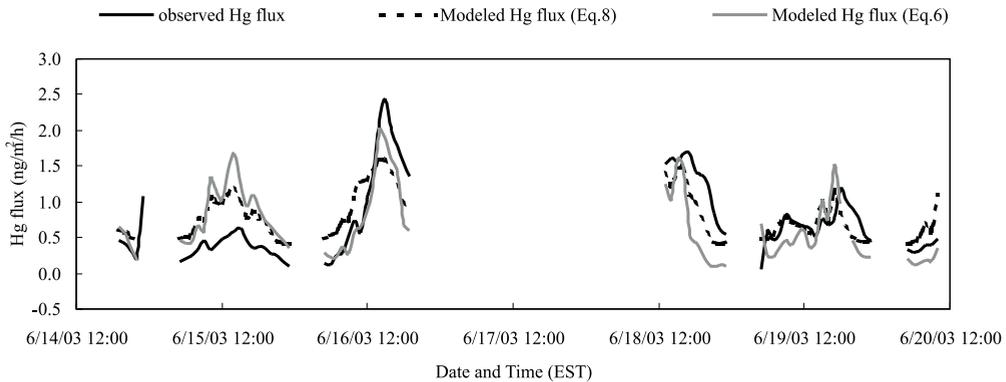
Sampling period	Indexes	equation 3	equation 5	equation 6	equation 7	equation 8
June 14~16, 2003	MAE	2.32	0.64	<b>0.26</b>	0.36	0.39
	RMSE	3.57	0.70	<b>0.38</b>	0.46	0.43
	NMSE	8.40	1.00	0.42	0.43	<b>0.37</b>
June 18~20, 2003	MAE	1.26	0.41	0.42	0.39	<b>0.26</b>
	RMSE	1.67	0.58	0.55	0.50	<b>0.35</b>
	NMSE	1.92	0.73	0.63	0.61	<b>0.22</b>

It is noticed from Table 3 that the newly developed models performed well compared with the original model (eq. 2). Hg flux using the original model (eq.2) on some day

was overestimated. For example, on June 15, the modeled flux using the original eq. (2) is one order greater than the observed one as shown in Figure 2.



**Figure 2.** The observed Hg flux and the original modeled flux (eq. 2) on June 15, 2003.



**Figure 3.** Observed and the predicted Hg flux using the newly developed models.

The newly developed models improved approximately 62%~95% compared with the original model (eq. 2), especially with equations (6) and (8). The time series of the observed flux and the modeled one using eqs. (6) and (8) is shown in Figure 3. As can be seen, Hg fluxes predicted by the newly improved models were of the same order as the measured value and have the similar pattern: the flux reaches maximum around late noon and minimum flux occurred during night or early morning.

## CONCLUSIONS

Hg air-water exchange flux was measured in the BSF wetlands in summer 2003. Several new models were developed and applied for air-water Hg flux estimation. The newly developed models performed well compared with the original model. These newly developed models could help us in predicting Hg emissions from water body in wetlands, which is an important part of mercury global budget.

## Acknowledgements

This project is sponsored by Nature Sciences and Engineering Research Council of Canada, Collaborative Mercury Research Network Initiative and Environment Canada.

## REFERENCES

- LISS, P. S. AND SLATER, P. G. (1974): Flux of gases across the air-sea interface; *Nature*, Vol. 247, pp.181-184.
- BOUDALA, F. S., FOLKINS, I., BEAUCHAMP, S., TORDON, R., NEIMA, J. AND JOHNSON, B. (2000): Mercury flux measurements over air and water in Kejimikujik national park, Nova scotia; *Water, Air, and Soil Pollution.*, Vol. 122, 183:202.
- POISSANT, L. AND CASIMIR, A. (1998): Water-air and soil-air exchange rate of total gaseous mercury measured at background sites; *Atmos. Environ.*, Vol. 32, pp. 883-893.
- POISSANT, L., AMYOT, M., PILOTE, M. AND LEAN, D. (2000): Mercury Water-Air Exchange over the Upper St. Lawrence River and Lake Ontario; *Environmental Science Technology.*, Vol. 34, pp. 3069-3078.

# Mercury Associated with Size-Segregated Airborne Particulate Matter

HUI ZHOU, XINJIE SONG<sup>[1]</sup>, JULIA LU<sup>[2]</sup>

Department of Chemistry and Biology, Ryerson University  
350 Victoria St. Toronto ON Canada

<sup>[1]</sup>Email: xsong@ryerson.ca

<sup>[2]</sup>Email: julialu@ryerson.ca

**Abstract:** Thermal desorption combined with Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) was used to determine the concentrations of total filterable mercury in Downtown Toronto in 2004. Simultaneously the concentrations of mercury associated with airborne particulate <2.5  $\mu\text{m}$  matter (PM<2.5) were measured by Tekran mercury speciation unit at the same location. The results so far obtained from Jan. to March 2004 showed that the concentrations of total filterable mercury range from 5.40 to 135.04  $\text{pg}/\text{m}^3$ . Those of PM<2.5 are from below detection limit ( $\sim 0.01 \text{ pg}/\text{m}^3$ ) to 56.59  $\text{pg}/\text{m}^3$ . The 61.54 % of PM<2.5 distributed to the concentration range from 10.00 to 50.00  $\text{pg}/\text{m}^3$ ; 73.08 % of PM>2.5 stood between the same range of mercury concentrations as PM<2.5. The surface air temperature was found to be inversely correlated with the concentrations of PM<2.5.

**Key words:** total filterable mercury; size-segregated airborne particulate mercury; thermal desorption; CVAFS

## INTRODUCTION

Mercury is one of the most toxic elements on the earth and it is widely distributed in the natural environment. More importantly, mercury can be transformed into much more toxic organic species that can be readily accumulated in the food chain. Therefore, mercury is one of the serious concerns for human health nowadays. The atmosphere is the major pathway of transporting mercury from sources of emission and distributing it in the environment. Even though particulate Hg generally constitutes only a small part of the total airborne Hg<sup>[1]</sup>, recent studies have shown the important role of particulate Hg

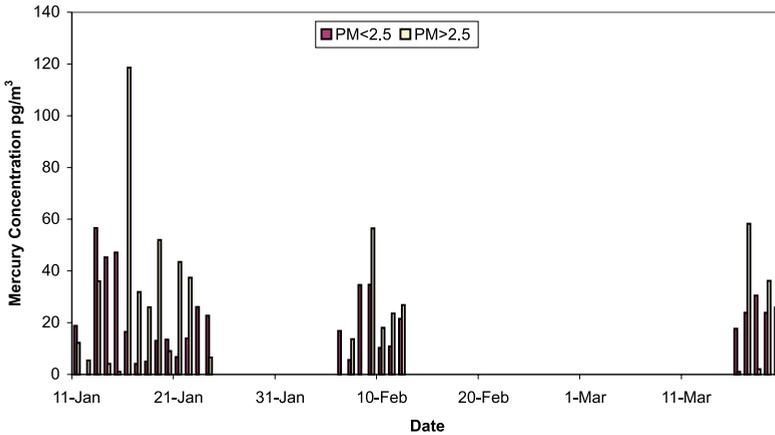
in determining both the wet and dry deposition flux of this toxic element <sup>[2,3]</sup>. Fine particles can stay in the atmosphere longer thus travel farther from sources of emission. These particles can enter human respiration system, causing health problems. Information on the distribution of mercury among airborne particles of different sizes is still scarce. In this study, the concentrations of total filterable mercury (TFM) and mercury associated with particles having size <2.5  $\mu\text{m}$  (PM<2.5) were measured in Downtown Toronto, Canada used methodologies based on thermal desorption and cold vapor atomic fluorescence spectrometry (CVAFS).

**RESULTS AND DISCUSSION**

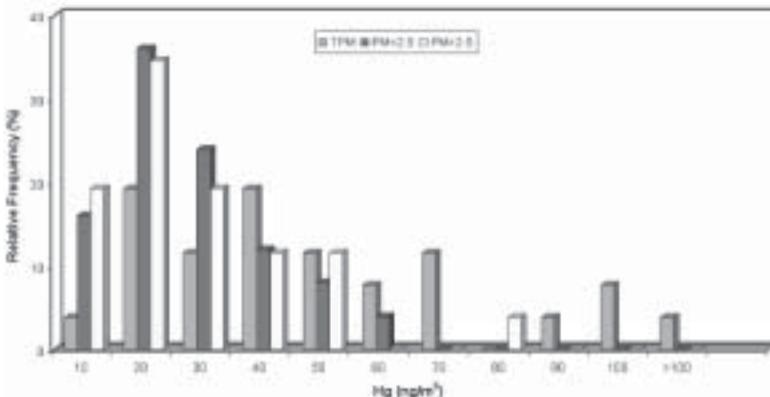
The results obtained from January to March 2004 showed that the concentrations of total filterable mercury (TFM) ranged from 5.40-135  $\mu\text{g}/\text{m}^3$ . Those of  $\text{PM}<2.5$  were from below the detection limit (BDL,  $\sim 0.01 \text{ pg}/\text{m}^3$ ) to 56.59  $\text{pg}/\text{m}^3$  and the concentrations of  $\text{PM}>2.5$  range from BDL to 119  $\text{pg}/\text{m}^3$  (Figure1). Figure 1 also showed that the majority of PM was the mercury associated with particulate whose size was bigger than 2.5  $\mu\text{m}$ .

Log-normal distribution pattern were clearly shown for  $\text{PM}<2.5$  and  $\text{PM}>2.5$  in Figure 2 while TPM has a relative random distribution. Table 1 summarized the monthly ranges of mercury distribution.

In addition, an anti-correlation between the daily concentration of  $\text{PM}<2.5$  and the surface temperature was observed during this period of experiments (Figure 3). Mercury condenses to the surface of the existing particles in the atmosphere when the air temperature drops, leading to the increase in the concentration of  $\text{PM}<2.5$ .



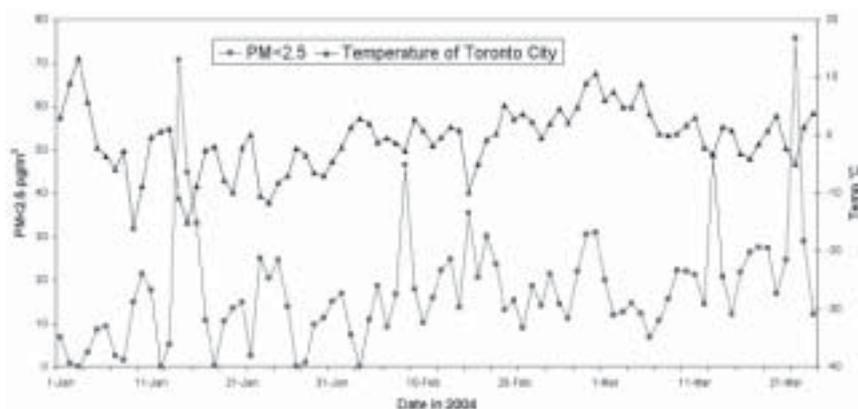
**Figure 1.** Comparison of daily  $\text{PM}<2.5$ ,  $\text{PM}>2.5$  from January- March 2004



**Figure 2.** Frequency distributions of TFM,  $\text{PM}<2.5$  and  $\text{PM}>2.5$

**Table 1.** Statistical summary of TFM and PM<2.5 frequency distributions January- March 2004 (RF- Relative Frequency)

		$\leq 10 \text{ pg/m}^3$	$10-50 \text{ pg/m}^3$	$50-100 \text{ pg/m}^3$	$\geq 100 \text{ pg/m}^3$
TFM	Jan.	1	8	4	1
	Feb.	0	6	1	0
	Mar.	0	2	3	0
	Total	1	16	8	1
	RF %	3.84	61.54	30.77	3.84
PM< 2.5	Jan.	4	8	1	0
	Feb.	1	6	0	0
	Mar.	0	5	0	0
	Total	5	19	1	0
	RF %	19.32	73.08	3.84	0.00

**Figure 3.** Time series of PM<2.5 and surface air temperature in downtown Toronto, Canada, January – March 2004

## CONCLUSIONS

The daily concentrations of TFM and PM<2.5 (and thus  $[\text{PM}>2.5] = \text{TFM} - [\text{PM}<2.5]$ ) were obtained by Thermal desorption combined with Cold Vapor Atomic Fluorescence Spectrometry (CVAFS), whose frequency distribution was analyzed in this study. The data showed certain relationship between the concentration of PM<2.5 and air-borne temperature.

## Acknowledgements

This work was supported by the Chinese Scholarship Council (CSC), the Metals in the Environment Research Network, Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Foundation for Innovation (CFI), and Ryerson University.

## REFERENCES

- <sup>[1]</sup> SCHROEDER, W. H., MUNTHE, J. (1998): Atmospheric mercury- An overview. *Atmospheric Environment* 32/5, pp. 809-822.
- <sup>[2]</sup> KEELER, G., GLINSORN, G., PIRRONE, N. (1995): Particulate mercury in the atmosphere: Its significance, transport, transformations and sources. *Water Air Soil Pollutant* 80, pp. 159-168.
- <sup>[3]</sup> LU, J. Y., SCHROEDER, W. H. (2004): Annual time series of Total Filterable Atmospheric Mercury Concentration in the Arctic. *Tellus*, in press.