3.4 MERCURY MONITORING IN THE VICINITY OF COAL-FIRED POWER PLANTS IN ALBERTA, CANADA

Rachel Mintz*, Maxwell Mazur, Monique Lapalme, Magdalena Scarlat, Sushmitha Gollapudi, Brian Wiens

Environment Canada

1.0 INTRODUCTION

The Lake Wabamun area in western Canada has the highest concentration of electricity generating coal-fired power plants in the country, with four power plants located within 500 km^2. Together they are the largest industrial source for atmospheric mercury emissions in the province of Alberta. Coal combustion accounts for over half of total global atmospheric mercury emissions (Wang et al., 2009). Coal-fired power plants with both standard and current technologies have been found to emit primarily vapor phase elemental mercury and reactive gaseous mercury (Pacyna et al., 2006). In addition to mercury, these power plants also emit large quantities of sulphur dioxide (SO_2) and oxides of nitrogen (NO_x) into the air (NPRI, 2006). The Lake Wabamun region therefore provides the unique opportunity to investigate ambient mercury concentrations in the vicinity of four coal-fired power plants due to the lack of other significant sources in the region. This study describes four months (January – April, 2009) of speciated mercury data in relation to air quality data collected near the coal-fired power plants. The study also compares the speciated mercury results to the Lake Wabamun total gaseous mercury (TGM) measurements and analysis described in Mazur et al. (2009).

2.0 MONITORING PROGRAM

The Lake Wabamun area is a rural area located in Parkland County (population 29,679; Parkland County, 2008). The primary industrial activities in the Lake Wabamun region are electrical power generation, involving the four coal-fired power plants, as well as associated coal mining and oil and gas production. There are thousands of oil and gas wells in central Alberta and these oil and gas wells are located in all directions surrounding the Lake Wabamun region. In addition to the industrial sources, the region is also influenced by agricultural activity. The nearest urban centre to the Lake Wabamun area is the city of Edmonton (population 752,412; City of Edmonton, 2008), located 60 km to the east.

Major emitters in the Edmonton area include oil refineries and chemical manufacturing plants, and these large facilities are located on the northeastern edge of Edmonton or in Fort Saskatchewan, an additional 15-40 km from the city centre. The city of Edmonton is predominantly downwind of the coal-fired power plants. To the west of the study region are small towns and foothills leading up to the Canadian Rocky Mountains and Jasper National Park. The location of the study region in Canada is shown in Figure 1 and a wind rose, calculated using hourly wind data from 2004 to 2008, is shown in Figure 2.

TGM and speciated mercury concentrations were recorded at the Genesee monitoring station. Prior to March 2009, TGM measurements were also taken at the Meadows station. The focus of this report is the Genesee air monitoring station, which is located 10 km southeast of Power Plant D, on agricultural land near an active mine producing coal for Power Plant D. The location of the monitoring station in relation to Power Plant D and the other coal-fired power plants A, B and C is shown in Figure 1. Table 1 presents the four power plants' NO_x, SO_2 and mercury air emissions for the year 2006, as reported to Environment Canada's National Pollutant Release Inventory (NPRI, 2007).

Table 1. Lake Wabamun air emissions reported to NPRI for 2007

Power Plant	NO_x (tonnes)	SO_2 (tonnes)	Hg (tonnes)
A	3,355	5,409	0.053
B	25,533	26,670	0.322
C	11,515	13,026	0.127
D	13,144	16,911	0.128
Total	53,547	62,016	0.630

*Corresponding author: Rachel Mintz, Environment Canada, Rm 200. 4999-98 Ave, Edmonton AB Canada, T6B 2X3; email: Rachel.Mintz@ec.gc.ca

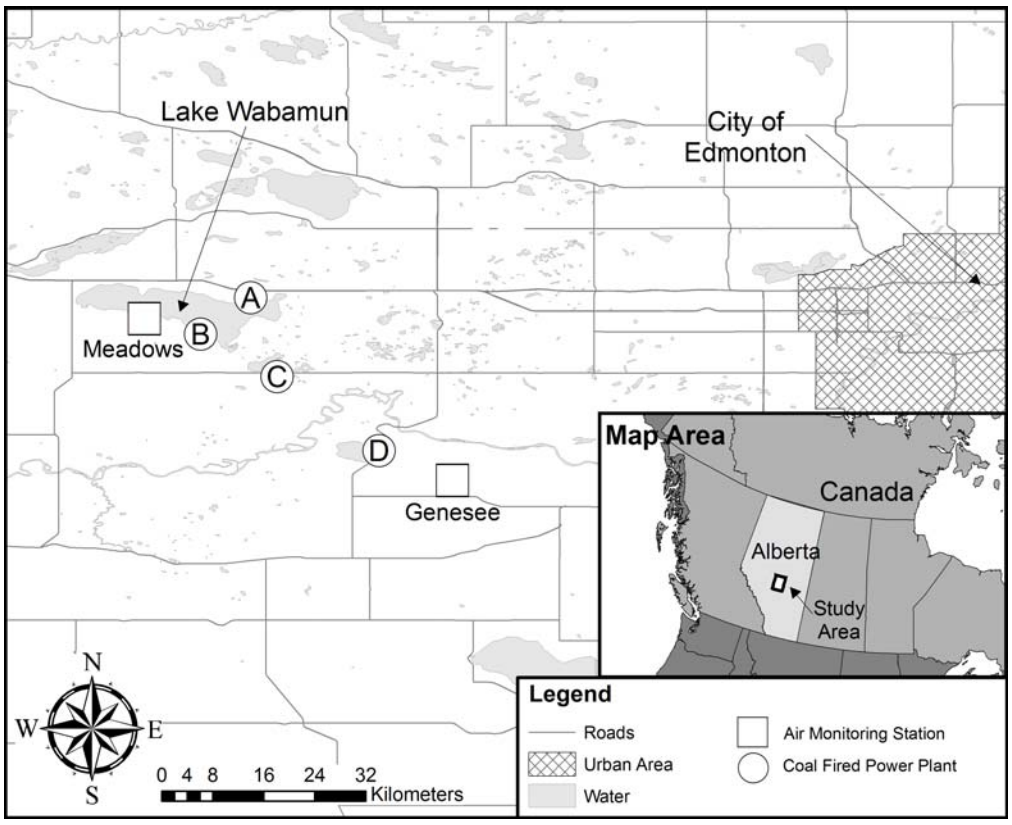

Figure. 1. Location of the air monitoring stations, coal-fired power plants and the city of Edmonton. Location of the study area within Western Canada is shown in the inset.

Environment Canada operates a Tekran Model 2537A Mercury vapor analyzer at Genesee, where this instrument has been providing continuous data since 2004. In January 2009, Environment Canada installed a Tekran 1130 and 1135 to measure speciated mercury {gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) and particulate mercury (PHg)}. The speciated mercury data was quality controlled using concurrent analysis of baseline voltage, sample volume, auto-calibration values and meteorological data. The West Central Airshed Society operates continuous NO_x, SO_2 and $PM_{2.5}$ monitors at the Genesee station. A TECO 42C is used to measure NO_x, a TECO 43BS is used to measure SO_2 and a TEOM (Tapered Element Oscillating Microbalance) instrument continuously monitors PM2.5. Additionally, wind speed and wind direction are monitored with a Climatronics 432 instrument. Data from the West Central Airshed Society was obtained through the Clean Air Strategic Alliance Data Warehouse, which provides quality controlled data for public use (CASA, 2008).

3.0 RESULTS AND DISCUSSION

The summary statistics for the speciated mercury data and other air quality parameters (NOx, SO_2 and PM2.5) collected during January – April, 2009, are shown in Table 2. The values of the speciated mercury concentrations were recorded continuously at Genesee station every two hours, and so the hourly data for NO_x, SO_2 and $PM_{2.5}$ were adjusted to match the recording time of the mercury data.

Figure 2 shows the prevailing winds in the Wabamun region to be from the west-northwest, with occasional winds from the southeast. As a result, Genesee is typically downwind of the coal-fired power plants.

The monitoring data was averaged over wind direction quadrants, as shown in Table 3. The SO_2 and RGM averages are noticeably higher from the 270° to 360° wind direction. The NOx and GEM are also elevated for the NW quadrant relative to the other quadrants. Table 3 also shows the ratios of NOx/GEM, SO_2/GEM and RGM/GEM.

Table 2. Concentration statistics for Genesee, January to April 2009*

Substance	Mean	Median	Std Dev	Max
GEM(ng/m3)	1.52	1.52	0.172	3.22
NO_x(ppm)	0.005	0.004	0.005	0.058
SO_2(ppm)	0.001	0	0.002	0.029
PM2.5(ug/m3)	3.61	3.00	2.96	28.4
RGM (pg/m3)	4.70	2.31	7.49	128.23
PHg (pg/m3)	5.91	4.07	9.46	156.19

* Number of hourly points is 1049.

Table 3. Average parameter concentrations for each wind direction quadrant Genesee, January to April 2009

Quadrant	NO_X (ppm)	PM2.5 (ug/m3)	SO_2 (ppm)	GEM (ng/m3)	PHg (pg/m3)	RGM (pg/m3)	NO_X/GEM (ug/ng)	SO_2/GEM (ug/ng)	RGM/GEM (pg/ng)
1 (0º-90º)	0.0047	4.0508	0.0005	1.5007	6.8404	3.6836	5.7970	0.8421	2.2398
2 (90º-180º)	0.0052	4.0715	0.0005	1.5271	6.7341	3.9112	6.6805	0.9261	2.5752
3 (180º-270º)	0.0044	2.8162	0.0005	1.4906	6.2312	4.1243	5.6475	0.7998	2.8064
4 (270º-360º)	0.0053	3.5729	0.0009	1.5512	4.7764	5.9973	6.3254	1.4549	3.7317

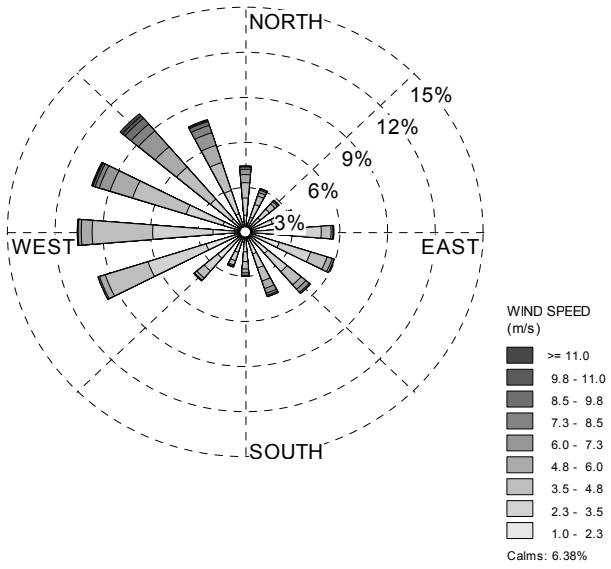

Fig. 2. Wind rose from the Genesee monitoring station, 2004-2008.

Table 4 summarizes the correlation coefficients (r^2) between the mercury species with NO_x and SO_2 concentrations for the entire data set. The RGM-NO_x correlation gives an r^2 value of 0.056, while the RGM-SO_2 relationship gives an r^2 value of 0.268. GEM has significantly lower correlations of 0.005 and 0.081 with NO_X and SO_2 respectively. This result is possibly due to the global nature of GEM, such that it has a long atmospheric lifetime and broader scale for variation (Manalopoulos et al., 2007). In comparison, the more reactive RGM has a shorter atmospheric lifetime since it is deposited quickly in close proximity to emission sources on a local or regional scale. The RGM-GEM relationship gives an r^2 value of 0.069. This relatively low value indicates that high RGM is not necessarily associated with high GEM values, and vice versa. It also lends further support to the difference in behavior between the two mercury species because of atmospheric residence time. Particulate mercury is found to be weakly correlated with NO_x, and has no correlation with GEM levels.

Table 4. Correlation coefficients between RGM, GEM and PHg values, and NO_x and SO_2 for the Genesee January to April 2009 dataset

	NO_X	SO_2	GEM
RGM	0.056	0.268	0.069
GEM	0.005	0.081	1
PHg	0.011	0.001	0

4.0 COMPARISON OF MERCURY STUDIES

Mazur et al. (2009) looked at the TGM concentrations in Lake Wabamun from 2004 to 2008. The lack of correlation between TGM and the other air quality parameters led Mazur et al. to investigate the high TGM episodes. The objective of the episode analysis was to find a relationship between the variables that might suggest a coal-fired power plant influence. Mazur et al. found episodes of elevated TGM, NO_x and SO_2 from the NW wind direction. Mazur et al. also confirmed the contribution of TGM from the coal-fired power plants with AERMOD modeling.

This study undergoes the same episode analysis technique from Mazur et al. in order to compare the RGM and GEM results to Mazur's TGM results. Since TGM = RGM and GEM and the majority of TGM is GEM (Ames et al.,1998), it was expected that this study's GEM results would be similar to Mazur's TGM results. A limitation to this comparison is that this study uses only four months of speciated data, whereas Mazur et al. used five years of TGM data.

Of particular interest are the high mercury levels with corresponding high NO_x and SO_2, due to the association of these pollutants with coal-fired power plant emissions. Mazur et al. approached the episode analysis using TGM as the marker. In this study, we conducted the episode analysis twice: once with GEM as the marker and once with RGM as the marker. In order to examine the high episodes, the data were divided into sub-sets based on GEM or RGM concentrations and wind direction. The first split in the Genesee data was chosen by defining a GEM or RGM threshold of higher than 2 standard deviations above the mean (>1.86 ng/m^3 for GEM and >19.68 pg/m^3 for

RGM). Data were then subsequently split into samples with northwest winds (270° – 360°), all other wind directions and data with NO_x and SO_2 greater than 1 standard deviation above the mean (NO_x >0.01 ppb and SO_2 >0.003ppb). Tables 5 and 6 summarize the statistics for each of the data sub-sets with GEM and RGM as the markers.

An episode may consist of contiguous hours on a given day with values above the GEM or RGM threshold. For example, applying the criterion for high RGM (>19.68 pg/m^3) over the four months of data collected at Genesee identified 38 hourly points, but from the 38 hourly points, 25 distinct episodes are identified.

Average NO_x/GEM and SO_2/GEM ratios were calculated for each of the data sub-sets and are presented in Tables 5 and 6. The ratios were determined, per episode, by finding the highest RGM or GEM concentration in the episode and then calculating the ratio from the corresponding GEM, NO_x and SO_2 concentrations.

As expected, Table 5 shows similar results to Mazur et al. since TGM consists mostly of GEM. There is elevated GEM from the NW wind direction, but there is higher GEM from the other wind directions. Only one episode was found in the sub-set with GEM above 2 standard deviations) and high NO_x and SO_2 (above 1 standard deviation). The ratio of NO_x/GEM and SO_2/GEM is slightly higher than the ratio determined for the similar sub-set in Mazur et al. (NO_x/TGM = 21.71 and SO_2/TGM = 19.98). The RGM for the one episode in this sub-set is considerably elevated above the average for the entire data set. Table 5 also shows that when the data is split into [GEM > 2 std dev and NW winds] and [GEM > 2 std dev and other wind direction], the resulting RGM averages for the sub-sets is approximately equal. This means that high RGM is not necessarily associated with winds from the NW.

Table 6 shows the episodes identified when RGM is focused on as the primary marker. In this case, more episodes are identified because RGM is the more local or regionally affected mercury species, and thus shows greater variability. There are a number of episodes with high RGM, and elevated NO_x and SO_2 associated with NW winds. The ratios of NO_x/GEM and SO_2/GEM using RGM as the marker result in values on par with the Mazur et al. study.

Note the NO_x/GEM and SO_2/GEM ratios where RGM or GEM > 2 std dev with NW winds and NO_X and SO_2 > 1 std dev, in Tables 5 and 6 as well as in Mazur's TGM ratios. An interesting finding here is that the values of the ratios NO_x/GEM:SO_2/GEM and NO_x/TGM :SO_2/TGM both approach 1. Looking back at Table 1, the annual reported emissions from the coal-fired power plants show an approximate 1:1 ratio between NO_x emissions and SO_2 emissions. Thus, despite the day-to-day variations in emitted species, the episodes analysis is identifying a representative proportion of NO_x and SO_2 to mercury (GEM or TGM).

Table 7 shows the percentage of episodes identified in each of the data sub-sets in the Mazur et al. study and in Tables 5 and 6. The Mazur paper data set consisted of 27,488 points, of which 815 hourly points had TGM values greater than two standard deviations, and 197 episodes were subsequently identified. In comparison, this study's dataset consisted of 1049 hourly points, 38 points with RGM greater than two standard deviations, and 25 distinct episodes. From the results of this study, 3.6% of total hourly points were high RGM, and 24% of the episodes were in the category of high RGM, northwest winds and high NO_x and SO_2. In the Mazur paper, 2.96% of total hourly points were high TGM, and 46% of the episodes were in the category of high TGM, northwest winds and high NO_x and SO_2. The percentage of episodes identified by high GEM or RGM with elevated NOx and SO_2 from the NW is smaller in this study than in Mazur et al. This can be attributed to the fact that our study's data only represents a winter/spring season.

This study found an abnormally high RGM concentration of 128.23 pg/m^3 on March 16, 2009. The concentrations of PHg, GEM, SO_2 and NO_x also increased up to when this high RGM value was recorded, after which they all dropped off significantly with the exception of PM2.5. PM2.5 remained relatively constant throughout this episode. The wind direction values were from the NW direction leading up to the high RGM value, but winds switched to the northeast direction at the time of the highest RGM measurement. For this reason, the episode was binned under "winds from the other wind direction" in Tables 5 and 6 even though there was influence from the NW wind direction leading up to the episode.

5.0 CONCLUSIONS

This study summarized the speciated mercury data measured at the Genesee station from January – April 2009. The data was compared to the Mazur et al. (2009) study that investigated TGM measurements at the Genesee station. The results were similar between the Mazur et al. and this study despite the limited number of data in the latter study, and the difference in measuring speciated mercury versus TGM mercury. This study also found a correlation between RGM and SO_2 at the Genesee station. This implies that RGM, as opposed to TGM and GEM, is a more sensitive indicator for coal-fired power plants.

Table 5. Statistics of parameter groups identified through splitting of Genesee dataset with focus on GEM

Dataset split	No. of episodes	Average GEM (ng/m3)	Average NO_X (ppm)	Average SO_2 (ppm)	Average PM2.5 (ug/m3)	Average PHg (pg/m3)	Average RGM (pg/m3)	NO_X/GEM (µg/ng)	SO_2/GEM (µg/ng)
All data	N/A	1.520	0.005	0.001	3.61	5.91	4.70	6.62	1.08
GEM > 2 std dev (>1.86 ng/m3)	10	2.341	0.011	0.005	4.91	18.54	20.24	11.40	7.83
GEM > 2 std dev and NW winds	6	1.997	0.013	0.007	3.28	7.53	21.49	12.79	8.63
GEM > 2 std dev and other wind direction	4	2.724	0.008	0.003	6.71	30.77	18.85	9.31	6.65
GEM > 2 std dev, NW winds, NO_X and SO_2 > 1 std dev	1	2.157	0.033	0.023	6.21	8.50	34.09	33.40	32.00
GEM > 2 std dev, other wind direction, NO_X and SO_2 > 1 std dev	1	2.550	0.036	0.025	7.58	10.61	128.23	26.20	26.12

Table 6. Statistics of parameter groups identified through splitting of Genesee dataset with focus on RGM

Dataset split	No. of episodes	Average GEM (ng/m3)	Average NO_X (ppm)	Average SO_2 (ppm)	Average PM2.5 (ug/m3)	Average PHg (pg/m3)	Average RGM (pg/m3)	NO_X/GEM (µg/ng) RGM marker	SO_2/GEM (µg/ng) RGM marker
All data	N/A	1.52	0.005	0.001	3.61	5.91	4.70		
RGM > 2 std dev (>19.68 pg/m3)	25	1.70	0.009	0.004	3.71	7.45	32.76	10.23	5.69
RGM > 2 std dev and NW winds	15	1.74	0.0104	0.005	2.37	7.64	31.29	12.45	6.50
RGM > 2 std dev and other wind direction	10	1.63	0.006	0.003	5.77	7.16	35.01	7.34	4.64
RGM > 2 std dev, NW winds, NO_X and SO_2 > 1 std dev	6	1.85	0.017	0.010	2.50	6.82	34.13	19.63	15.37
RGM > 2 std dev, other wind direction, NO_X and SO_2 > 1 std dev	1	2.55	0.036	0.025	7.58	10.61	128.23	26.20	26.12

Table 7. Comparison of percentages of hourly points and episodes for TGM and speciated mercury species

	Mazur et al.		RGM marker		GEM marker
High TGM (% of hourly points)	2.96	High RGM (% of hourly points)	3.60	High GEM (% of hourly points)	1.81
High TGM, NW winds and high NO_X and SO_2 (% of episodes)	46	High RGM, NW winds and high NO_X and SO_2 (% of episodes)	24	High GEM, NW winds and high NO_X and SO_2 (% of episodes)	10

6.0 REFERENCES

Ames, M., Gullu, G., Olmez, I., 1998: Atmospheric mercury in the vapor phase, and in fine and coarse particulate matter at Perch River New York. *Atmos. Environ*., 32, 5, 865-872.

Clean Air Strategic Alliance (CASA): The Clean Air Strategic Alliance Data Warehouse. http://www.casadata.org (Accessed: November, 2009).

Manolopoulos, H., Snyder, D., Schauer, J., Hill, J., Turner, J., Olson, M., Krabbenhoft, D., 2007: Sources of speciated atmospheric mercury at a residential neighborhood impacted by industrial sources. *Environ. Sci. Technol*., 41, 5626-5633.

Mazur, M., Mintz, R., Lapalme, M., Wiens, B., 2009: Ambient air total gaseous mercury concentrations in the vicinity of coal-fired power plants in Alberta, Canada. *Sci. Total Environ*., 408, 2, 373-381.

National Pollutant Release Inventory (NPRI), Environment Canada, 2007: NPRI Reviewed Data Release. http://www.ec.gc.ca/pdb/npri/ (Accessed: November, 2009).

Pacyna, E., Pacyna, J., Steenhuisen, F., Wilson, S., 2006: Global anthropogenic mercury emission inventory for 2000. *Atmos. Environ*., 40, 4048-4063.

Wang, S., Zhang, L., Li, G., Wu, Y., Hao, J., Pirrone, N., Sprovieri, F., Ancora, M.P., 2009: Mercury emission and speciation of coal-fired power plants in China*. Atmos. Chem. Phys. Discuss*., 9, 24051-24083.