2006 - 2007 Measurements of Atmospheric Mercury Species at a Coastal Site in Atlantic Canada

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Abstract

Environment Canada has been continuously measuring the levels of three gaseous Hg species - gaseous elemental mercury (GEM), reactive gaseous mercury (RGM), particulate (P-Hg) fine fraction (<2.5 µm) - at an urban coastal site since January 2006. This poster illustrates and discusses data collected at our site in Halifax, Nova Scotia (Canada) from January 2006 to June 2007. The 18 month data set show GEM (5 minute sampling) having a median of ≈ 1.7 ng m^{-3} and a range of 0.72 to 46.5 ng m^{-3}; RGM (3 hour sample) a median of ≈ 2.5 pg m^{-3} with a range from the detection limit (dl) to 140 pg m^{-3} and P-Hg (3 hour sample) a median of 1.73 pg m^{-3} and a range from dl to 31 pg m^{-3}. The median levels of RGM and P-Hg are only a small percentage of the Total Gaseous Mercury (TGM), 0.14% for RGM and 0.10% for P-Hg.

Temporal trends of elevated GEM were noted in the spring and early summer with uniform levels observed in winter months. P-Hg events were more predominant in winter and early spring periods. For RGM, elevated levels occurred during the spring and early summer. A diurnal trend in RGM shows elevated levels beginning near mid day and continuing through the evening and night time period. The lowest levels of RGM are generally measured in the early morning to about noon. A diurnal trend for P-Hg was not evident.

RGM did show significant associations with air temperature, solar radiation and relative humidity. An observed trend of decreased levels of RGM during precipitation events coincided with the negative relationship observed with relative humidity. The significance of wind direction contributing to RGM levels was also observed and attributed to an effect from local sources. An analysis of air quality parameters versus Hg species show ozone having its most significant association with RGM and an inverse association with GEM. Also noted, were $PM_{2.5}$ and NO_2 have varying degrees of association with all three Hg species.

Methods

Atmospheric Hg species (Hg^0, RGM, and fine fraction <2.5 µm P-Hg) were sampled in the Halifax Regional Municipality from a third floor roof platform on a building located in Halifax, Nova Scotia (Canada). This site is located within one km from an active commercial harbour and a city population base of ~360,000.

The mercury analysis was carried out using the Tekran system incorporating the 2537A analyser and the 1130/1135 speciation sampling units. A Tekran air dryer unit (Model 1102) was used with the 1130 zero air supply to eliminate analytical artifacts. Our method sampled for a 3 hour composite RGM and P-Hg sample at a flow of 10 l/min. The RGM fraction was collected on a KCl-coated quartz denuder and the P-Hg was collected on the quartz filter. During the 3 hour sampling period, 5 minute integrated samples of Hg^0 were continuously quantified with the 2537A analysis unit.

The desorption cycle of one hour was a sequential transfer of the collected P-Hg and RGM to the 2537A analyser. During the first step, a pyrolyzer oven was heated to 850°C, to ensure complete decomposition of Hg compounds eluded from the P-Hg filter and RGM denuder. First the P-Hg filter was heated to 850° followed by the denuder (RGM) heated to 500°, each sequentially desorbed for 15 minutes. The Hg from the P-Hg and RGM samplers were quantified as Hg^0 by the 2537A unit. After this desorption step, the 1130/1135 sampling units were cooled for 10 minutes before the beginning of the next sampling cycle. The denuder, quartz filter unit (Quartz Regenerable Particulate Filter assembly RPF) and impact disk were changed out biweekly. Prior to the first analysis cycle after "change out", both the denuder and RPF units were conditioned with a heating cycle (500°C denuder; 850°C RPF) of 30 minutes with zero air flow, followed by 15 minutes of cooling. The in-line sample filter (1µm glass fibre) was changed weekly.

For each analysis cycle, the analytical blanks for the 1130 (RGM) and 1135 (P-Hg) were determined from the average of the last two zero air values of each analysis cycle. The zero air mean value for the speciation units (1130 and 1135) was determined to be 0.07 pg m^{-3} (standard deviation 0.3 n=334). Our method detection limit for RGM and P-Hg was calculated to be ~0.83 pg m^{-3}. The detection limit for Hg^0 is ~0.2 ng m^{-3} (from Tekran).

Meteorological measurements (MET) were collected from May 2006 concurrently with the atmospheric mercury sampling. The MET data - air temperature, relative humidity (Campbell Scientific™ CS-500 temperature/RH sensor), solar radiation (LiCor LI200S solar pyranometer 400-1100 nm) and wind speed-direction (RM Young 05103) - was collected with 5 minute resolution. In May 2007, a Davis weather system (Vantage Pro2) replaced the Campbell weather system.

Illustration of the Tekran sampling apparatus and Davis weather system on the roof deck.

Results & Discussion

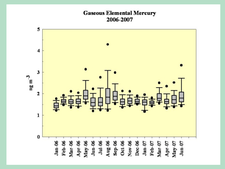
Statistical Summary of GEM, RGM and P-Hg measured is illustrated in the table to the right. The median concentration for GEM, RGM and P-Hg were 1.67 ng m^{-3} (0.72 to 46.5 ng m^{-3}), 2.42 pg m^{-3} (detection limit (dl) to 140 pg m^{-3}), and 1.73 pg m^{-3} (dl to 30.8 pg m^{-3}), respectively. The median levels of RGM and P-Hg were a small percentage of the GEM, 0.2% for RGM and 0.1% for P-Hg These results are similar to other recent studies where clean marine air was sampled.

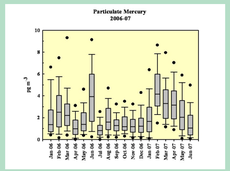
	GEM (3 hr avg) ng m^{-3}	RGM pg m^{-3}	P-Hg pg m^{-3}	GEM (5 min) ng m^{-3}
Min	0.91	dl	dl	0.72
Max	9.30	140	30.8	46.5
Mean	1.79	4.62	2.37	1.77
Median	1.69	2.42	1.73	1.67
SD	0.45	7.61	2.30	0.61
Sample #	2835	2835	2835	106283

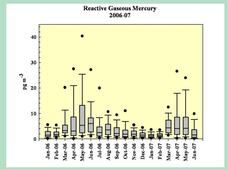
Temporal Trends (yellow whisker plots below)

GEM - elevated in the spring and early summer with lower levels in winter months

P-Hg - elevated events were more predominant in the winter and early spring periods







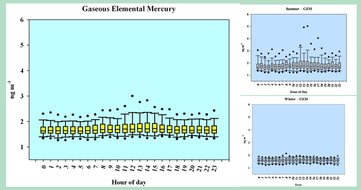
In the Temporal and Diurnal wisker-box plots the box boundary indicates 25th to 75th percentile with the line in the box marking the median, whisker lines illustrate the 10th to 90th percentiles and the data points outside the box are 5th to 95th

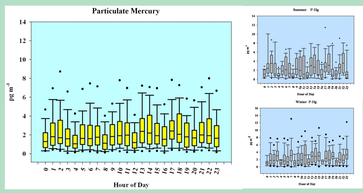
Diurnal Trends (blue whisker plots below)

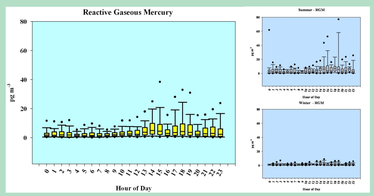
GEM - increase levels near midday and with more elevated events observed in summer while during winter little diurnal trend evident

P-Hg - little trend was evident in the diurnal cycle for this species and trend was likely due to the lack of significant local sources and/or the impact of the cleaner air from our coastal marine boundary layer

RGM - elevated levels begin near mid day and continue through the evening and night time period. The lowest levels of RGM were generally seen from early morning to about noon. The seasonal winter and summer diurnal trend in RGM show summer months as the period for RGM production in the Halifax air shed.







Meteorological data versus GEM, RGM and P-Hg in the table below show significant associations between RGM and air temperature, solar radiation and relative humidity. A trend of decreased levels of RGM during precipitation and fog events coincided with the negative relationship were observed in the data. Also, the significance of wind direction contributing to RGM levels was attributed to local anthro and non-anthropogenic sources.

	RH	Solar_Rad	W_spd	W_Dir	GEM	P-Hg	RGM
TEMP	0.0782	0.144	0.0703	0.214	0.347	-0.201	0.241
P	*0.000*	*0.000*	*0.002*	*0.000*	*0.000*	*0.000*	*0.000*
RH		-0.381	-0.0913	0.163	0.04	-0.388	-0.334
P		*0.000*	*0.000*	*0.000*	***0.074***	*0.000*	*0.000*
Solar_Rad			0.255	0.0774	0.0578	0.0573	0.0775
P			*0.000*	*0.000*	*0.010*	*0.011*	*0.000*
W_spd				0.497	-0.136	-0.0768	-0.0201
P				*0.000*	*0.000*	*0.000*	***0.370***
W_Dir					0.0304	-0.0482	0.193
P					***0.174***	*0.033*	*0.000*
GEM						0.0175	0.212
P						***0.439***	*0.000*
P-Hg							0.482
P							*0.000*

Air Quality Parameters versus GEM, RGM and P-Hg in the table below indicated for GEM versus SO_2; P-Hg versus O_3 and CO, no significant relationship exists between these Hg species and these air quality parameters. Ozone did have its most significant association with RGM and an inverse association with GEM. Also noted, was $PM_{2.5}$ and NO_2 have varying degrees of association with all three Hg species.

Spearman Rank Order Correlation matrix of coefficients and their P values for the atmospheric mercury species versus the MET and air quality data, pairs with P values > 0.05 (marked in bold), no significant relationship between the two

	P-Hg	RGM	SO_2	NO	NO_2	O_3	CO	PM_2.5
GEM	0.0325	0.249	0.0163	0.174	0.21	-0.0422	0.145	0.187
P	***0.091***	*0.000*	***0.388***	*0.000*	*0.000*	*0.025*	*0.000*	*0.000*
P-Hg		0.425	0.055	0.213	0.154	-0.0266	0.0125	0.247
P		*0.000*	*0.004*	*0.000*	*0.000*	***0.166***	***0.529***	*0.000*
RGM			0.0474	0.0969	0.174	0.194	0.223	0.286
P			*0.012*	*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
SO_2				0.194	0.308	-0.189	0.147	0.254
P				*0.000*	*0.000*	*0.000*	*0.000*	*0.000*
NO					0.798	-0.533	0.281	0.142
P					*0.000*	*0.000*	*0.000*	*0.000*
NO_2						-0.464	0.442	0.307
P						*0.000*	*0.000*	*0.000*
O_3							-0.0759	-0.052
P							*0.000*	*0.021*
CO								0.153
P								*0.000*

Future Work

Sampling will now be conducted in a rural location located in Kejimkujik National Park (Nova Scotia, Canada) starting in late October 2008.

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