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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Source-receptor relationships for speciated atmospheric mercury at the remote experimental lakes area, Northwestern Ontario, Canada" *by* I. Cheng et al.

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We greatly appreciate many detailed specific comments, which helped us to improve the paper. We have revised the paper accordingly as detailed below.

RC- Review Comments; AC – Authors' Comments

RC: In a number places, the authors attribute a correlation between elevated RGM and O3 to photochemical production. This may not always be the case, especially when elevated RGM and O3 are correlated with low RH. Elevated RGM, O3, and low RH are thought to be a signature of free tropospheric air (e.g. Weiss-Penzias et al., 2009, JGR) and this explanation needs to included. Based on 7Be and Hg simulations, Amos et al.

(2011, ACPD) suggests that springtime RGM at ELA is influence by free tropospheric air.

AC: We did not attribute a correlation between RGM and O3 to photochemical production. Instead we used the findings from Sillman et al. (2007) and examined correlations between GEM and RGM. Sillman et al. (2007) suggested positive GEM-RGM correlations could indicate RGM is directly emitted from sources, whereas negative correlations suggest photochemical production.

We have included a discussion on elevated RGM, O3, and low RH as indicators of free troposphere air in the revised paper (Sect. 3.1.3 Diurnal variability), as suggested by the reviewer.

"Elevated RGM and O3 concentrations and low relative humidity may be a signature of free troposphere air as discussed in Swartzendruber et al. (2006) and Weiss-Penzias et al. (2009). At the Mt. Bachelor Observatory site in Oregon, U.S., maximum diel RGM concentrations (>50 pg m-3) typically occurred at night along with elevated ozone (up to 60 ppb) and low water vapor (2.2 g/kg) (Swartzendruber et al., 2006). Maximum diel RGM concentrations for the three sites in Nevada, U.S. ranged from 55-140 pg m-3 during daytime along with higher ozone (ranging from 50-60 ppb) and low relative humidity ranging from 12-55% (Weiss-Penzias et al., 2009). Compared to the ELA site, the maximum diel RGM and O3 concentrations were on average 2.6 pg m-3 and 37 ppb, and relative humidity ranged from 56-83%. The large differences observed may be due to the different location, altitude and atmospheric circulation patterns affecting the sites. The downward transport of free troposphere air is believed to be driven by katabatic winds from mountains (Swartzendruber et al., 2006) and subtropical high pressure system affecting higher altitude western U.S. sites (Fiore et al., 2003; Weiss-Penzias et al., 2009) and tropical deserts (Arkian et al., 2010).

Surface measurements of beryllium-7 (7Be), a cosmogenic radioactive nuclide found mainly in the stratosphere, and RGM may be useful for examining whether the free

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troposphere is a source of RGM (Amos et al., 2012). But RGM concentrations can still be affected by anthropogenic sources and other processes, such as wet deposition and photochemical production by atmospheric oxidants. Similarly, many factors, such as season, location, atmospheric circulation, and wet scavenging, can also affect surface 7Be activity (Yoshimori, 2007; Arkian et al., 2010)."

RC: Lastly, a minor comment on the style of the paper. There are a number of very long sentences and paragraphs that I suggest the authors break up to improve the readability of the text. These are pointed out in the Specific Comments.

AC: We have shortened the paragraphs in the revised paper.

Specific Comments

RC: Page 31433, Title: Should "experimental lakes area" be capitalized? It is referred to as the "Experimental Lakes Area" in other publications (e.g. Graydon et al., 2008, ES&T). It's also capitalized in the first sentence of your abstract.

AC: Yes, experimental lakes area should be capitalized. Revised according to your suggestion.

RC: Page 31434, line 12-13: I suggest, ". . . like ELA. . ." instead of ". . .like the ELA".

AC: Revised according to your suggestion.

RC: Page 31435, lines 2-7: Consider breaking "Source-based methods require. . ." into two sentences for clarity.

AC: Revised according to your suggestion.

RC: Page 31436, line 4: "Combination" should be changed to "combinations". Also consider creating a new paragraph break at "Combinations of the. . .".

AC: Revised according to your suggestions.

RC: Page 31438, lines 1-2: Are the major ions associated with total particulate matter,

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or just fine particulate matter?

AC: The major ions are associated with total particulate matter, includes both fine and coarse particles. The sentence was revised to: "...total particulate Ca2+, K+, Mg2+, Na+, Cl-, SO42-, NO3-, and NH4+ since the 1980s (ELA, 2010)."

RC: Page 31438, section 2.2: It would be appropriate to include your study period (May 2005 – December 2006) here.

AC: Revised according to your suggestion.

RC: Page 31439, line 2: Consider adding a new paragraph break at "Although the accuracy. . .".

AC: Revised according to your suggestion.

RC: Page 31439, line 7: replace "Furthermore to the issue are uncertainties. . ." with "Furthermore there are uncertainties. . ."

AC: Revised according to your suggestion.

RC: Page 31440, line 5: How is "seasonal" defined here? Monthly averages? Three months averages (e.g. DJJ, MAM, JJA, SON)? Please be clear.

AC: The following explanation was added: "Spearman's rank correlation coefficient was used in correlation analysis of the daily averaged data for each season (i.e., winter = DJF, spring = MAM, summer = JJA, fall = SON)."

RC: Page 31440, line 24: What qualifies as a "high" factor loading? Can you be more quantitative?

AC: The sentence was revised to, "The variables with high factor loadings (>0.5) were identified and used to interpret the potential sources of Hg."

RC: Page 31441, line 3: StatSoft (2011) doesn't seem like the most appropriate reference to cite for the definition of K-means and hierarchical cluster analysis. I suggest

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citing work from the statistics literature (or a textbook) instead.

AC: Statsoft is an electronic version of a statistics textbook. The printed version citation is included in the reference. "(Printed Version): Hill, T. & Lewicki, P. (2007). STATISTICS: Methods and Applications. StatSoft, Tulsa, OK.)."

RC: Sections 2.4.2-2.4.4: The authors provide a very clear, concise summary of how each methods works, but what is lack from these sections is why are the authors using these methods. I suggest adding 1-2 brief sentences to each section communicating to the reader why the authors are using the methods described.

AC: Revised according to your suggestion. The following sentences were added to sections 2.4.2-2.4.4:

"PCA was chosen for this study because it can be used to analyse multiple pollutant and meteorological variables at once and has been used in several source-receptor studies of atmospheric Hg."

"Cluster analysis was chosen for this study because the data clusters can be directly compared to the factors generated from PCA. This comparison is useful for evaluating PCA, since it is often applied on its own to air pollutants data."

"In addition to PCA and cluster analysis, back trajectories were generated to simulate the airflow from the ELA site. This can be used to identify and locate the specific types of anthropogenic sources that were interpreted from the PCA factors and K-means and Hierarchical clusters."

RC: Pages 31442-31444: The paragraph that begins on page 31442 line 24 and ends on page 31444 line 5 is very long and difficult to follow. I suggest breaking it up into three separate paragraphs about GEM, RGM, and PHg.

AC: Revised according to your suggestion.

RC: Page 31443 line 1: Low RH and high O3 suggests may be a signature of free

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tropospheric air. This could be important to consider, in addition to soil emissions and coal combustion.

AC: see our replies to the very first comment.

RC: Page 31446, lines 19-20: Change “the lack of correlation” to “a lack of correlation”.

AC: Revised according to your suggestion.

RC : Page 31447, line 15: Poissant et al. (2005) should also be referenced.

AC: The study by Poissant et al. (2005) was referenced.

RC: Page 31449, lines 7-11: I strongly suggest removing, “Recent studies in marine environments. . . . far away from polar regions.” Discussing marine environments and high Arctic sites seems irrelevant and you dismiss the mechanisms happening at these sites anyways. These three sentences distract from the main message of the paragraph.

AC: Based on this and another comment below, we simply stated that GEM oxidation by reactive halogen species is possible on a global scale (Seigneur and Lohman, 2008; Holmes et al., 2010) in the revised paper.

RC: Page 31449, lines 20-21: “There is also a strong influence on this factor by temperature, which enhances the surface emission process.” Which surface emission processes are the authors referring to here? Temperature is related to the emission of Hg(0) from surface soils (e.g Poissant and Casimir, 1998), but I am not aware of any studies showing a relationship between temperature and surface emissions of PHg. If the authors are aware of such studies, they should cite them.

AC: The phrase, “which enhances the surface emission process” has been removed, but there may be indirect link on how temperature might enhance PHg. There are more wildfires during warmer seasons and temperatures, which generate more particulate matter; unfortunately, the particulate matter concentrations were not measured at ELA

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site to confirm this. Previous studies suggest biomass burning and wood combustion (indicated by K+ in PCA-3) are sources of GEM and RGM. The higher particulate matter concentrations from wildfires could provide more surface area for absorption of RGM (Huang et al., 2010, ES&T).

RC: Page 31449, lines 25-26: It is not clear why a five-cluster solution was chosen over four- and six-cluster solutions.

AC: The following explanation was added: "The five-cluster solution was most ideal because the four PCA factors did not explain all of the variance in the data set; thus choosing five clusters might help to explain the remaining variance. The six-cluster solution contained two clusters that have similar profiles."

RC: Page 31451, line 31451: What is "fairly high"? Please provide the percentage.

AC: The percentage was added to the sentence: "The percentage of data with elevated RGM concentrations was fairly high (66%) for HCA-4 as well."

RC: Page 31452, lines 25-26: The discussion of marine environments does not seem relevant at ELA, which is in the middle of the North American continent. It would be more appropriate to cite studies showing that Hg(0) oxidation by halogens is possible on a global scale and not just in marine environments (e.g. Holmes et al., 2010).

AC: In the revised paper, we cited the global-model studies to explain the possibility of Hg(0) oxidation by halogens at an in-land siet like ELA.

RC: Page 31456, lines 18-21: "That is, the transport of industrial/combustion emissions was often occurring simultaneously with photochemical production of RGM or crustal/soil emissions, suggesting this type of Hg source was well-represented in the data." This sentence is confusing.

AC: The sentence was revised to, "That is, the transport of industrial/combustion emissions was often occurring simultaneously with photochemical production of RGM or crustal/soil emissions, suggesting this type of source was a constant influence on GEM

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concentrations at ELA site."

RC: Page 31456, line 29: Consider changing ". . . halogen species as they are also important. . ." to ". . .halogen species since they may also be important. . ."

AC: Revised according to your suggestion.

RC: Page 31457, lines1-2: Other oxidants (e.g. Br) have also been shown to be potentially important on a global scale (e.g. Holmes et al., 2010).

AC: The sentence was revised to, "Recent studies suggest other oxidants (e.g. Br, BrO) are potentially important in regions with active bromine chemistry, such as polar regions and MBL (Holmes et al., 2009; Obrist et al., 2011), and on a global scale (Holmes et al. 2010)."

RC: Page 31457, line 6: Consider adding a brief summary the strengths and weaknesses of the methods you've used here.

AC: We have already summarized the strengths and weaknesses of the various methods throughout the conclusion.

Additional references:

Amos, H. M., Jacob, D. J., Holmes, C. D., Fisher, J. A., Wang, Q., Yantosca, R. M., Corbitt, E. S., Galarneau, E., Rutter, A. P., Gustin, M.S., Steffen, A., Schauer, J.J., Graydon, J. A., St. Louis, V. L., Talbot, R. W., Edgerton, E. S. and Sunderland, E. M.: Gas-particle partitioning of atmospheric Hg(II) and its effect on global mercury deposition, Atmos. Chem. Phys. 12, 591-603.

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Holmes, C. D., Jacob, D. J., Mason, R. P., and Jaffe, D. A.: Sources and deposition of reactive gaseous mercury in the marine atmosphere, Atmos. Environ., 43, 2278–2285, 2009.

Holmes, C. D., Jacob, D. J., Corbitt, E. S., Mao, J., Yang, X., Talbot, R., and Slemr, F.: Global atmospheric model for mercury including oxidation by bromine atoms, Atmos. Chem. Phys., 10, 12037-12057, doi:10.5194/acp-10-12037-2010, 2010.

Seigneur, C., and Lohman, K.: Effect of bromine chemistry on the atmospheric mercury cycle, J.Geophys. Res., 113, D23309, doi:10.1029/2008JD010262, 2008.

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Weiss-Penzias, P., Gustin, M.S., Lyman, S.N.: Observations of speciated atmospheric mercury at three sites in Nevada: Evidence for a free tropospheric source of reactive gaseous mercury, J. Geophys. Res., 114, D14302, doi:10.1029/2008JD011607, 2009.

Yoshimori, M.: Atmospheric Transport Inferred from Seasonal Variations in Cosmogenic Be-7 Concentrations, Proceedings of the 30th International Cosmic Ray Conference, Merida, Mexico, 3-11 July 2007, 224, 2007.

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